Edited by Axel H. E. Müller
and Krzysztof Matyjaszewski

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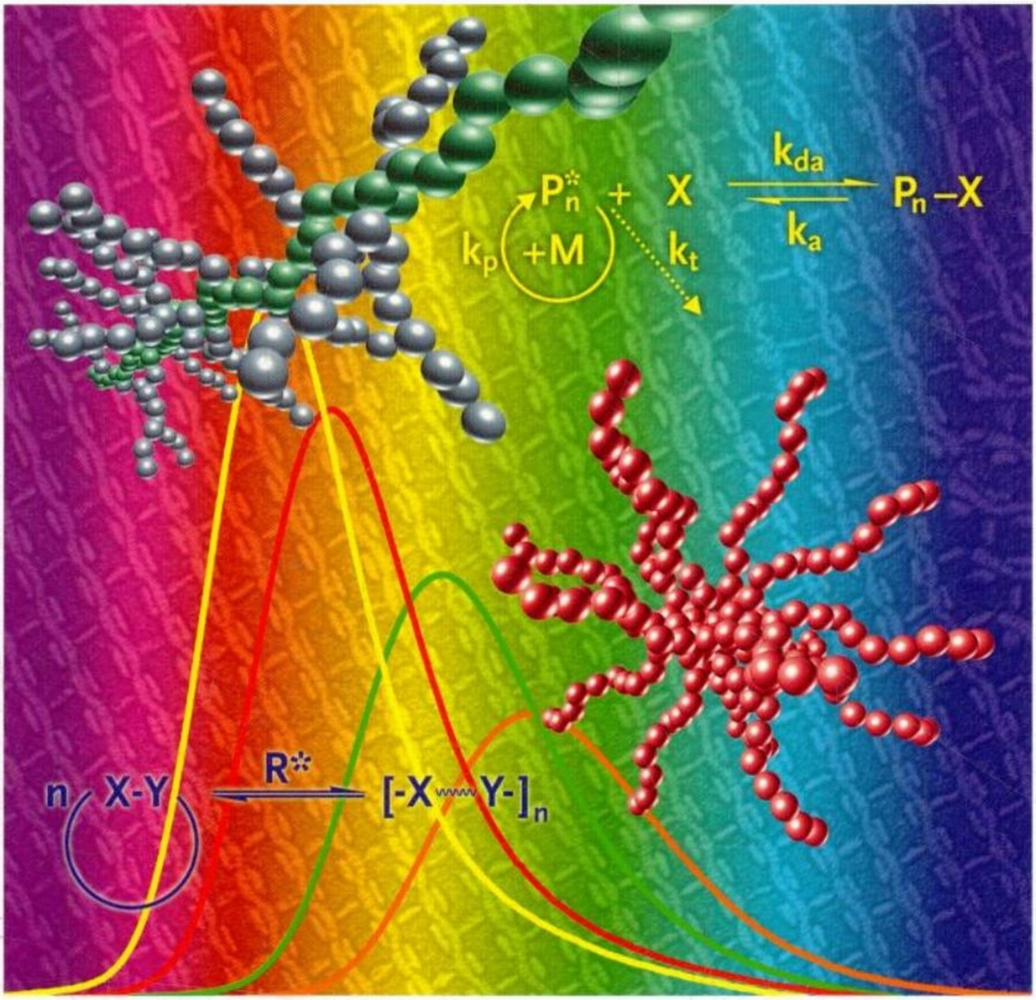
Controlled and Living Polymerizations

From Mechanisms to Applications



Controlled and Living Polymerizations

Methods and Materials

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Preface: Controlled and Living Polymerizations

The discovery of living anionic polymerization and subsequently other controlled/living polymerizations has had tremendous impact on polymer and materials science. It facilitated major developments not only in synthetic polymer chemistry but also in polymer physics as it opened an avenue to the preparation of well-defined polymers with precisely designed molecular architectures and nanostructured morphologies. As an example, block copolymers synthesized via sequential monomer addition by Szwarc *et al.* more than 50 years ago [1] have inspired a generation of polymer physicists due to their potential to self-organize in bulk or solution. They were successfully commercialized as thermoplastic elastomers, compatibilizers, surfactants, or components of medical and personal care products, to name just a few applications. Thermoplastic elastomers, first commercialized under the trade name Kraton®, are landmark materials made by living anionic polymerization and they are applied in many compounding applications, including footwear, pressure-sensitive adhesives, cables, soft-touch overmolding, cushions, lubricants, gels, coatings, or in flexographic printing and road marking. It is anticipated that materials made by other controlled/living processes will lead to more applications with even larger market impact. Many details on the current and potential future applications of polymers made by controlled/living polymerization can be found in all chapters of this book.

The term *living polymer* was coined by Michael Szwarc to describe the products of the anionic polymerization of styrene initiated by electron transfer in tetrahydrofuran [1, 2]. In this context, ‘‘living’’ denotes the ability of a polymer chain to further add monomer after the initial batch of monomer has been consumed, and this means that the polymer chains do not undergo irreversible chain breaking reactions, such as termination or chain transfer. The IUPAC Gold Book [3] defines ‘‘living polymerization’’ as *a chain polymerization from which chain transfer and chain termination are absent.* It adds (although this is not part of the definition) the following: *In many cases, the rate of chain initiation is fast compared with the rate of chain propagation, so that the number of kinetic-chain carriers is essentially constant throughout the polymerization.* Typically, such a process should lead to a very narrow (Poisson) molecular weight distribution

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(MWD). However, a slow initiation process can have a considerable impact on the molecular weights achieved and on the MWD.

It has been discussed how strict one should regard the absence of termination and transfer. For example, it is impossible to completely suppress termination in radical polymerization. Thus, Szwarc later modified his definition [4] saying that *a polymerization is living when the resulting polymer retains its integrity for a sufficiently long time to allow the operator to complete its task, whether a synthesis or any desired observation or measurement. Even in that time some decomposition or isomerization may occur, provided it is virtually undetectable and does not affect the results.*

The term *controlled polymerization* introduced by us in 1987 [5] can be defined as a synthetic method to prepare polymers, which are well-defined with respect to topology (e.g., linear, star-shaped, comb-shaped, dendritic, and cyclic), terminal functionality, composition, and arrangement of comonomers (e.g., statistical, periodic, block, graft, and gradient), and which have molecular weights predetermined by the ratio of concentrations of reacted monomer to introduced initiator, as well as a designed (not necessarily narrow) MWD.

Thus, a living polymerization is not always controlled and a controlled polymerization is not always strictly living, according to the definitions given above. In the ideal case, a living polymerization is also controlled; however, in some systems such as in a radical polymerization, termination can never be entirely avoided but its contribution can be sometimes significantly reduced.

The feature of livingness was discovered in carbanionic polymerization in 1956. Many efforts were made in other polymerization methodologies to achieve a level of control attainable in living carbanionic polymerization. However, it took nearly 20 years until living cationic ring-opening polymerization was developed (living anionic ring-opening polymerization was known already for some time). Group transfer polymerization (GTP; a process close to anionic polymerization) was reported in 1983 and the living carbocationic polymerization in 1984. Subsequently, living ring-opening metathesis polymerization (ROMP) was reported in 1986 and various controlled/living radical polymerization mechanisms were reported in the 1990s. Finally, even coordination polymerization of olefins was made living.

It is intriguing that almost all new controlled/living systems have one common feature, which is the coexistence of active and inactive (“dormant”) species, being in a dynamic equilibrium, either via *reversible deactivation* processes or via *reversible (degenerative) transfer.*

Reversible deactivation is a process where active species (ions, ion pairs, or radicals), *P**, are in a dynamic equilibrium with inactive (dormant), typically covalent species, *P*,

$$\sim\sim\sim\sim P\,(+C) \underset{k_{\mathrm{deact}}}{\overset{k_{\mathrm{act}}}{\rightleftharpoons}} \sim\sim\sim\sim P^{*}(+D)$$

Here, *C* is a catalyst (coinitiator/activator) and *D* is a deactivator or product of the activation process. As an example, in atom transfer radical polymerization (ATRP), *P* can be a bromine-terminated chain end, *C* can be a Cu(I) compound, P^* is the propagating radical, and *D* is a Cu(II) compound (Chapter 3). In GTP, *P* is a silylketene acetal, *C* can be a bifluoride anion, P^* can be an enolate, and *D* is a silyl fluoride (Chapter 1).

Reversible transfer is a bimolecular reaction between a dormant and an active polymer chain, which only differ in their degree of polymerization (degenerative transfer, i.e., equilibrium constant $K_{ex} = 1$), leading to a direct exchange of activity between two chain ends:

$$\sim\sim\sim\sim P_{\mathrm{n}} + \sim\sim\sim\sim P^*_{\mathrm{m}} \underset{k_{\mathrm{ex}}}{\overset{k_{\mathrm{ex}}}{\rightleftarrows}} \sim\sim\sim\sim P^*_{\mathrm{n}} + \sim\sim\sim\sim P_{\mathrm{m}}$$

A typical example is the exchange reaction between an iodine-terminated chain end and a propagating radical. Reversible addition–fragmentation chain transfer (RAFT) polymerization is also closely related to such a process (Chapter 3).

As a consequence of these processes, the MWD may be considerably broader than the Poisson distribution, where the polydispersity index, PDI $= M_{\mathrm{w}}/M_{\mathrm{n}}$, is close to unity. The PDI depends on the ratio of the rate constants of propagation to deactivation (or exchange) and decreases with monomer conversion [6]. If deactivation/exchange is slow relative to propagation, broad MWDs are observed. Many such systems have been called nonliving, because broad MWDs were assumed to originate in chain breaking reactions.

The first four chapters in this book present the mechanisms and the most recent advances in controlled/living polymerization of vinyl monomers. The first chapter summarizes anionic polymerization using classic systems and also recent developments employing equilibria between active and dormant species that enabled reduction of the rate of polymerization of styrene and also controlled polymerization of (meth)acrylates. The second chapter is devoted to carbocationic polymerization and illustrates examples of equilibria between carbocations and various dormant species and their applications to synthesis of well-defined (co)polymers. The third chapter describes a state of the art in controlled radical polymerizations, predominantly in stable free radical polymerization, atom transfer radical polymerization, and degenerative systems such as RAFT, and also presents how controlled molecular architecture can lead to new applications. The fourth chapter is focused on controlled/living coordination polymerization of olefins and presents some new materials prepared by this technique.

The next two chapters are focused on ring-opening polymerization. Chapter 5 presents recent advances in both anionic and cationic polymerization of heterocyclics together with examples of well-defined (co)polymers and their applications. Chapter 6 is focused on ROMP of cycloolefins and a variety of resulting new materials prepared by ROMP.

Chapters 7 and 8 illustrate how various controlled/living polymerizations can be employed to precisely control various elements of macromolecular architecture, such as chain composition and microstructure, chain topology and functionality, including block and graft copolymers. Chapter 9 presents how segmented copolymers self-organize in bulk, thin films, and solution into various nanostructured morphologies and how precise synthesis and processing can generate new materials with exciting properties.

Finally, the last chapter provides not only a state-of-the-art summary of current and forthcoming applications of Kraton, a large-volume block copolymer prepared by anionic vinyl polymerization, but also (co)polymers prepared by other controlled/living techniques.

We are confident that this book provides an excellent overview of various controlled/living polymerization techniques and hope that it will stimulate new discoveries and will facilitate developments of new polymeric materials for many exciting applications.

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1
Anionic Vinyl Polymerization

Durairaj Baskaran and Axel H.E. Müller

1.1
Introduction

1.1.1
The Discovery of Living Anionic Polymerization

The concept of anionic polymerization was first developed by Ziegler and Schlenk in early 1910. Their pioneering work on the polymerization of diene initiated with sodium metal set the stage for the use of alkali metal containing aromatic hydrocarbon complexes as initiators for various α-olefins. In 1939, Scott and coworkers used for the first time the alkali metal complexes of aromatic hydrocarbon as initiators for the polymerization of styrene and diene. However, in 1956, it was Michael Szwarc who demonstrated unambiguously the mechanism of anionic polymerization of styrene, which drew significant and unprecedented attention to the field of anionic polymerization of vinyl monomers [1, 2]. Michael Szwarc used sodium naphthalenide as an initiator for the polymerization of styrene in tetrahydrofuran (THF). Upon contact with styrene, the green color of the radical anions immediately turned into red indicating formation of styryl anions. He suggested that the initiation occurs via electron transfer from the sodium naphthalenide radical anion to styrene monomer. The styryl radical anion forms upon addition of an electron from the sodium naphthalenide and dimerizes to form a dianion (Scheme 1.1).

After the incorporation of all the monomer, the red color of the reaction mixture persists, indicating that the chain ends remain intact and active for further propagation. This was demonstrated by the resumption of propagation with a fresh addition of another portion of styrene. After determining the relative viscosity of the first polymerized solution at its full conversion, another portion of styrene monomer was added and polymerization was continued. Thus, Szwarc characterized this behavior of the polymerization as *living polymerization* and called the polymers as *living polymers* [2]. Here, the term *living* refers to the ability of the chain ends of these polymers retaining

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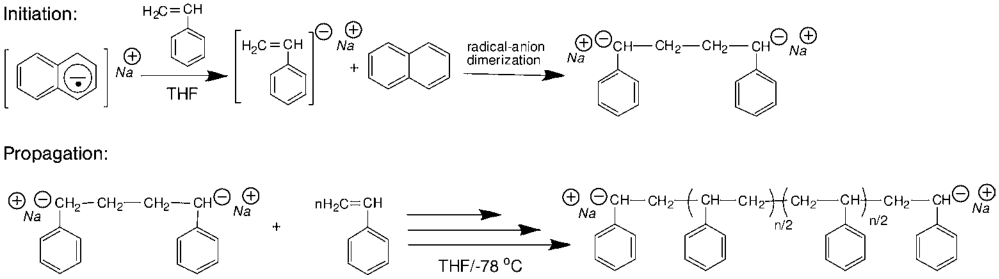
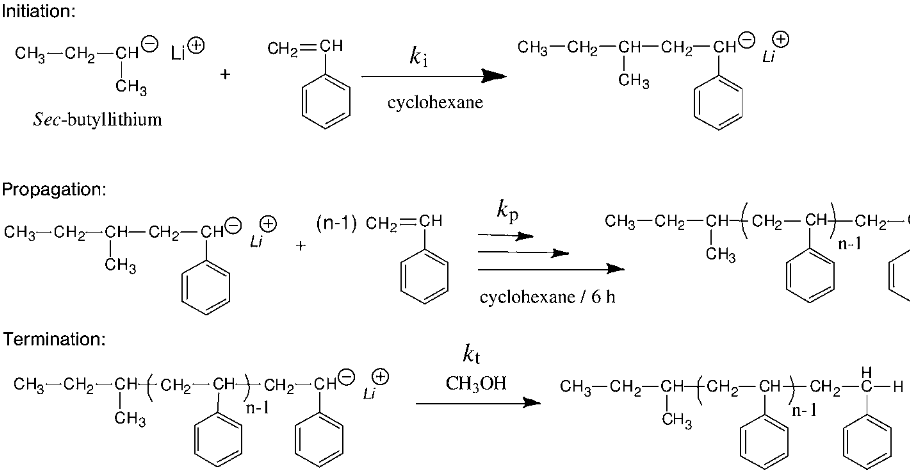


Scheme 1.1 Anionic polymerization of styrene using sodium naphthalene as initiator in THF.



Scheme 1.2 Anionic polymerization of styrene using *sec*-butyllithium as initiator.

their reactivity for a sufficient time enabling continued propagation without termination and transfer reactions.

Szwarc's first report of living anionic polymerization of styrene free from termination and transfer reactions in THF marks the beginning of lively research activities in this field [1–5]. Subsequent work on the anionic polymerization of styrene and dienes in hydrocarbons using alkyllithium initiators stimulated interest in this field [6–8]. Scheme 1.2 shows the anionic polymerization of styrene initiated by *sec*-butyllithium.

1.1.2
Consequences of Termination- and Transfer-Free Polymerization

Detailed kinetic measurements confirm that the polymerization of styrene in fact is free from termination and transfer reactions [1, 2]. Assuming a fast

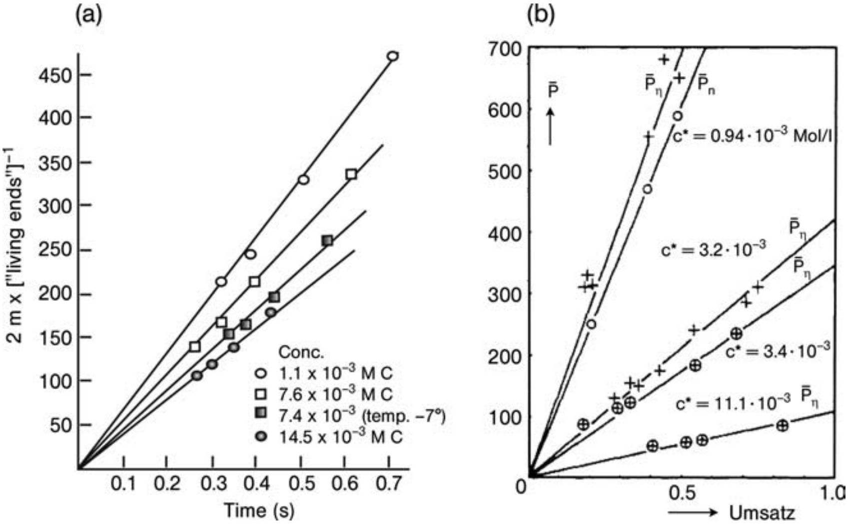


Figure 1.1 (a) Rate of polymerization of polystyrene in THF at 25 °C ('m' corresponds to $[M]_0/[M]_t$) [9]. (b) Number- and viscosity-average degrees of polymerization of polystyrene vs. conversion at various chain-end concentrations, c^* [10]. (Reprinted with permission from Wiley-VCH.)

initiation step, the rate of polymerization is given by

$$R_p = -\frac{d[M]}{dt} = k_p \cdot [P^*] \cdot [M] \tag{1.1}$$

where $[M]$ is the monomer concentration, k_p is the rate constant of propagation, and $[P^*]$ is the concentration of active chain ends. In the absence of termination, $[P^*]$ is constant, and the product $k_\text{p}[P^*] = k_\text{app}$ can be regarded as an apparent first-order rate constant. Introducing monomer conversion, $x_\text{p} = ([M]_0 - [M]_t)/[M]_0$, integration of Eq. (1.1) leads to

$$\ln \frac{[M]_0}{[M]_t} = -\ln(1 - x_\text{p}) = k_\text{p} \cdot [P^*] \cdot t = k_\text{app} t \tag{1.2}$$

Figure 1.1a shows a historic plot of such a first-order time-conversion relation. The linearity indicates that the active center concentration remains constant throughout the polymerization. In case of termination, $[P^*]$ depletes and thus the slope of the first-order plot decreases. It must be noted that this plot does not give evidence for the absence of transfer, since in this case the concentration of active chain ends remains constant.

The absence of transfer can be demonstrated by the linearity of a plot of the number-average degree of polymerization, DP_n, vs. conversion:

$$\overline{\text{DP}}_n = \frac{\text{concentration of consumed monomers}}{\text{concentration of chains}}$$

$$= \frac{[M]_0 - [M]_t}{[P]} = \frac{[M]_0}{[P]} \cdot x_p \tag{1.3}$$

where $[P]$ denotes the *total* number of chains, active and inactive ones, which are generated in the transfer process. In an ideal polymerization $[P] = [P^*] = f[I]_0$, where $[I]_0$ is the initial initiator concentration and f the initiator efficiency. In case of transfer, $[P]$ increases and the slope of the plot decreases. Figure 1.1b shows a historical plot from Schulz *et al.* [10]. This indicated that the propagating anions are free from transfer and the molecular weight of the chains correspond to theoretical molecular weight depending on the monomer conversion [11].

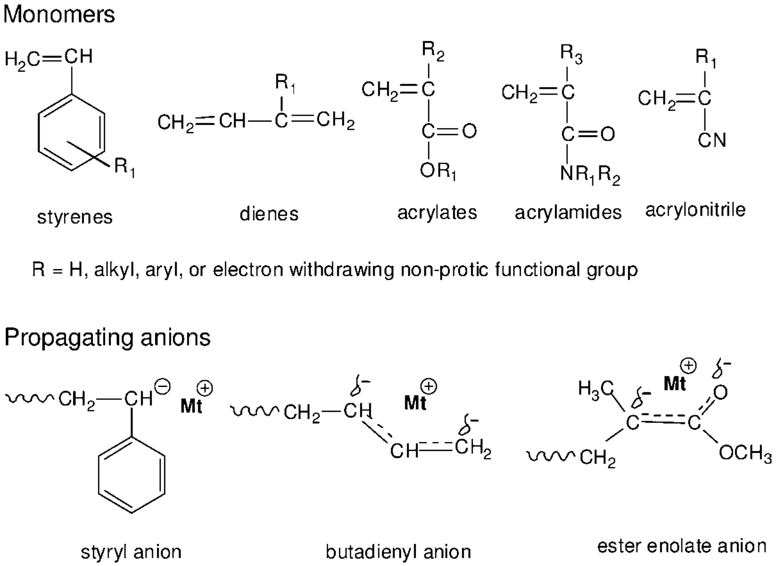
The absence of termination and transfer reactions has two important consequences: (i) the number-average molecular weight, M_n, of the resulting polymer is determined by the amount of consumed monomer and the initiator used for the polymerization[12] and (ii) all the chains at any time, t, propagate at the same rate and acquire the same length after a subsequent time interval, $t + \Delta t$. This leads to a linear growth of polymer chains with respect to the monomer consumption, leading to a narrow distribution of chain lengths characterized by a *Poisson* distribution; the polydispersity index is given by

$$\mathrm{PDI} = \frac{\overline{M}_w}{\overline{M}_n} \approx 1 + \frac{1}{\overline{\mathrm{DP}}_n} \tag{1.4}$$

This distribution had already been derived by Flory in 1940 for the ring-opening polymerization of ethylene oxide [13]. This was experimentally confirmed by Schulz and coworkers who determined the polydispersity index, M_w/M_n, of Szwarc's samples and found that they were in the range of 1.06–1.12 [14].

Monomer resumption experiment is another way to show the absence of termination. Here, a second batch of monomer is added after a certain period has elapsed after full monomer conversion. In case of termination, one will find a bimodal distribution, one peak from the terminated chains and another from the active chains that participated in chain extension with the second batch of monomer.

It is important to note that not all living polymerizations lead to narrow molecular weight distributions (MWDs). First, a *Poisson* distribution is obtained only if the rate of initiation is much faster than that of propagation. Second, as is discussed later, many chain ends in anionic polymerizations (and also in other types of living polymerizations) can exist in various states, e.g., covalent species, aggregates, various types of ion pairs, or free anions, which propagate at different rates or are inactive ("dormant"). Different types of chain ends in anionic polymerization exist in equilibrium with each other and a chain end can change its state depending on the reaction condition such as the polarity of solvent and the temperature. If the rate of exchange between these species is slow compared to the rate of propagation, this can lead to a significant broadening of the MWD.


Monomers

Propagating anions

Figure 1.2 Major class of vinyl monomers and their corresponding propagating anions.

1.1.3
Suitable Monomers

A variety of α-olefins substituted with an electron withdrawing group have been subjected to anionic polymerization [15, 16]. Several substituted α-olefin monomers can be polymerized via anionic polymerization except the ones with functional groups bearing acidic protons (or other electrophiles) for the obvious reason that electrophiles react with carbanions and thus either quench the initiator or terminate anionic propagation. However, after appropriate protection, those monomers can be polymerized [17–19]. Hydrocarbon monomers such as dienes and styrene, polar vinyl monomers such as vinyl pyridines, (meth)acrylates, vinyl ketones, acrylonitriles, and cyclic monomers containing oxirane, lactones, carbonates, and siloxanes have been polymerized using anionic initiators [16]. The anionic polymerization of heterocyclic monomers is discussed in Chapter 5. A list of major classes of substituted α-olefin monomers with their corresponding propagating anions is given in Figure 1.2. The reactivity of these propagating anions and their nature of ion pairs are dependent on reaction conditions. The substitution (R_1, R_2, R_3) in the olefin monomers can vary from H, alkyl, aryl, and protected silyl group, leading to numerous monomers that are amenable for anionic polymerization [20, 21]. Various other monomers that are anionically polymerizable with limited control over the polymerization include ethylene, phenyl acetylene, vinyl ketones, and vinyl sulfones and α-olefins with other electron withdrawing group such as $-CN$ and $-NO_2$. A detailed list of monomers for anionic polymerization is given in various books and reviews [21, 22].

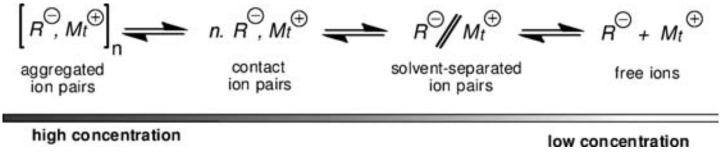
In the following, we first discuss characteristics of carbanions and their ion pairs in different conditions and their function as initiators and chain ends in the anionic polymerization of vinyl monomers. As our intention is to cover the fundamental aspects related to the mechanism of anionic vinyl polymerization in this chapter, the architectural controls using active chain-end manipulations and copolymerization have not been included; they will be covered in other chapters of this book. The existence of different forms of ion pairs in polar and nonpolar solvents and their dynamic equilibrium will be described. Subsequently, the detailed mechanism of anionic polymerization of styrene, dienes, and acrylic monomers in polar and nonpolar solvents will be discussed. Finally, we present some examples of industrial and scientific applications of anionic polymerization.

1.2
Structure of Carbanions

The rate of anionic polymerization of styrene using alkyllithium as initiator strongly depends on the solvent. It is very fast in polar solvents like THF. It is much slower in aromatic hydrocarbons such as benzene and even slower in aliphatic hydrocarbons such as cyclohexane. This is due to the different states of solvation and aggregation of carbanions in these solvents [23, 24]. Therefore, the mechanism of anionic polymerization is complicated due to the contribution of different forms of ion pairs. Thus, we will first examine the various forms of carbanions used in polar and nonpolar solvents before analyzing the mechanisms of initiation and polymerization.

Various factors affect the reactivity of carbanions, and it is important to understand the properties of carbanions that assume different structures depending on the environment. The polarity of the solvent in which anion is prepared and used, the intermolecular ionic interactions, and the size of metallic counterion all dictate the characteristics of a particular carbanion. The stabilization of anions through intermolecular interaction leads to the formation of different associated states called *aggregates*. The nature of anion aggregation is governed by various factors such as the charge density of anion, interionic distances, the dielectric constant, and the donating properties of the solvent [25]. Thus, the aggregated anions always exist in dynamic equilibrium with nonaggregated ones.

Fuoss [26, 27] and Winstein *et al.* [28] independently proposed the existence of two different forms of ion pairs based on the interionic distance. Accordingly, the anion present in solution may be tightly associated with counterion or loosely with solvated counterion. They named a tightly associated anion with cation as contact ion pair and a loosely associated anion with solvent-coordinated cation as solvent-separated ion pair. The different forms of ion pairs that are in equilibrium with each other are shown in Scheme 1.3. Depending on the concentration, the solvent-separated ion pairs can dissociate



Scheme 1.3 Fuoss–Winstein spectrum of anion pairs in a polar solvent.

into free ions and they can also associate intermolecularly to form triple ions. The reactivity of the free ions and solvent-separated ion pairs is very high when compared to that of contact ion pairs. The position of this equilibrium is controlled by the polarity of the solvent as well as the concentration of ion pairs used for the polymerization (Scheme 1.3).

Low temperature favors the formation of solvent-separated ion pairs due to the higher dielectric constant of the solvents at low temperatures. Spectroscopic evidence for the existence of contact- and solvent-separated ion pairs was found by Smid and Hogen-Esch. Two distinct temperature-dependent ultraviolet absorption bands were found for fluorenyl sodium solution in THF [29–31].

The ion pair equilibrium shifts to the formation of free ions, especially at low concentration of ion pairs and in highly solvating media. Although the dissociation of contact- or solvent-separated ion pairs into free ions occurs to a very low extent in polar solvent, their participation in propagation increases the reaction rate tremendously [32, 33]. The participation of free ions during the propagation can be suppressed by addition of a highly dissociating salt containing a common ion, e.g., a tetraphenylborate. The presence of free ions can be identified through conductivity measurement, as the free ions are conductive compared to the nonconductive ion pairs [27, 34].

Although contact ion pair solutions do not show conductance at low concentration, Fuoss found high equivalent conductance at higher concentration [35, 36]. Fuoss and Kraus suggested the formation of a new type of ion pair through intermolecular association called *triple ion* [35–37]. The presence of free anions, ion pairs, triple ions, and aggregated ion pairs plays an important role in anionic polymerization carried out in polar media, as will be seen later.

In nonpolar solvents, the ion pairs exist mostly in the aggregated state in equilibrium with a small amount of contact ion pairs. Of course, initiation and propagation are controlled by the reactive nonaggregated ion pairs irrespective of their concentration as they exist in fast equilibrium with aggregated ones.

1.3
Initiation

In general, the anionic polymerization like in other vinyl polymerization methods consists of three main reactions: (i) initiation, (ii) propagation, and (iii) termination, as described in Scheme 1.2. However, termination is brought about intentionally using a suitable electrophile, which can be useful for end group modification.

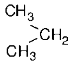
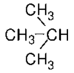
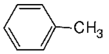
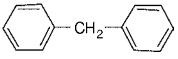
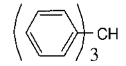
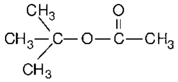
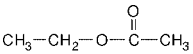
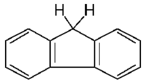
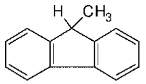
For a well-controlled anionic vinyl polymerization, the initiation reaction is generally fast and is not reflected in the overall rate of the polymerization. The kinetics of the polymerization is predominantly controlled by the propagation step. However, some initiators initiate vinyl monomer slowly over a period of time or with induction period and have significant influence on over all reaction rate as well as affect the MWD of the polymers [38–40]. The kinetics is complicated with the behavior of propagating ion pairs and their association and interaction with solvent molecules (see below). The interaction of propagating ion pairs with functional groups of the vinyl monomer or the polymer chain can affect the propagation rate and in some cases induces side reactions that can cease the polymerization. In a side reaction-free anionic vinyl polymerization, the termination is a simple rapid reaction wherein anions are quenched through acidic hydrogen or another suitable electrophile.

It is important to judiciously choose an appropriate anionic initiator for the polymerization of a particular type of vinyl monomer. This is because the characteristics of carbanions differ significantly by their nucleophilicity and depend on the solvent polarity. The rate of initiation is strongly influenced by the aggregation state of anion and the intermolecular interactions of ion pairs that are formed through opening of the vinyl bond of the monomer and the formation of new propagating species. Hence, it is important to match the reactivity of the initiator with the propagating species in order to have fast and homogeneous initiation. A suitable measure of nucleophilicity is the pK_a value of the corresponding protonated mother compound of the chain end, e.g., butane for butyllithium, ethylbenzene for styrene, or methyl propionate for methyl acrylate polymerization (Table 1.1). Typically, the pK_a of the (protonated) initiator should be comparable to or higher than that of the propagating anion.

1.3.1
Anionic Initiators

Initiators for the anionic polymerization of vinyl monomers can be broadly classified into (i) radical anions, (ii) carbanions, and (iii) oxyanions, including their thio derivatives. As described above, the direct use of radical anions such as sodium naphthalenide in polar solvent for the polymerization of styrene forms dimerized bifunctional anionic propagating species during propagation [2]. Several aromatic hydrocarbons and α-olefins containing aromatic substitution can react with alkali metals to form radical anions. For example, the reaction of sodium metal and 1,1-diphenylethylene (DPE) generates a radical anion in polar solvent, which can be used as initiator for the anionic polymerization [43]. Similarly, the reaction of sodium with α-methylstyrene yields a radical anion in polar solvent, which oligomerizes to the tetramer at room temperature [44, 45]. The general mechanism of the formation of these types

Table 1.1 pK_a values of most important carbon acids related to anionic vinyl polymerization in dimethylsulfoxide solution [41, 42].

Carbon Acids	pK_a
CH_4	(56)
	$(51)^a$
	$(53)^a$
$CH_2{=}CH{-}CH_3$	(44)
	(43)
	32.2
	30.6
	(30.3)
 $CH_3{-}CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_3$	($\sim$30)
	22.6
	22.3

^{a} Determined in water.
Values in parenthesis are extrapolated estimates.

of initiators is a transfer of an electron from the surface of the alkali metal to the electron deficient aromatic hydrocarbon or monomer.

Alkali metals were used as initiators for the anionic polymerization of dienes in the past. The synthesis of Buna S rubber is a well-known example for the metal-initiated polymerization [46]. However, metals generate radical anions through electron transfer to the surface adsorbed monomer in a heterogeneous state. The generated monomer radical anions rapidly undergo dimerization to form new dianions, which then initiate monomer to bifunctional anionic propagation. Electron transfer initiators work efficiently in polar solvents providing fast generation of bifunctional growing chains. However, electron transfer is inefficient in nonpolar solvents due to the lack of solvation and it is not possible to prepare radical anions in nonpolar solvents. In the case of polymerization initiated by alkyllithiums in polar solvents, the initiating carbanions and the propagating carbanions are solvated and significantly less aggregated.

Another important class of initiator is simple carbanions; in particular, alkyllithiums derived directly from the reaction of alkylhalide and lithium [7, 8, 47, 48]. Alkyllithiums generally exist in aggregated form in hydrocarbons. The behavior of carbanions and their ion pairs is strictly controlled by their solvation with solvent molecules. The reactivity of carbanions differs significantly depending on the solvent polarity. The structure and reactivity of a carbanion also depend on the size of its counter cation, since it determines the interionic distance in a contact ion pair and the extent of solvation and intermolecular association. Alkyllithiums are highly reactive and unstable in polar solvents and at least the initiation step has to be performed at low temperature (−78 °C).

The intermolecular association of alkyllithium in solid state as well as in solution is well known [49–51]. The extent of aggregation depends strongly on the polarity of the solvent. As alkyllithiums are known to exist in different forms with different degree of intermolecular aggregation, an appropriate initiator should be used for the polymerization in order to have efficient initiation [22, 52–55]. Alkyllithium initiators are especially efficient in nonpolar solvents in the polymerization of hydrocarbon monomers [16].

The aggregation of initiators in nonpolar medium affects the efficiency of initiation of hydrocarbon monomers. The anionic polymerization of styrene and dienes using *n*-butyllithium as initiator in hydrocarbon medium is sluggish and the initiation is often incomplete due to the high degree of aggregation. The highly aggregated *n*-butyllithium shows incomplete initiation of styrene in cyclohexane. At complete monomer conversion, ~30% and ~42% of unreacted *n*-BuLi and *t*-BuLi, respectively, present in the polymerization. On the other hand, the less aggregated *sec*-BuLi undergoes fast initiation within a short time enabling proper control of the polymerization [23, 56–58].

In the case of alkyl (meth)acrylate polymerization, less nucleophilic anions should be used (often in conjunction with moderating ligands) to avoid attack of the monomer carbonyl group. Here, the charge distribution over two or three phenyl rings (e.g., 1,1-diphenylhexyl [59] or triphenylmethyl anions [60]) or larger aromatic systems (e.g., fluorenyl anions) [61, 62] attenuates the nucleophilicity enough. However, these initiators are not always nucleophilic enough to efficiently initiate the polymerization of hydrocarbon monomers. (An exception is 1,1-diphenylhexyllithium, which slowly initiates the polymerization of styrene [63, 64].) Ester enolates, which mimic the structure of the chain end, are also good initiators for (meth)acrylates. In conclusion, the selection of an initiator for the polymerization of a particular monomer is very important in order to obtain control of the propagation.

Alkylsodium and alkylpotassium are not frequently used, mostly in the initiation of diene polymerization [65]. However, sodium, potassium, and cesium salts of aromatic anions (e.g., benzyl, cumyl, diphenylmethyl, triphenylmethyl, and fluorenyl) [62, 66, 67] have been used quite frequently to initiate the polymerization of polar monomers such as alkyl(methacryalates). The complexity of the anionic polymerization arises mainly from the charge density of the anionic center in the initiator or in the propagating chain end as they are known to assume multiple configurations and conformations depending on the nature of medium in which they participate in the reaction [68, 69].

1.3.2
Experimental Considerations

Owing to the high nucleophilicity of the carb- or oxyanionic chain ends, the polymerizations must be conducted under inert conditions, i.e., in the absence of moisture or other electrophiles. Oxygen must also be avoided (even in the quenching agent!), since it undergoes electron transfer with carbanions, leading to chain coupling [70]. Thus, monomers, solvents, and reaction vessels must be thoroughly purged and filled with nitrogen or argon. For very high molecular weight polymers (needing very low initiator concentrations), reactions should be performed under high vacuum using special all glass vessels with glass break seals [71]. Some polymerizations proceed extremely fast in polar solvents (half-lives below 1 s). For those, flow-tube reactors with short mixing times have been developed [72]. Alternatively, the monomer should be added very slowly via the gas phase. An overview of experimental details is given by Fontanille and Müller [73].

1.4
Mechanism of Styrene and Diene Polymerization

1.4.1
Polymerization of Styrene in Polar Solvents: Ions and Ion Pairs

The first example of the polymerization of styrene in THF using sodium napthalenide at low temperature proceeded smoothly without any side reaction [1, 2]. Szwarc and his coworkers proved the transfer- and termination-free nature of the propagation through monomer resumption and kinetic experiments (Figure 1.1). They observed a resumption of the polymerization with a second dose of fresh monomer leading to 100% chain extension and also obtained a linear first-order time-conversion plot indicating the absence of termination during the propagation [9]. The observed experimentally determined (apparent) rate constant $k_{\mathrm{p,app}} = k_{\mathrm{app}}/[P^*]$ (i.e., the slope of the first-order time-conversion plot k_{app} divided by the concentration of active centers $[P^*]$) of the polymerization in THF increased with decreasing concentration of active centers [9]. This suggested the presence of different forms of ion pairs depending on the concentration of initiator.

Subsequently, intensive kinetics studies by Szwarc, Schulz, Ivin, and Bywater revealed that the apparent propagation rate constant of styrene with sodium counterion strongly depends on the ability of the solvent to solvate the counterion, decreasing from dimethoxyethane (DME) over THF and tetrahydropyran (THP) to dioxane [9, 10, 74–81]. This indicated that the structure of the propagating ion pairs of polystyryllithium distinctly depends on the nature of the solvent. It was shown that the experimentally determined rate constant of styrene polymerization, in the presence of various alkali metal counterions, increases linearly with the reciprocal square root of propagating chain-end concentration (Figure 1.3) [10, 82].

This behavior was attributed to the equilibrium of free ions and ion pairs, where the propagation rate constant of free anions, k_-, is much higher than that of the ion pairs, $k_\pm$ (Scheme 1.4). The mole fractions of free ions and ion pairs participating in the propagation are α and $1-\alpha$, respectively [75, 83–86]. These can be calculated from Ostwald's law, using the dissociation constant, $K_{\text{diss}} = k_i/k_a$, and the total concentration of the ion pairs, $[P^*]$,

$$\frac{\alpha^2}{(1-\alpha)} = \frac{K_{\text{diss}}}{[P^*]} \tag{1.5}$$

Since $K_{\text{diss}} \ll 1$ (typically below 10^{-7} M),

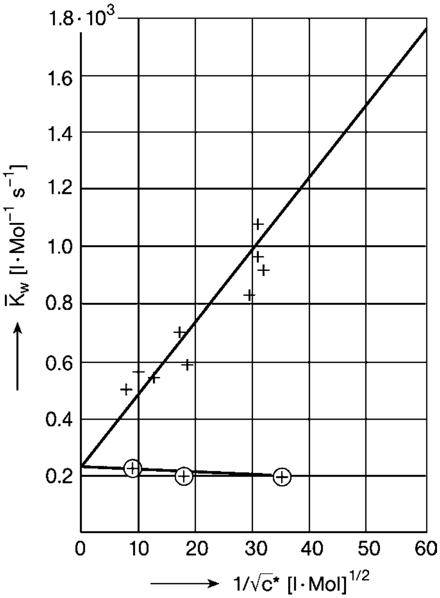
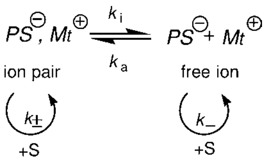


Figure 1.3 Dependence of the experimental rate constant of the anionic polymerization of styrene, $k_{p,\text{exp}}$, in THF with sodium counterion on the concentration of active chain ends, $[P^*]$. Circles denote experiments in the presence of sodium tetraphenylborate [10]. (Reprinted with permission from Wiley-VCH.)



Scheme 1.4 Participation of free ions in the anionic polymerization of styrene in THF.

$$\alpha \approx \sqrt{K_{\text{diss}}/[P^*]} \ll 1 \tag{1.6}$$

The apparent (i.e., experimentally determined) propagation rate constant is

$$k_{\text{p,exp}} = \alpha \cdot k_{-} + (1-\alpha) \cdot k_{\pm} \tag{1.7}$$

leading to

$$k_{\text{p,exp}} = k_{\pm} + (k_{-} - k_{\pm}) \cdot \sqrt{K_{\text{diss}}/[P^*]} \tag{1.8}$$

Thus, the slope of a plot of $k_{\text{p,exp}}$ vs. $[P^*]$ gives $(k_{-} - k_{\pm}) \cdot \sqrt{K_{\text{diss}}}$ and the intercept gives the corresponding $k_{\pm}$ ("Szwarc–Schulz plot"; Figure 1.3) [75, 83–86]. Thus, the equilibrium constant of dissociation determines the apparent rate constant of propagation in anionic polymerization in polar solvents and this depends on the polarity of the solvent. The dissociation of the ion pairs can be efficiently suppressed by adding a common ion salt with higher degree of dissociation, e.g., sodium tetraphenylborate (Figure 1.3) [10, 75]. A plot of $k_{\text{p,exp}}$ vs. $[\text{Na}^+]^{-1}$ according to Eq. (1.9) can also be used to determine the dissociation constant, K_{diss}, independent of conductivity measurements.

$$k_{\text{p,exp}} = k_{\pm} + (k_{-} + k_{\pm}) \cdot (K_{\text{diss}}/[\text{Na}^+]) \tag{1.9}$$

With the knowledge of K_{diss}, the propagation rate constant of free anions was determined and found to be independent of counterion and solvent used, according to expectations [87].

The dynamics of the dissociation equilibrium has a slight effect on the MWD [88]. By analyzing the MWD of polymers obtained in the polymerization of styrene in THF, Figini *et al.* were able to determine the rate constants of dissociation and association separately [83, 88].

In the case of dioxane, a low dielectric medium ($\varepsilon = 2.25$), the propagation rate constants of ion pairs increase with increasing crystal radius of the cation [84, 89], which is attributed to easier charge separation in the transition state for larger cations. It was also expected and confirmed that for a given counterion, the ion pair propagation rate constants depend on the polarity of the solvent due to solvation of the counterion [89]. However, unexpectedly, in THF and in other polar solvents, the propagation rate constants of polystyryl ion pairs follow a reverse order with respect to the size of counterions; cesium ions leading to the slowest propagation. This led to a closer inspection of the nature of the ion pairs involved.

1.4.2
Contact and Solvent-Separated Ion Pairs

Szwarc and Schulz carried out kinetics of the propagation of polystyrylsodium in a variety of polar solvents over a large temperature range. Figure 1.4 shows

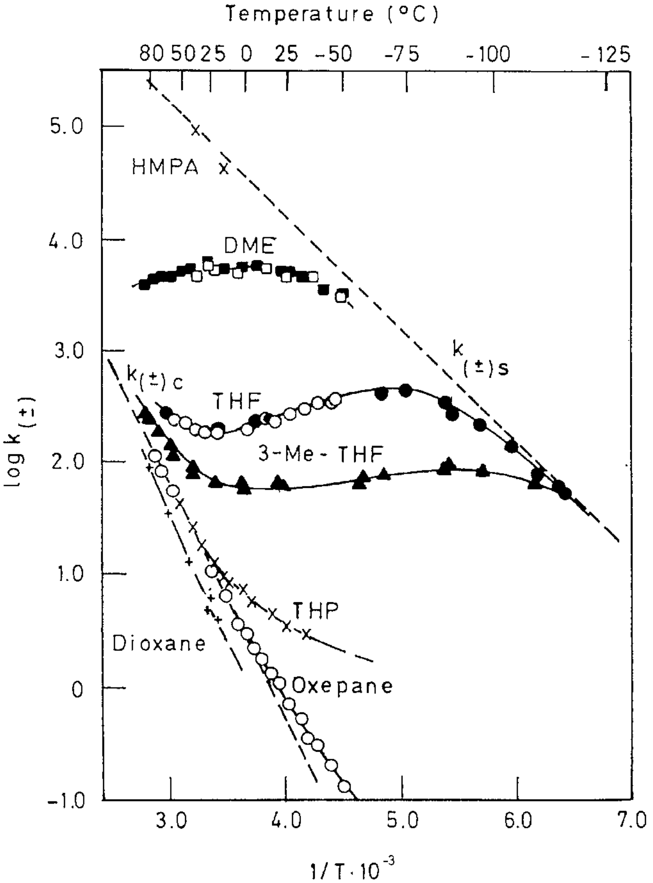
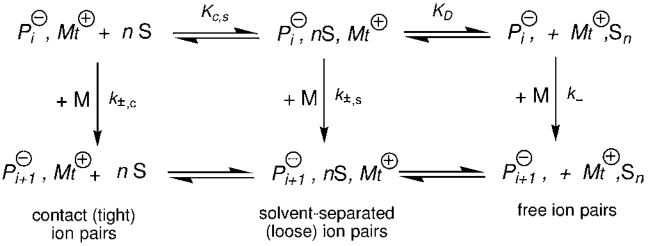


Figure 1.4 Arrhenius plot of the ion pair propagation rate constant in the polymerization of styrene with sodium counterion in polar solvents. (Reprinted with permission from Elsevier [87, 92].)

the Arrhenius plots of the ion pair propagation rate constants, $k_{\pm}$, for various solvents, exhibiting strongly *S-shaped* curves. In DME and THF, the rate constants even increase with decreasing temperature, which would lead to an apparently negative activation energy. Independently, Arest-Yakubovich and Medvedev found that the propagation rate of polybutadienylsodium in THF is independent of temperature below −56 °C and attributed this to a change in the structure of Na^+ solvation [90]. These results suggested the participation of another temperature-dependent equilibrium between two kinds of ion pairs, identified as contact ion pairs and solvent-separated ones [81, 91] (Scheme 1.5). The existence of solvent-separated ion pairs as distinct thermodynamically stable species was already outlined in Section 1.2.



Scheme 1.5 Three-state mechanism of styrene polymerization involving contact- and solvent-separated ion pairs and free anions with $k_{\pm,c} \ll k_{\pm,s} < k_-$.

Here, the overall (experimental) ion pair rate constant, $\overline{k_\pm}$, is given by

$$\overline{k_\pm} = \frac{k_{\pm,c} + K_{c,s} \cdot k_{\pm,s}}{1 + K_{c,s}} \approx K_{c,s} \cdot k_{\pm,s} \tag{1.10}$$

where $K_{c,s}$ is the equilibrium constant for the interconversion of contact(c)- to solvent-separated(s) ion pairs and typically $K_{c,s} \ll 1$. This interconversion is exothermic since the polarity of the solvent increases with decreasing temperature. Thus, at low temperature, the more reactive solvent-separated ion pairs are favored and the overall rate constant increases until the majority of monomer additions occur via the solvent-separated ion pairs.

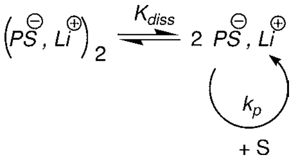
In dioxane, a poorly solvating medium, such a behavior was not observed, whereas in the strongly solvating medium, hexamethylphosphortriamide (HMPA), only solvent-separated ion pairs are found, which supports the above argument that the participation of different types of ion pairs depends on the polarity of the solvent.

In the presence of cesium counterions the participation of *triple ions* was observed in propagation. Results are reviewed by Smid *et al.* [93].

1.4.3
Polymerization of Styrene in Nonpolar Solvents: Aggregation Equilibria

1.4.3.1 Polymerization in Pure Solvents

Initiation and propagation of styrene and diene monomers in hydrocarbon solvent are significantly influenced by the aggregates of alkyllithium compounds [16, 94]. The nature of the alkyl group governs the degree of aggregation. Studies related to the kinetics of polymerization of *styrene* in benzene using *n*-BuLi as initiator began with the work of Worsfold and Bywater in 1960 [95]. The reaction order with respect to propagating anions is 0.5 in benzene, toluene, and cyclohexane [96–99]. This indicated that the growing polystyryllithium anions exist as less reactive dimers in equilibrium with reactive unimers in hydrocarbon solvents. Since the dissociation of lithium ion pairs into free ions is not possible in nonpolar solvent, the assumption



Scheme 1.6 Dimers and unimers in the anionic polymerization of styrene in nonpolar solvent.

of less active dimeric aggregates with coexisting minute amounts of reactive unimer was accepted as a plausible mechanism (Scheme 1.6).

Since the MWD of the polymers is very narrow, the interconversion rate between dimer and unimer must be very high relative to the propagation. As a result, a unimer with high reactivity dominates the propagation in the anionic polymerization of styrene in hydrocarbon solvents. The apparent rate constant of propagation (i.e., the slope of the first-order time-conversion plot) is given as

$$k_{\mathrm{app}} = k_{\mathrm{p,exp}}[P^*] = k_{\mathrm{p}}[\mathrm{P^-Li^+}] = \alpha k_{\mathrm{p}}[P^*] \tag{1.11}$$

where the fraction of unimers, α, is given as

$$\alpha = \frac{[\mathrm{P^-Li^+}]}{[(\mathrm{P^-Li^+})_2] + [\mathrm{P^-Li^+}]} \approx \frac{[\mathrm{P^-Li^+}]}{[P^*]/2} = \sqrt{K_{\mathrm{diss}}/2[P^*]} \ll 1 \tag{1.12}$$

and K_{diss} is the dissociation constant of the dimers to unimers. This leads to

$$k_{\mathrm{app}} = k_{\mathrm{p}}(K_{\mathrm{diss}}/2)^{1/2}[P^*]^{1/2} \tag{1.13}$$

Studies of Morton and coworkers on the viscosity of living polystyryllithium supported the existence of dimeric association [6]. They found that the viscosity of high molecular weight living polystyryllithium solution was 10 times higher as compared to the solution after termination with a drop of methanol. Since the viscosity of a semidilute polymer solution is proportional to $M^{3.4}$, association of two living polymer chains should lead to a viscosity increase by a factor of $2^{3.4}$, ~10.5. Light scattering studies of living and terminated chains confirmed this observation [68, 100].

1.4.3.2 **Polymerization in Nonpolar Solvent in the Presence of Ligands**

Lewis Bases (σ-Ligands) Owing to their ability to solvate lithium ions, electron donors, such as ethers or amines, have a dramatic effect on the polymerization of styrene in nonpolar solvents. The addition of THF to the polymerization of styrene in benzene strongly increases the rate of polymerization [101, 102]. When adding more than one equivalent of THF, the rates decrease and level off to a level that is higher than the original one (Figure 1.5). This was explained by the formation of two new species, the very reactive monoetherate and a less reactive dietherate, as seen in Scheme 1.7.

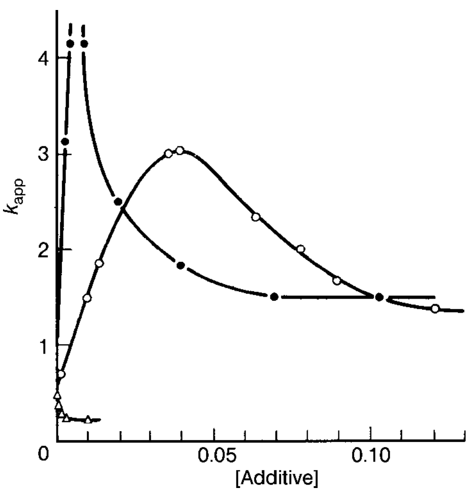


Figure 1.5 Effect of THF (●), 1,4-dioxane (○), and lithium *tert*-butoxide (△) on the polymerization of styrene in benzene, $c = 10^{-3}$ M [102]. (Reprinted with permission from the Canadian Society for Chemistry.)

$$(P\text{-}Li)_2 + 2\,\text{THF} \rightleftharpoons 2\,P\text{-}Li\cdot\text{THF} \xrightleftharpoons{2\,\text{THF}} 2\,P\text{-}Li\cdot 2\,\text{THF}$$

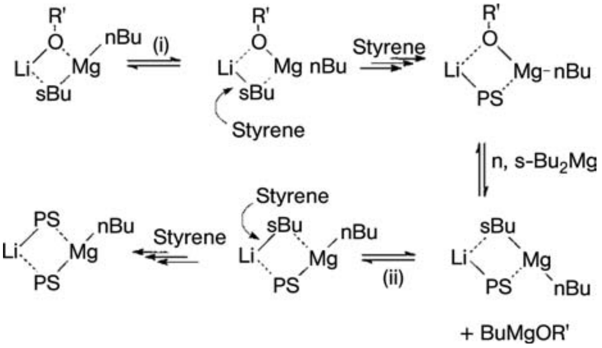
Scheme 1.7 Equilibria in the polymerization of styrene in benzene in the presence of THF.

Depending on the concentration, tertiary amines such as N, N, N', N'-tetramethylethylenediamine (TMEDA) can lead to an increase or decrease in the rate of polymerization [24, 103]. This is due to the fact that the reaction order in the absence of TMEDA is 1/2, whereas it is unity in its presence. The two lines of a plot of log $k_{\text{p,exp}}$ vs. log c intersect at a certain critical concentration.

Nonpolar ligands with high electron density, such as durene (tetramethylstyrene) or tetraphenylethylene, also affect the aggregation equilibrium and lead to an increase in the rate of polymerization followed by a decrease at higher concentrations. This is explained in terms of the formation of 1 : 1 and 2 : 1 π-complexes with the living chain ends [104].

Lewis Acids (μ-Ligands): Retarded Anionic Polymerization Lewis acids such as alkyl aluminum, alkyl zinc, alkyl magnesium, and lithium alkoxides form mixed aggregates with living chain ends of carbanions and significantly stabilize the ion pairs. In general, the addition of lithium alkoxides and other Lewis acids decreases the rate of polymerization of styrene and dienes (Scheme 1.8) [101, 105–107]. Since lithium alkoxides are even more strongly aggregated than the polystyryllithium chain ends, this leads to the formation of mixed aggregates (μ-complexes).

Addition of lithium chloride leads to a complex behavior, which was explained by the formation of mixed triple ions. These results are reviewed by Smid *et al.* [93].



Scheme 1.8 Mechanism of retarded anionic polymerization of styrene in the presence of dibutylmagnesium [109].

Alkali metal alkoxides (with Li, Na, and K counterions) also strongly affect the stereoregulation of diene polymerization as well as reactivity ratios in the copolymerization with styrene [16, 108].

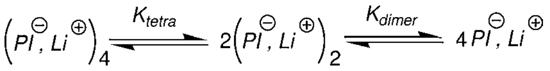
More recently, Deffieux and his collaborators have used a variety of magnesium and aluminum alkyls to retard the polymerization of styrene and at the same time stabilize the chain ends so significantly that they conducted the polymerization in bulk at temperatures of 100 °C and higher [110, 111]. They proposed a mechanism (Scheme 1.8) that involves the formation of mixed aggregates (''ate'' complexes). They also showed that a combination of various alkali hydrides and magnesium or aluminum alkyls can be used to efficiently initiate the polymerization of styrene [109, 112, 113] and butadiene [114]. These results present a significant progress, enabling an industrial polymerization of styrene with inexpensive initiators in conventional reactors.

1.4.4
Anionic Polymerization of Dienes in Nonpolar Solvent

1.4.4.1 Kinetics

The anionic polymerization of dienes proceeds without side reactions in hydrocarbon solvents. Kinetic measurements indicated that the propagation is fractional order with respect to the active chain-end concentration [6, 48, 96, 99, 107, 115–119], again supporting the presence of inactive aggregated species. The reaction order with respect to the active center concentration was observed to be in the range of 0.16–0.25 for butadiene [16, 22], indicating hexameric or tetrameric aggregates. Viscosity studies gave ambiguous results, hinting to dimeric aggregates [120].

The aggregation number of living polyisoprenyllithium in benzene depends on the concentration of active centers [121]. The reaction order with respect to active center changes from ~0.25 to ~0.5 with decreasing concentration



$$\left(\overset{\ominus}{PI},\overset{\oplus}{Li}\right)_4 \overset{K_{tetra}}{\rightleftharpoons} 2\left(\overset{\ominus}{PI},\overset{\oplus}{Li}\right)_2 \overset{K_{dimer}}{\rightleftharpoons} 4\,\overset{\ominus}{PI},\overset{\oplus}{Li}$$

Scheme 1.9 Aggregation equilibrium of polyisopropenyllithium in hydrocarbon solvent.

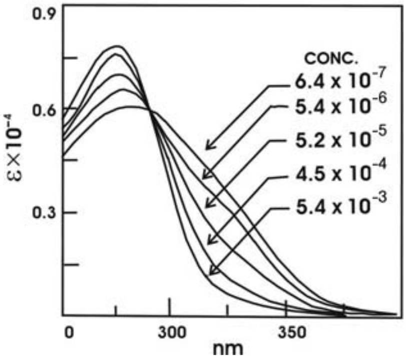


Figure 1.6 UV spectra of living polyisoprenyllithium in benzene solution at various concentrations [123]. (Reprinted with permission from Elsevier.)

[122], indicating a tetramer–dimer aggregation equilibrium (Scheme 1.9). The ultraviolet (UV) spectra of various concentrations exhibit two distinct absorptions at ~275 and ~325 nm with an isosbestic point, indicating a stoichiometric relation between the species formed at high and low concentration (Figure 1.6) [123].

There has been a long-standing, controversial debate in the literature on the nature of the active species in nonpolar solvents based on conflicting evidence from kinetics and direct observation of aggregation by viscosity, light scattering, and small-angle neutron scattering (SANS). SANS results of Fetters and coworkers indicated the existence of huge cylindrical micellar aggregates of polydienyllithium along with dimers and tetramers in dilute solution supporting their claim that dimers are the active species in polymerization [124–127]. These claims were questioned by others [128, 129]. In a recent SANS study, Hashimoto and his coworkers did not find evidence for the presence of such a large aggregates [130].

1.4.4.2 **Regiochemistry**

The regioselection of the diene addition to the ion pairs is controlled by the position of counterion (in particular lithium) and their coordination with incoming monomer, leading to different proportions of 1,2-, 3,4-, and 1,4-addition (the latter in cis or trans). For rubber applications, a high *cis*-1,4 content is important for a low glass transition temperature. This is achieved in nonpolar solvents and low temperatures. Ion pairs with counterions other than lithium have less effect on regiochemistry. The lithium ion undergoes specific solvation due to a short interionic distance compared to bulker metals.

Polar solvents or the addition of Lewis bases in hydrocarbon solvent occupy the coordination sites around the lithium ion and hinder monomer addition to the chain end. Instead, addition in the γ position is favored, leading to an increased fraction of 1,2-units (Scheme 1.10) [16].

The delocalization of ion pairs depends on the extent of solvation of counterion, and hence 1,2-addition of diene increases with increasing concentration of Lewis bases. As an example, equimolar amounts relative to the chain-end concentration of bispiperidinoethane can shift the structure of polybutadiene formed in hexane at room temperature from ~8% 1,2-units to ~99% [131]. More details of the effect of polar additives on the stereochemistry of polydiene and the kinetics of diene polymerization in nonpolar solvent can be found in the textbook of Hsieh and Quirk [16].

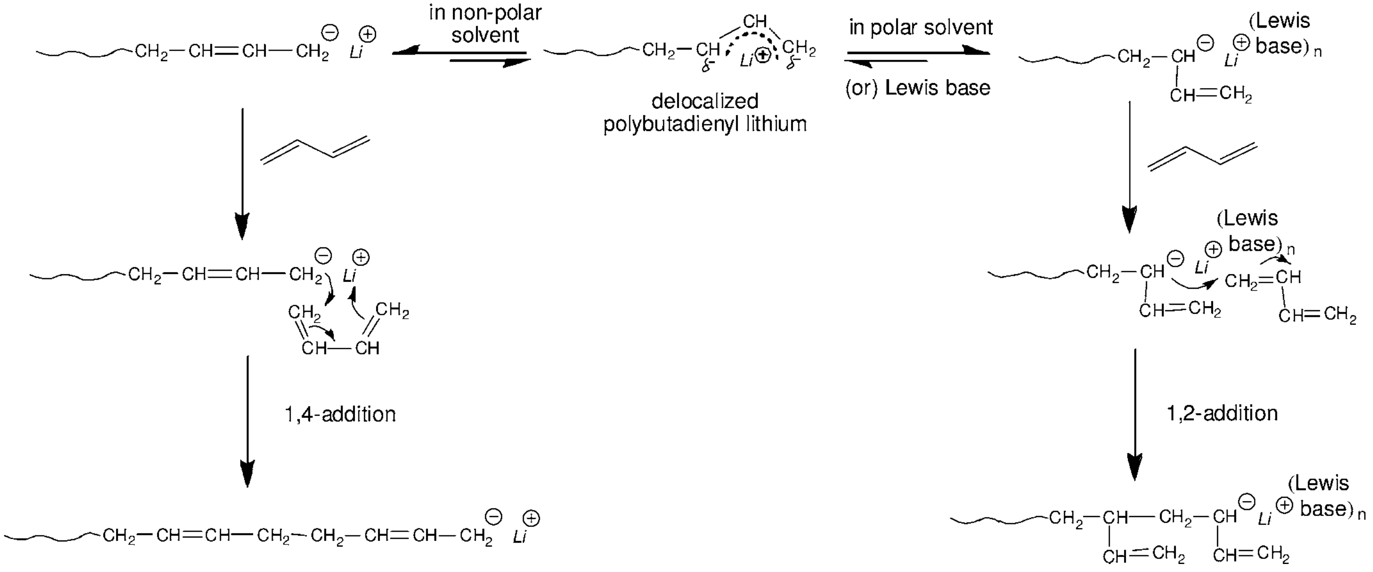
Many more mechanistic details, as well as the regio- and stereochemistry of diene polymerization (mechanism of formation 1,4-*cis* and *trans* isomers), and the kinetics of copolymerization of styrene with dienes can be found in a number of reviews and books [16, 22, 33, 92–94, 132–139].

1.4.5
Architectural Control Using Chain-End Functionalization

Architectural control through coupling of macrocarbanion chain ends opens endless possibilities in anionic vinyl polymerization to produce various type of branched homo or block copolymers (Figure 1.7). Termination of polymeric carbanions, especially, polystyryl and polydienyl, using chlorosilane reagents in nonpolar solvent is an efficient way to produce block and star copolymers. The coupling of chlorosilane with polymeric anion proceeds in a controlled manner through step by step elimination of halogen [140, 141]. Mays and Hadjichristidis and their coworkers pioneered chlorosilane coupling chemistry and synthesized various types of branched polymers, consisting of miktoarm stars, H-shaped polymers, multigrafts, and dendrimers [140, 142–144]. Similarly, Hirao, Quirk, and many others used alkylhalide-functional 1,1-diphenylethylene (DPE) as electrophilic coupling reagent to functionalize polymers to form macromonomers with DPE end group [145–150]. Through successive reinitiation and termination of DPE-functionalized chains, it is possible to synthesize well-defined stars, dendrimers, and hyperbranched polymers and copolymers. More details can be found in Chapter 7.

1.5
Mechanism of Anionic Polymerization of Acrylic Monomers

The most important classes of acrylic monomers are alkyl acrylates and methacrylates. Since some of their polymers, in particular poly(methyl methacrylate) (PMMA), are commercially very important, their polymerization



Scheme 1.10 Anionic propagation of 1,3-butadiene in nonpolar and polar medium and the control of microstructures through delocalization of ion pairs.

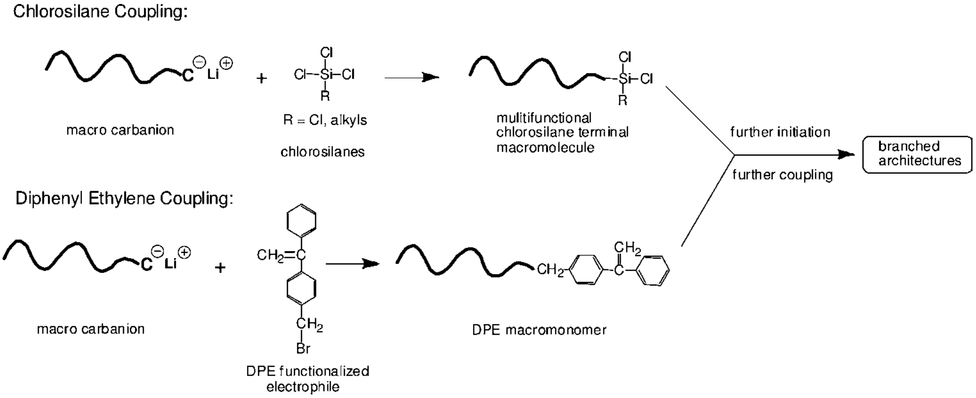


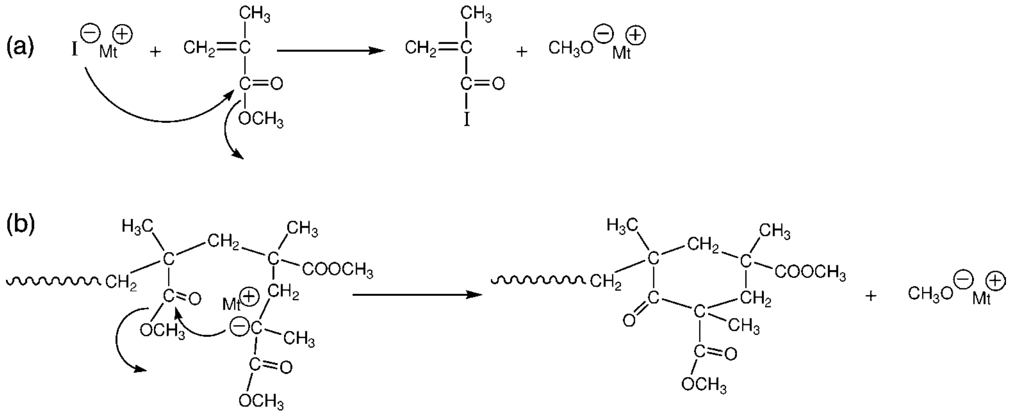
Figure 1.7 Strategies for the synthesis of various branched homo and block copolymer architectures using coupling reactions of multifunctional chlorosilanes and functional diphenylethylenes with polymeric carbanions.

has been investigated in great detail with respect to both kinetics and stereochemistry. More recently, the polymerization of *N*, *N*-dialkylacrylamides has found interest due to the interesting solution properties of the corresponding polymers and their dependence on tacticity.

1.5.1
Side Reactions of Alkyl (Meth)acrylate Polymerization

The initiation of alkyl (meth)acrylates with classical initiators like butyllithium is not straightforward and proceeds with several side reactions, yielding polymers of broad MWD with low conversion [151–158]. The nature of solvent and the size of cation influence the course of alkyl (meth)acrylate polymerization significantly. It proceeds in a controlled way in polar solvents with appropriate initiators (see above) at temperatures below −60 °C. In nonpolar solvents, the polymerization is complicated with incomplete monomer conversion and broad MWD. The occurrence of such side reactions has been experimentally confirmed by many authors [156–167]. The nonideal behavior of alkyl (meth)acrylates is basically due to two facts:

1. Side reactions by the nucleophilic attack of the initiator or the active chain end onto the monomer or polymer ester group, as proposed by Schreiber [152] and Goode *et al.* [61, 154] (Scheme 1.11a) and the intramolecular backbiting reaction (Scheme 1.11b).
2. Aggregation of the active chain ends, having an ester enolate structure. In contrast to nonpolar monomers, this occurs even in polar solvents such as THF and the consequences are discussed below.



Scheme 1.11 Side reactions in the polymerization of methyl methacrylate: (a) Initiator attack onto the monomer ester group and (b) backbiting reaction of propagating enolate anion.

The main termination reaction during *propagation* is the attack of the propagating enolate anion into the antepenultimate ester carbonyl group forming a cyclic β-ketoester (Scheme 1.11b) that was identified by infrared (IR) spectroscopy as a distinct band at 1712 cm^{-1} [154]. Evidence for the formation of vinylketone chain ends, the elimination of unreactive methoxide, and the formation of β-keto cyclic ester through the backbiting reaction was documented by several authors [154, 159–162, 168–172]. The side reactions were substantially reduced by using bulky and delocalized carbanions or Grignard reagents as initiators [161, 173–178]. 1,1′-Diphenylhexyllithium (DPHLi), the addition product of butyllithium and 1,1-diphenylethylene (DPE) [173], a nonpolymerizable monomer, diphenylmethyl [174], triphenylmethyl [60] and fluorenyl [179] anions have been used for the controlled polymerization of (meth)acrylates.

Ester enolates, in particular alkyl α-lithioisobutyrates, were introduced as initiators for methyl methacrylate (MMA) polymerization in polar and nonpolar solvents by Lochmann *et al.* [171, 180, 181]. As these initiators can be considered as a model for the propagating species in the anionic polymerization of alkyl (meth)acrylate, the rate of initiation and propagation was expected to be similar, which, in turn, should lead to polymers with narrow MWD. However, the ester enolate-initiated polymerization of MMA exhibited incomplete initiator efficiency, attributed to the presence of a higher degree of aggregation in both polar and nonpolar solvents [170, 181].

Using delocalized anions and large counterions (e.g., cesium), alkyl methacrylates can be polymerized in polar solvents, especially in THF or DME, at low temperature. However, with lithium as counterion, only moderate control is achieved. This is even worse for alkyl acrylates, in particular *n*-alkyl esters.

Several new initiating systems have been identified during the last two decades for the living polymerization of alkyl (meth)acrylates [182]. There are three main approaches employed for achieving living polymerization:

1. Use of various σ-type (Lewis base) and μ-type (Lewis acid) ligands that can form complexes with the counterion or with the propagating ion pair. This leads to a favorable aggregation dynamics for ligand-complexed ion pairs.
2. Use of nonmetal counterions. This class includes *group transfer polymerization* (GTP) with silyl ketene acetals (silyl ester enolates) as initiators and *metal-free anionic polymerization* using initiators with, e.g., tetrabutylammonium and phosphorous-containing counterions. This suppresses aggregation of ion pairs.
3. Coordinative-anionic systems involving aluminum porphyrin and zirconocene or lanthanocene initiators. This eliminates the ionic character of the propagating enolate and provides control of the polymerization through coordinative monomer insertion.

All these initiating systems enhance the livingness of the alkyl(meth)acrylate polymerization to varying degree to suppress secondary reactions and to achieve manipulations of active chain ends such as chain extension, block copolymerization, and functionalization. In addition, they moderate the position and the dynamics of the association equilibrium. The details of the polymerization of alkyl(meth)acrylates using these new initiating systems have been reviewed in detail by Baskaran [182]. Hence, we will briefly describe the behavior of classical enolate ion pairs, and then examine the newly developed strategies for the advancement of alkyl (meth)acrylate polymerization.

1.5.2
Alkyl (Meth)acrylate Polymerization in THF

1.5.2.1 Propagation by Solvated Ion Pairs

First mechanistic investigations of a living polymerization of MMA were published by Roig *et al.* [183, 184], Löhr and Schulz [185, 186], and Mita *et al.* [187] using sodium or better cesium counterions in THF at low temperature. Schulz, Höcker, Müller, *et al.* studied the effect of different counterions (Li^+, Na^+, K^+, and Cs^+) in the anionic polymerization of MMA in THF [179, 185, 188–191] and found living behavior at low temperatures (indicated by linear first-order time-conversion plots, linear plots of DP_n vs. conversion, and narrow MWD). They also observed a strong dependence of rate constants on the counterion size (except for K^+ and Cs^+; Figure 1.8) and obtained linear Arrhenius plots for the propagation rate constant, much in contrast to the kinetics of styrene polymerization in THF (Figure 1.4). Solvent polarity and

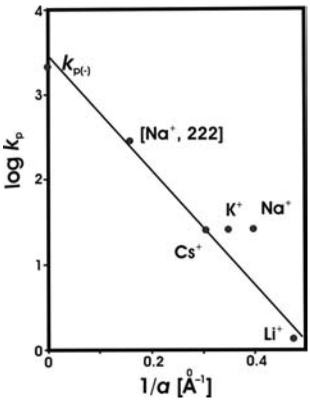


Figure 1.8 Dependence of propagation rate constant on the interionic distance, *a*, in the anionic polymerization of MMA in THF at −100 °C [191]. (Reprinted with permission from Wiley-VCH.)

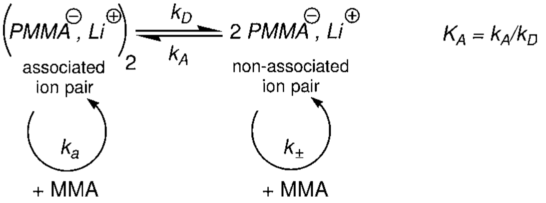
counterion size largely influence the rate of polymerization and affect the tacticity of the methacrylates [192].

The polymerization of MMA exhibits a good control in polar solvents such as THF and DME. *Glusker et al.* and Schulz *et al.* suggested that the polymerization is controlled due to the absence of intramolecular solvation of the counterion. In highly solvating media such as DME, the counterion is externally solvated with solvent coordination, thereby suppressing intramolecular termination via backbiting reaction at low temperature [155, 156, 189, 193]. Their results suggested that only one kind of active species is involved in the MMA polymerization, which they assigned as a peripherally solvated contact ion pair. Owing to a much stronger bond between the enolate oxygen and the counterion, solvent-separated ion pairs were not observed.

1.5.2.2 **Association of Enolate Ion Pairs and Their Equilibrium Dynamics**

The experimentally measured propagation rate constant, $k_{\mathrm{p,exp}}$, of the MMA polymerization for Li^+ and Na^+ counterions was found to decrease with increasing concentration of active centers, $[P^*]$ [194]. The participation of dissociated free enolate ion pairs in the propagation was rolled out as the addition of common ion salt had no or insignificant effect on the rate constants. Thus, the behavior was attributed to the coexistence of associated and nonassociated contact ion pairs propagating at two different rates.

Müller, Tsvetanov, and Lochmann found that the propagation rate constant of associated ion pairs, k_a, is much smaller than that of the nonassociated ion pairs, $k_\pm$, in alkyl (meth)acrylate polymerization (Scheme 1.12). The aggregation of chain ends was further confirmed by quantum-chemical calculations of ester enolates as models of chain ends [170, 195–197]. Aggregation of chain ends in a polar solvent is a feature that differs from the carbanionic ones, which associate only in nonpolar solvents.



Scheme 1.12 Equilibrium between associated and non-associated ion pairs.

The apparent rate constant of propagation, k_{app}, is determined by the rate constants of ion pair, $k_\pm$, the associates, k_a, and the fraction of nonaggregated species, α (Eqs. 1.14–1.16)

$$\begin{aligned} k_{\text{app}} &= [P^*]\left\{\alpha \cdot k_\pm + \frac{1}{2} \cdot (1-\alpha) \cdot k_a\right\} \\ &= [P^*]\left\{\frac{1}{2} \cdot k_a + \left(k_\pm - \frac{1}{2} \cdot k_a\right) \cdot \alpha\right\} \end{aligned} \tag{1.14}$$

and the fraction of nonassociated ion pairs, α, is given by [39, 196]

$$\alpha = \frac{[P_\pm{}^*]}{[P^*]} = \frac{(1 + 8K_A[P^*])^{1/2} - 1}{4 \cdot K_A[P^*]} \tag{1.15}$$

where K_A is the equilibrium constant of association. For $k_a[(P^*)_2] \ll k_\pm[P_\pm{}^*]$, Eq. (1.14) becomes

$$k_{\text{app}} \approx k_\pm[P_\pm] = \alpha k_\pm[P^*] = k_\pm \cdot \frac{(1 + 8 \cdot K_A \cdot [P^*])^{1/2} - 1}{4 \cdot K_A} \tag{1.16}$$

For a limiting case of high chain-end concentration, where $K_A[P^*] \gg 1$, Eqs. (1.15) and (1.16) become

$$\alpha = \frac{1}{\sqrt{2 \cdot K_A \cdot [P^*]}} \propto [P^*]^{-1/2} \tag{1.17}$$

$$k_{\text{app}} = \frac{k_\pm}{\sqrt{2 \cdot K_A}}\sqrt{[P^*]} \tag{1.18}$$

which leads to a reaction order of 0.5 with respect to $[P^*]$. For low chain-end concentrations, $K_A[P^*] \ll 1$, the aggregated ion pairs disappear ($\alpha \approx 1$) and $k_{\text{app}} \approx k_\pm \cdot [P^*]$, leading to a reaction order of unity with respect to $[P^*]$.

In fact, kinetic experiments of polymerization of MMA with lithium counterion in THF at −65 °C showed that the reaction order changes from 0.58 to 0.75 in the concentration range from 2.5 to 0.12 mM [197], allowing for the determination of $k_\pm$ and K_A and proving that aggregation is an important factor in the polymerization of alkyl (meth)acrylates in a polar solvent such as THF.

1.5.2.3 **Effect of Dynamics of the Association Equilibrium on the MWD**

The rate of interconversion between associated and nonassociated ion pairs in alkyl (meth)acrylate polymerization has a profound effect on the MWD of the polymer synthesized. Although the reactivity of aggregated lithium enolate chain ends is much lower than that of the nonassociated ones, a slow rate of interconversion between active species would allow both species to participate in propagation at two different rates. This leads to the formation of two different populations of polymers with a broad or bimodal MWD depending on the dynamics of the equilibrium. Broad or bimodal MWD was obtained in the polymerization of various (meth)acrylates with lithium counterion at −65 °C (Figure 1.9). Kunkel *et al.* [197] attributed the two peaks in the MWD of poly(*tert*-butyl acrylate) to aggregated and nonaggregated enolate chain ends. They also showed that the high polydispersity is not due to termination but due to the slow association phenomena.

Figini [88, 198] and others [199–202] have shown that, for a two-state mechanism, a slow exchange between various active (or between active and dormant) species leads to a broadening of the MWD (increase of polydispersity index, PDI) as given in Eq. (1.19):

$$\mathrm{PDI} = \frac{M_w}{M_n} = \left(\frac{M_w}{M_n}\right)_{\mathrm{Poisson}} + U_{\mathrm{ex}} \approx 1 + U_{\mathrm{ex}} \tag{1.19}$$

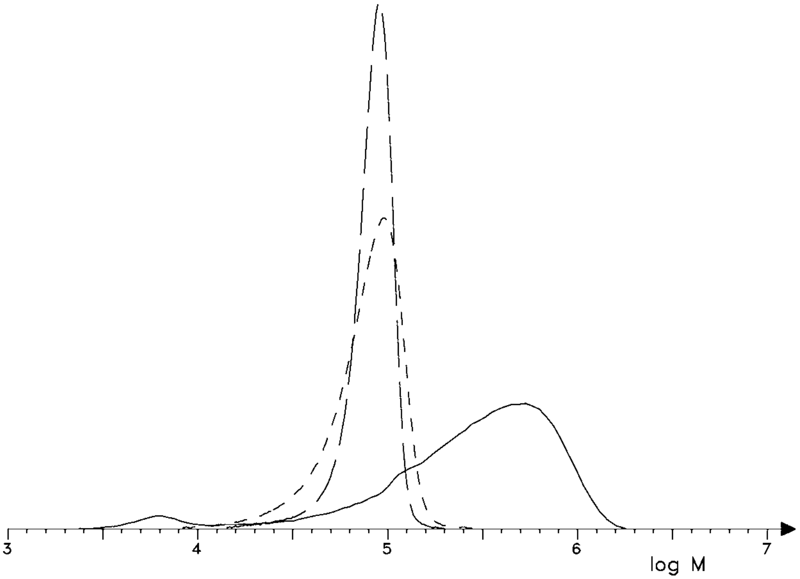


Figure 1.9 MWD obtained in the polymerization of MMA (·····, PDI = 1.3), *tert*-butyl methacrylate (-----; PDI = 1.1), and *tert*-butyl acrylate (——; PDI = 7.9) initiated by methyl α-lithioisobutyrate in THF at −65 °C [197]. (Reprinted with permission from Wiley-VCH.)

where U_{ex} is an additional nonuniformity that depends on the rate of exchange relative to the rate of propagation. The excess term, U_{ex}, is given by [203–205]

$$U_{\mathrm{ex}} \cong \frac{2\langle n\rangle}{\overline{\mathrm{DP}}_n} \tag{1.20}$$

where $\langle n\rangle$ is the number of monomer additions between two exchange processes, averaged over the whole polymerization process, and DP_n is the number-average degree of polymerization. At a given conversion, n is identical to the ratio of the rates of polymerization and association [197]:

$$n = \frac{R_{\mathrm{p}}}{R_{\mathrm{A}}} = \frac{k_{\pm}\cdot[M]\cdot[P^{*}{\pm}]}{k_{\mathrm{A}}\cdot[P^{*}{\pm}]^{2}} = \frac{k_{\pm}\cdot[M]}{k_{\mathrm{A}}\cdot[P^{*}{\pm}]} \tag{1.21}$$

Averaging of "n" over the monomer concentrations up to a given monomer conversion, x_{p}, gives

$$\langle n\rangle = \frac{k_{\pm}}{2\,k_{\mathrm{A}}\cdot[P^{*}{\pm}]}\cdot([M]+[M]_0) = \frac{k_{\pm}\cdot[M]_0}{2\,k_{\mathrm{A}}\cdot[P^{*}{\pm}]}\cdot(2-x_{\mathrm{p}}) \tag{1.22}$$

Introducing $\overline{\mathrm{DP}}_n = [M]_0 x_{\mathrm{p}}/[P^{*}]$ and combining with Eq. (1.20) leads to

$$U_{\mathrm{ex}} = \frac{k_{\pm}}{\alpha k_{\mathrm{A}}}(2/x_{\mathrm{p}}-1) \tag{1.23}$$

and Eq. (1.19) becomes

$$\frac{M_w}{M_n} = 1 + \frac{k_{\pm}}{\alpha k_{\mathrm{A}}}(2/x_{\mathrm{p}}-1) \tag{1.24}$$

For full monomer conversion ($x_{\mathrm{p}} = 1$), Eq. (1.22) becomes

$$\frac{M_w}{M_n} = 1 + \frac{k_{\pm}}{\alpha k_{\mathrm{A}}} \tag{1.25}$$

Thus, it is required to have high rates of association and high conversions to obtain polymers with narrow MWD in a polymerization system involving associated and nonassociated active species.

Kunkel *et al.* determined all the rate constants involved in this process [197]. They showed that the broad MWD obtained in the polymerization of *tert*-butyl acrylate (*t*BA) is only due to the fact that both the rate constants of association and dissociation are comparable to those for MMA polymerization, but that the rate constant of propagation is 50 times higher.

The concept of slow equilibria between various active and dormant species was later elaborated in more detail (including nonequilibrium initial conditions) and generalized to other kinds of exchange processes by Litvinenko and Müller [39, 206–209]. These calculations have been useful for various other living/controlled processes.

1.5.3
Modification of Enolate Ion Pairs with Ligands: Ligated Anionic Polymerization

The equilibrium dynamics of propagating ester enolate ion pairs in alkyl (meth)acrylates' polymerization both in polar and nonpolar solvents can be modified favorably in the presence of coordinating ligands. Several new ligands capable of coordinating with either the cation or the enolate ion pairs were reported in the literature. In general, the coordination of ligands with enolate ion pairs enhances the rate of interconversion between aggregated and nonaggregated chain ends, thereby altering the kinetics of propagation and to some extent suppressing the side reactions [174, 190, 210–226]. Wang *et al.* [227] have classified the coordination of ligands with enolate ion pairs into the following types:

1. σ-type coordination with Lewis bases such as crown ethers [212, 213], cryptands [190], or tertiary amines [216–219];
2. μ-type coordination with Lewis acids such as alkali alkoxides [228–231], lithium halides [197, 211, 232], lithium perchlorate [215, 233], aluminum alkyls [221–224], boron alkyls [225] and zinc alkyls [174];
3. $\sigma\mu$,-type coordination with alkoxyalkoxides [226, 234–236], aminoalkoxides [237], and silanolates [238].

1.5.3.1 Lewis Base (σ-Type) Coordination

The coordination of σ-type ligands such as various *tertiary diamines* (linear and cyclic) and cyclic ethers provides enhanced living character to alkyl (meth)acrylates polymerization through peripheral solvation depending on the sterics and number of coordination sites that are present in the ligand. The influence on the propagation and termination reaction varies on the strength of ligand coordination. For example, the addition of TMEDA was shown to increase the stability of the active centers of MMA polymerization in THF using the monomer resumption method [218] and in kinetic studies [216, 217]. The reaction order with respect to chain ends is 0.5, indicating that chelation of the lithium cation does not effectively perturb the aggregation state of the enolate ion pair. No significant difference in the rate of the polymerization was observed in the presence and in the absence of TMEDA at −20 °C. It was assumed that the chelation only replaces the THF molecules in the dimeric enolate ion pair retaining the peripheral coordination with lithium during propagation.

If a reactive initiator is used, it can metalate the ligand to mediate anionic polymerization. For example, the polymerization of MMA with *n*-butyllithium in pyridine or in a pyridine–toluene mixed solvent leads to monodisperse PMMA indicating a living character from −78 to −20 °C [219, 239, 240]. ^{1}H NMR showed the presence of the dihydropyridine end group in the polymer, indicating that the actual initiator is not the alkyllithium but an adduct with pyridine. In THF, a hindered alkyllithium initiator must be used to maintain molecular weight control.

Various *crown ethers* were used as ligands for the Na^+ counterion in the polymerization of MMA and *t*BA initiated by diphenylmethylsodium in toluene and in THF [212, 213]. The crown ethers substantially increase the monomer conversion, initiator efficiency, and improve the MWD of the resulting PMMA. It is assumed that the crown ether peripherally solvates the counterion, limiting the possibility of backbiting termination. No kinetic studies have been published so far.

Addition of *cryptand* 2.2.2 in the polymerization of MMA with Na^+ counterion in THF increases the propagation rate constants by orders of magnitude, indicating the presence of ligand-separated ion pairs [190].

Quantum-chemical calculations showed that a variety of structures can be formed by the various σ-ligands, including dimers and triple ions [241].

1.5.3.2 **Lewis Acid (μ-Type) Coordination**

Alkali alkoxides have a significant effect on the polymerization of alkyl (meth)acrylates [228–231]. Lochmann and Müller found that the addition of *lithium t-butoxide* strongly affects the rates of propagation and backbiting termination in the oligomerization of MMA [230] and *t*BA [242, 243] in THF at +20 °C (Figure 1.10). For MMA, the rate constant of propagation is decreased by one order of magnitude, but the termination rate constant is decreased by two orders. Thus, the enolate–alkoxide adduct has a 10 times lower tendency to undergo termination than the noncomplexed ion pair.

However, although *tert*-butoxide increases the livingness of polymerization, the MWD of the resulting polymers becomes broader [243], unless the alkoxide

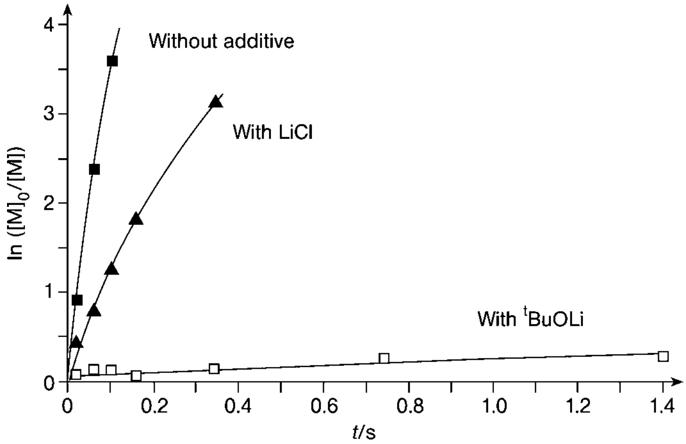


Figure 1.10 First-order time-conversion plots of the anionic polymerization of *tert*-butyl acrylate initiated by *tert*-butyl α-lithioisobutyrate in THF at +20 °C [243]. (Reprinted with permission from Wiley-VCH.)

is added in large (10 : 1) excess [244–246]. This is explained by the existence of various mixed tetrameric (or higher) aggregates in 3 : 1, 2 : 2, and 1 : 3 ratios of the enolate chain end and *t*-butoxide, which are in slow equilibrium with each other. In the 3 : 1 adduct, the degree of aggregation is even higher than in the noncomplexed dimer. Only in the presence of a large excess of alkoxide, the equilibrium is shifted to the side of the 1 : 3 adduct with only one kind of chain end.

Until the late 1980s, the controlled polymerization of alkyl acrylates had not been possible. Incomplete polymerization and very broad MWD (Figure 1.9) were reported. It was assumed that this might be due to both backbiting termination and a transfer reaction between the anion and a hydrogen alpha to an in-chain ester group. However, evidence for the latter has never been reported. In 1987, Teyssié and his coworkers [210, 247] reported for the first time the living anionic polymerization of *t*BA in THF in the presence of an excess of *lithium chloride,* leading to polymers with narrow MWD (Figure 1.11). It was assumed that the beneficial effect of LiCl is due to complexation with chain ends, which suppresses backbiting termination.

Kinetic experiments of Müller and coworkers, however, showed that LiCl affects the rate of propagation, but not the amount of termination [197, 242, 243]. The observed rate constant of propagation passes a slight maximum and then decreases with increasing LiCl/[P^*] ratio (Figure 1.12). Simultaneously, a strong decrease in the polydispersity index was observed with increasing concentration of LiCl. These observations were explained by the formation of 1 : 1 and 2 : 1 adducts of differing activity (Scheme 1.13). Quantum-chemical

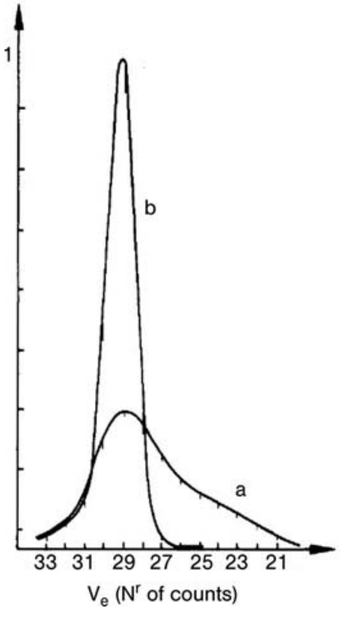


Figure 1.11 Size exclusion chromatography (SEC) traces of poly(*tert*-butyl acrylate) synthesized in the absence (a; PDI = 3.6) and in the presence of excess LiCl (b; PDI = 1.2) in THF using monofunctional α-methylstyryllithium as initiator [210]. (Reprinted with permission from the American Chemical Society.)

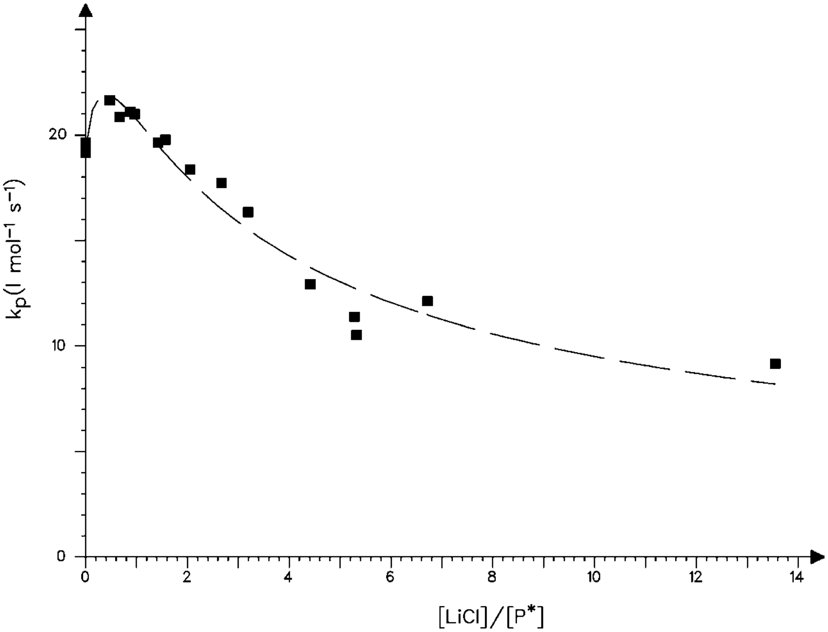


Figure 1.12 Effect of LiCl on the observed rate constant of polymerization in the anionic polymerization of MMA in THF at −65 °C initiated with methyl α-lithioisobutyrate. (Reprinted with permission from Wiley-VCH [197].)

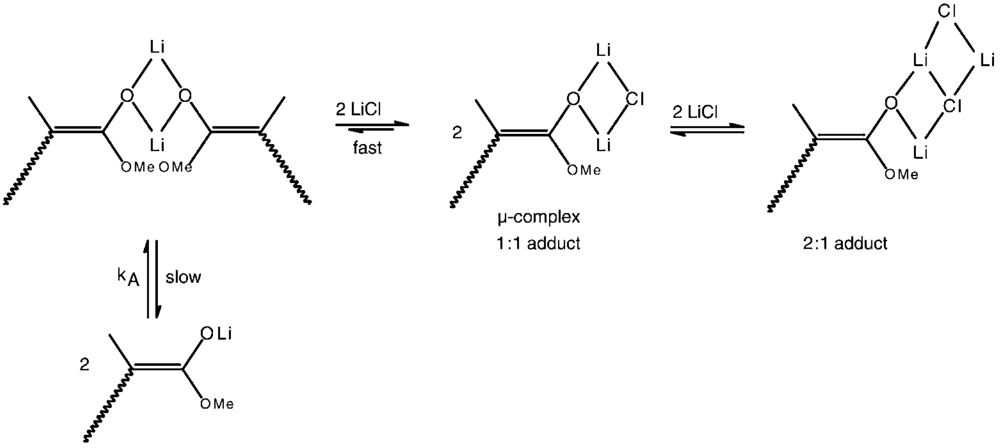
calculations confirmed that the 1 : 1 complex is more stable by 4 kJ mol^{-1} than the noncomplexed dimer [248]. The equilibrium between noncomplexed dimer and unimer is slow, whereas it is faster between the dimer and the LiCl-complexed unimer. The inefficiency of LiCl to control termination is demonstrated by the fact that one cannot control the polymerization on *n*-butyl acrylate (*n*BA) with this ligand. However, aluminum alkyls and σ, μ-ligands can lead to a living polymerization (see below).

Thus, the position of the equilibria between nonassociated, associated, and complexed ion pairs determines the rate of polymerization, whereas the dynamics of interconversion between species governs the polydispersity [197, 242, 243].

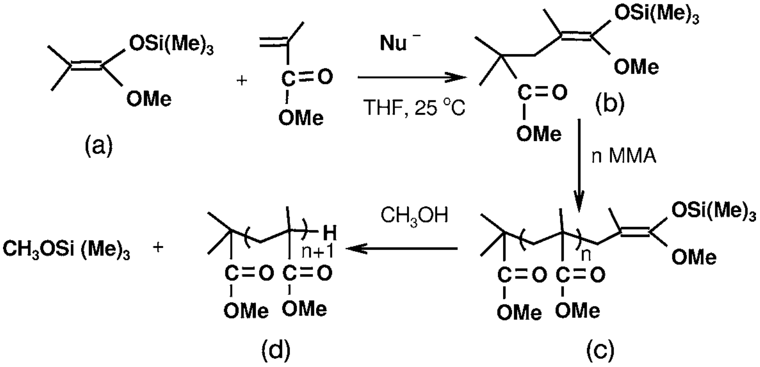
1.5.4
Metal-Free Anionic Polymerization

1.5.4.1 Group Transfer Polymerization (GTP)

In 1983, Webster and coworkers at DuPont demonstrated for the first time that a silyl ketene acetal (silyl ester enolate, Scheme 1.14a) is an initiator for the controlled polymerization of alkyl (meth)acrylates *at room temperature* [249].



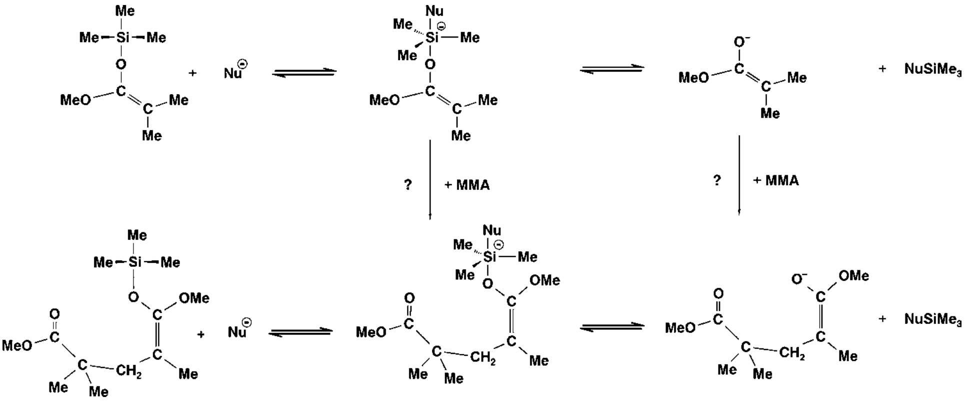
Scheme 1.13 Equilibria in the polymerization of (meth)acrylates in the presence of LiCl.



Scheme 1.14 Group transfer polymerization of MMA with nucleophilic catalyst.

The presence of a small amount of a nucleophilic or Lewis acid catalyst is necessary, leading to poly(alkyl methacrylates) with narrow MWD. The process was called *group transfer polymerization (GTP)* on the basis of the proposed mechanism, which involves the transfer of the trimethylsilyl group coordinated with a nucleophilic catalyst from the initiator or propagating chain end to the carbonyl oxygen of the incoming monomer (Scheme 1.14). It was proposed that the intramolecular transfer takes place via an eight-membered transition state in every insertion of monomer.

Various nucleophilic anions and Lewis acids have been identified as catalysts to promote GTP [249–257]. The relative efficiency of a nucleophilic catalyst strongly depends on the corresponding acidity (pK_a value) of the acid from which it is derived [251, 258, 259]. The Lewis acids are believed to activate monomers by coordination with carbonyl oxygen of acrylates, as indicated by the large amount of Lewis acid necessary (10% based on monomer) for a controlled polymerization [249, 260–262].

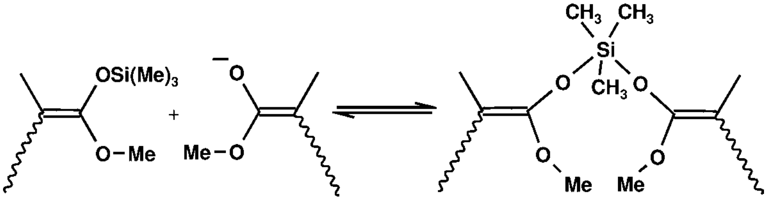


Scheme 1.15 Associative and dissociative mechanisms of GTP of MMA.

There has been a long discussion on the mechanism of GTP, which seems to depend on the type of catalyst used for the polymerization [251, 253, 259, 263–269]. This was originally proposed by Webster and Sogah. Double-labeling experiments supported a direct transfer of the pentacoordinated siliconate from a chain end to the incoming monomer's carbonyl group, named *associative* mechanism [270], though several questions related to this mechanism remained unanswered [271–276]. Kinetic experiments enabled Mai and Müller [259, 266, 277] to propose a modified two-stage associative mechanism in which the monomer adds to the α-carbon of pentacoordinated siliconate chain end and subsequently silyl group migration takes place to the carbonyl oxygen of the monomer. According to this mechanism, a fast exchange of catalyst between the dormant and active chain ends (Scheme 1.15, left equilibrium) is essential to have control on MWD. This exchange is essential because the catalyst concentration is typically in the range of 0.1–10% of that of the initiator concentration. They showed that the rate of polymerization is determined by the concentration of catalyst and the equilibrium constant of activation, whereas the polydispersity, if given by the dynamics of this equilibrium, is very similar to other living polymerization processes.

Quirk proposed a "dissociative" process where the pentacoordinated siliconate dissociates into an ester enolate anion and the corresponding trimethylsilyl–nucleophile compound (Scheme 1.15, right equilibrium) [272, 278]. The two equilibria ensure the necessary exchange of activity between dormant silyl ketene acetal and active enolate chain ends, leading to a control of molecular weight and MWD. Alternately, if dissociation is irreversible, the free enolate anion can exchange activity only in a direct reaction between an active enolate and a dormant silyl ketene acetal (degenerative transfer; Scheme 1.16) [272].

It is very important to note that the mechanism of GTP differs with the type of catalyst used for the polymerization. Moreover, it was found that



Scheme 1.16 Intermolecular activity exchange of an enolate anion with a silylketene acetal [272].

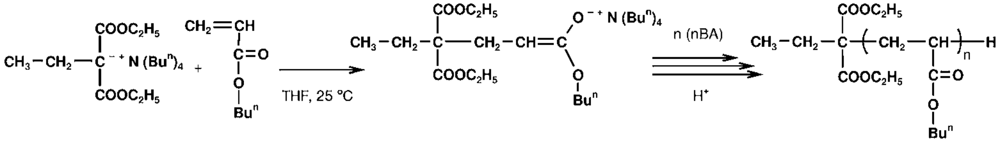
the reaction order with respect to catalyst concentration for the GTP of MMA obtained by different research groups varied depending on the nature of catalyst and its concentration [251, 253, 259, 266, 277]. Comparing the experimental data and the calculations of Müller, Litvinenko let to the conclusion that the mechanism of GTP strongly depends on the nature of the nucleophilic catalyst [39, 206–209, 268]. Catalysts that bind very strongly to silicon, such as bifluoride, seem to undergo an irreversible dissociative (enolate) mechanism, whereas less "silicophilic" catalysts, such as oxyanions, may add via both pathways.

The participation of enolate anions as intermediate during propagation goes along with the backbiting side reaction similar to classical anionic polymerization, although its significance is lower in GTP [279]. It was proposed that the silylalkoxide formed in the backbiting reaction might reversibly open the β-ketoester to reform the active chain end. The active centers of GTP of MMA undergo chain transfer reaction with various carbon acids ($18 < \mathrm{p}K_a < 25$) [264, 280], which indicated its higher reactivity analogous to ester enolate active centers ($\mathrm{p}K_a \sim 30-31$) (Table 1.1) [42] in the classical anionic polymerization.

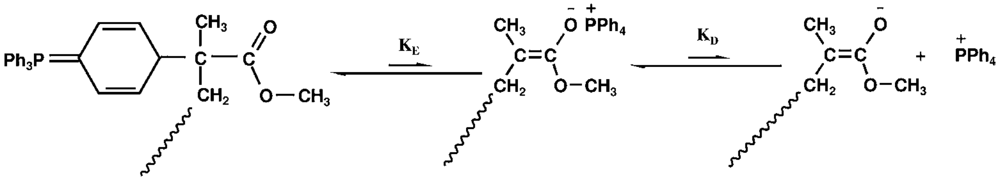
GTP has been used to synthesize a number of structures, including block copolymers [250], macromonomers [281], stars [282, 283], hyperbranched polymers [284, 285], or networks [286]. More detailed discussions on the mechanism and the applications can be found in a number of reviews on GTP [259, 287–290], in particular a very recent one by Webster [291].

1.5.4.2 Tetraalkylammonium Counterions

Reetz and coworkers [292–294] first used metal-free carbon, nitrogen, or sulfur nucleophiles as initiators for the controlled anionic polymerization of *n*BA. It was thought that replacing metal counterion in the polymerization would reduce the problem associated with aggregation and improve the control over the polymerization. Tetrabutylammonium salts of malonate derivatives provided poly(*n*-butyl acrylate) (P*n*BA) of relatively narrow MWD at room temperature (Scheme 1.17). Many metal-free initiators for the polymerization of alkyl (meth)acrylates using a variety of anions and cations have been reported [272, 295–299].



Scheme 1.17 Metal-free anionic polymerization of *n*BA with tetrabutylammonium counterions in THF at 25 °C.



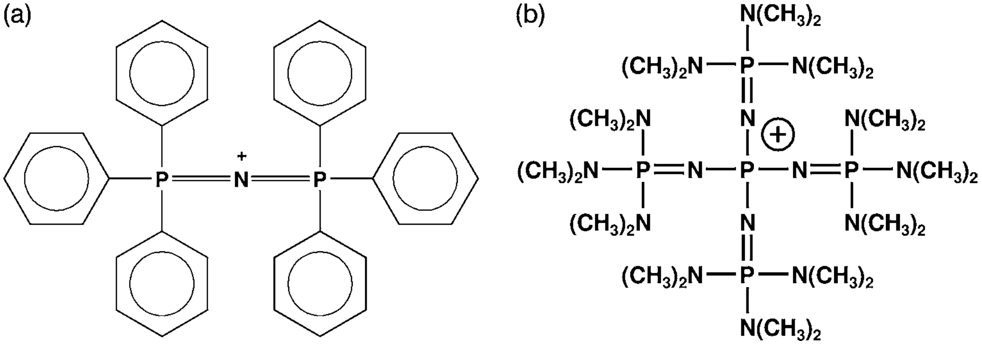
Scheme 1.18 Dynamic equilibrium between ylide, enolate ion pair, and enolate anion.

1.5.4.3 **Phosphorous-Containing Counterions**

Zagala and Hogen-Esch [300] used the tetraphenylphosphonium (TPP$^+$) counterion in the anionic polymerization of MMA at ambient temperature in THF and produced PMMA in quantitative yield with narrow MWD. Unexpectedly, the reaction solution during the polymerization was characterized by an orange-red color. A detailed kinetic study of the polymerization of MMA using trityl TPP$^+$ showed that the polymerization is very fast (half-lives at room temperature in the second range); however, the rate constants are two orders of magnitude lower than expected for such a large counterion [301]. It was concluded that the active centers exist in equilibrium with a dormant species. Nuclear magnetic resonance (NMR) and UV investigations on the model compound of the growing PMMA chain end, i.e., methyl tetraphenylphosphonium isobutyrate revealed the existence of a phosphor ylide as dormant species (Scheme 1.18) [302].

This system is different compared to tetrabutylammonium counterion as the phenyl group in the counterion undergoes nucleophilic attack by the enolate ion and forms ylide intermediate. The yilde is unstable and exists in equilibrium with enolate ion pairs. According to the kinetic and spectroscopic data, the fraction of active enolate chain ends is only 1%. The bis(triphenylphosphoranilydene)ammonium (PNP$^+$) cation (Scheme 1.19a) shows a lower tendency for ylide formation and leads to higher rates [303], whereas the (1-naphthyl)triphenylphosphonium (NTPP$^+$) cation has a strong tendency for ylide formation and propagates extremely slowly [304].

The phosphorous-containing cation that cannot form ylide, the tetrakis[tris (dimethylamino)phosphoranylidenamino] phosphonium (P$_5$$^+$) counterion (Scheme 1.19b) showed fast polymerization with the half-lives that are in the 0.1 s range and the rate constants are in the expected order of magnitude



Scheme 1.19 (a) PNP^+ and (b) $P_5{}^+$ cations.

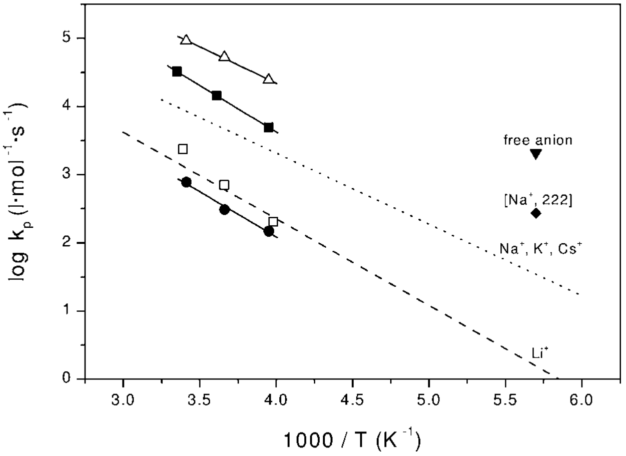


Figure 1.13 Arrhenius plot for the polymerization of MMA in THF with various counterions: (-----) Li^+; (·····) Na^+, K^+, Cs^+; (●) $Ph_3C^-TPP^+$ (K^+ precursor), (■) $Ph_3C^-PNP^+$ (K^+ precursor), (□) $Ph_3C^-PNP^+$ (Li^+ precursor), (△) $DPH^-P_5{}^+$ (Li^+ precursor) [303, 305]. (Reprinted with permission from Wiley-VCH.)

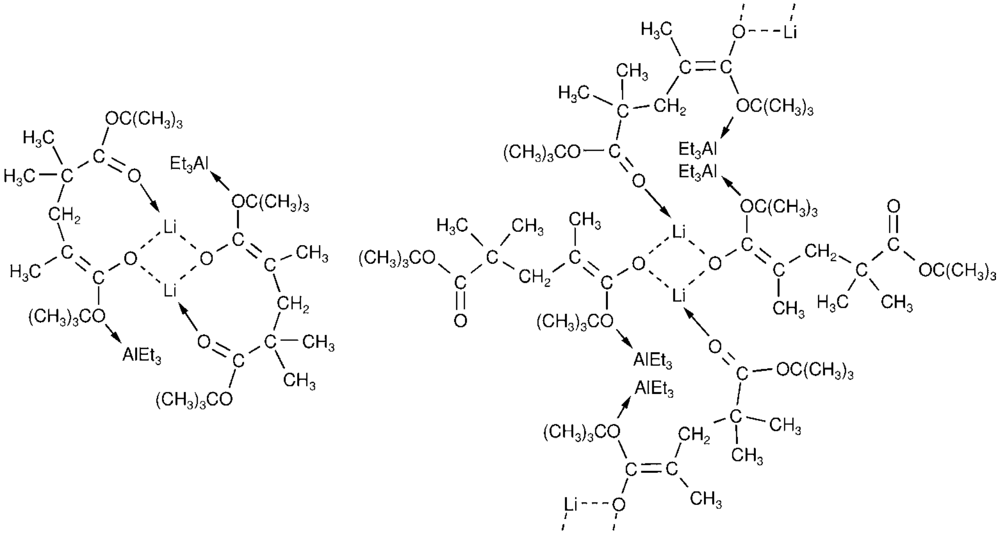
due to the absence of dormant ylide formation [305]. Figure 1.13 shows how these large counterions fit into the Arrhenius plot obtained with various metallic counterions, the cryptated sodium ion and the free anion. Quantum-chemical calculations have confirmed the ylide structure of various phosphorous-containing counterions [306].

1.5.5
Polymerization of Alkyl (Meth)acrylates in Nonpolar Solvents

In nonpolar solvents, the anionic polymerization of alkyl (meth)acrylates is complicated by the slow dynamics of the equilibria between multiple aggregates of ion pairs leading to very broad MWDs. In addition, it leads to more isotactic polymers, which have much lower glass transition temperatures than syndiotactic ones. Thus, a controlled polymerization has only been possible in the presence of ligands.

1.5.5.1 μ-Type Coordination

Hatada and coworkers [221, 307–311] first employed various aluminum alkyls, in particular triethylaluminum, Et_3Al, as additives and *tert*-butyllithium as initiator in the polymerization of MMA in toluene at −78 °C. They obtained syndiotactic polymers with controlled molecular weight and narrow MWD. The complexation of the aluminum compound with the initiator as well as the propagating center is essential to have a proper control of the polymerization. Ballard and his coworkers [222] demonstrated the living nature of MMA polymerization at ambient temperature in the presence of bulky diaryloxyalkyl aluminum. NMR and quantum-chemical investigations [312–314] on the model active center (i.e., ethyl α-lithioisobutyrate, EIBLi) in the presence of MMA and trialkylaluminum confirmed the coordination of the aluminum to the ester oxygen in the dimer of the lithium enolate. The mechanism is complicated by the fact that Et_3Al also forms complexes with the carbonyl groups of the monomer and the polymer. In addition, other carbonyl groups can coordinate with free coordination sites of the lithium atoms (Scheme 1.20). This leads to a physical gel at higher conversion and a downward kink in the time-conversion plot.



Scheme 1.20 Structures of intra- and intermolecular coordination leading to a coordinative network of living polymer chains in the presence of Et_3Al [314].

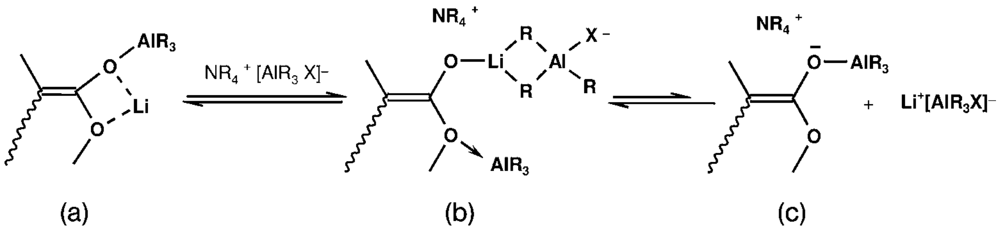
Schlaad *et al.* [223, 315] used several Lewis bases to attach to the free coordination sites of the lithium ion, thus suppressing the network formation during the polymerization. Linear first-order time-conversion plots with higher rates and polymers with much narrower MWD were obtained in the presence of excess methyl pivalate and methyl benzoate. A further improvement was the use of tetraalkylammonium halides as additives, forming a complex with trialkylaluminum, e.g., $NBu_4^+[Al_2Et_6Br]$. They observed linear first-order time-conversion plots using EIBLi as initiator in the presence of high concentration of $NBu_4^+[Al_2Et_6Br]$. The rate of the polymerization is two orders of magnitude higher as compared to the EIBLi/$AlEt_3$ initiating system in toluene/methyl pivalate (3 : 1 v/v) mixed solvent [224, 316]. Similarly, cesium halides can be used as co-ligand [317]. This system combines the advantages of a nonpolar solvent (toluene), convenient temperatures (−20 °C), with easily controllable rates (minutes to hours) and very narrow MWD (PDI < 1.1).

The rather complex kinetics of the process were attributed to an equilibrium between the trialkylaluminum–enolate complex (or its dimer) (Scheme 1.21a), a trialkylaluminum–halide–enolate "ate" complex with tetrabutylammonium counterion (Scheme 1.21b), and a tetraalkylammonium trialkylaluminum enolate (Scheme 1.21c) [314, 316].

This system is also useful for the controlled polymerization of *n*BA below −65 °C, in particular when using cesium fluoride/triethylaluminum as ligand [317, 318]. *n*BA had eluded a controlled anionic polymerization so far, except for the use of lithium alkoxyalkoxides as σ, μ-ligands (see below).

The triethylaluminum system was further modified by Kitayama's group who revived the Ballard system of bulky diphenoxyalkylaluminum ligands and found that these systems lead to a very high control of stereoregularity [319–321]. A further improvement was obtained by Hamada *et al.* by adding multidentate σ-ligands to these systems, allowing for the living polymerization of MMA and even *n*BA at 0 °C [322–325]. At present this system seems to be the most useful one to polymerize *n*-alkyl acrylates in a controlled way.

Recently, Ihara *et al.* reported the use of triisobutylaluminum in combination with potassium *tert*-butoxide for the living anionic polymerization of *t*BA and MMA in toluene at 0 °C [326, 327].



Scheme 1.21 Equilibria between various species in the polymerization of MMA in the presence of trialkylaluminum and tetraalkylammonium halide.

1.5.5.2 σ, μ-Type Coordination

Polydentate lithium alkoxyalkoxides and aminoalkoxides, as well as dilithium alkoxyalkoxides, have been used as powerful additives in the alkyl (meth)acrylate polymerization [214, 226, 234, 236, 237, 328]. In the presence of these ligands, living polymerization of even primary acrylates proceeded in a controlled manner in THF, in toluene, and in toluene–THF (9:1 v/v) mixed solvent at −78 °C [329]. The rate of MMA polymerization in the presence of lithium 2-methoxyethoxide (LiOEM) in toluene is extremely high ($k_p > 10^4\,\mathrm{l\,mol^{-1}\,s^{-1}}$) [236]. The polymerization proceeds with half-lives in the subsecond range without termination at 0 °C. Baskaran reported the use of dilithium triethylene glycoxide as ligand to achieve control over the living anionic polymerization of MMA using DPHLi as initiator at 0 °C [226], resulting in quantitative conversion, relatively narrow MWD ($1.29 \leq M_w/M_n \leq 1.37$), and high initiator efficiency ($0.81 \leq f \leq 1$). The enhanced living character brought by polydentate dilithium alkoxide ligand was attributed to the formation of a sterically hindered mixed aggregate whose equilibrium dynamics between the complexed ion pairs and uncomplexed ion pairs is high enough to produce narrow MWD PMMA at 0 °C [226, 236]. The complex structure of the chain end, involving tetrameric and hexameric aggregates with coordination of the ether oxygens with lithium, was also confirmed by quantum-chemical calculations [330]. This polymerization has been recently commercialized by Arkema (former Elf-Atochem) to synthesize polystyrene-*b*-polybutadiene-*b*-poly(methyl methacrylate) (SBM), where the PMMA block is synthesized in a flow-tube reactor [331].

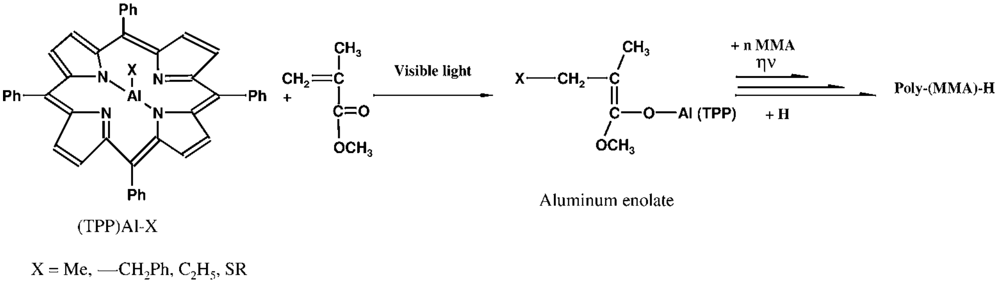
The polymerization of *n*BA is also living at −20 °C in the presence of LiOEM in toluene. The polymerization is so fast (half-lives in the millisecond range) that it can be controlled only in a flow-tube reactor [236].

1.5.6
Coordinative-Anionic Initiating Systems

1.5.6.1 Aluminum Porphyrins

Inoue and his coworkers found that methyl (tetraphenylporphyrinato) aluminum (TPP)AlMe initiates the living polymerization of alkyl (meth)acrylates upon irradiation by visible light (Scheme 1.22) [332]. PMMA was obtained in quantitative conversion and with narrow MWD ($1.06 < M_w/M_n < 1.2$).

The effect of light is observed not only in the initiation step but also in the propagation steps. NMR studies confirmed that the polymerization proceeds via a concerted mechanism, where the MMA coordinates to the aluminum atom leading to the conjugate addition of methyl group of initiator to monomer to form an aluminum enolate. Aluminum enolate once again coordinates with MMA and propagation occurs through a Michael addition process. Visible light accelerates this initiation and propagation to yield quantitative conversion. Later, it was found that the reaction can also be accelerated by Lewis acids,



Scheme 1.22 Aluminum porphyrin-initiated MMA polymerization.

presumably through monomer activation [333–337]. More details can be found in reviews by Aida [138] and Sugimoto and Inoue [338].

1.5.6.2 Metallocenes

Metallocenes with various rare earth central atoms, such as $((C_5Me_5)_2SmH)_2$ or the complexes derived from $(C_5Me_5)_2Yb(THF)_2$, show high catalytic activity in the polymerization of MMA in toluene between 40 °C and −78 °C, leading to syndiotactic PMMA with narrow MWD [339–341]. The living nature of the chain ends at room temperature was demonstrated by monomer resumption experiments. The living MMA dimer was crystallized and X-ray diffraction showed that the samarium central atom is coordinated to the enolate oxygen of the chain end and to the carbonyl group of the penultimate monomer unit. Later, it was shown that a living polymerization of acrylates can also be obtained [342]. More details can be found in a review by Yasuda [343]. Zirconocenes have also been used as initiators for the polymerization of (meth)acrylates [344, 345]. A review was recently published by Chen [346].

1.5.7
Polymerization of *N*,*N*-Dialkylacrylamides

Polymers of mono- and dialkylacrylamides are gaining increasing interest due to their thermoresponsive properties in aqueous solution [347, 348]. However, the anionic polymerization of *N*, *N*-dimethylacrylamide (DMAAm) and *N*, *N*-diethylacrylamide (DEAAm) in polar and nonpolar solvents using alkyllithium initiators is complicated due to the presence of slow aggregation dynamics of the propagating amido enolate ion pairs similar to ester enolate ion pairs in alkyl (meth)acrylate polymerization. Attempts were made to use different initiator in combination with coordinating ligands to control the polymerization and only minimum control on molecular weight, MWD, and the stereostructure of the polymers were obtained [349–354].

Major advances were reported by Nakahama *et al.* for the anionic polymerization of DMAAm and DEAAm by the use of organolithium and organopotassium initiators in the presence of Lewis acids (Et_2Zn and Et_3B) in THF [352, 355, 356]. Similarly, Et_3Al was used [353, 357]. The great influence of the system initiator/additive/solvent on the tacticity and the solubility of the resulting polymer was clearly demonstrated. The authors suggested that the coordination of the amidoenolate with the Lewis acid leads to a change of the stereostructure of the final polymer along with the retardation of the polymerization. Highly isotactic poly(*N*, *N*-diethylacrylamide) (PDEAAm) was obtained by using LiCl with organolithium initiator whereas highly syndiotactic and atactic polymers were obtained in the presence of Et_2Zn and Et_3B, respectively. Polymers rich in syndiotactic triads were not soluble in water whereas other microstructures lead to hydrophilic polymers [356]. Ishizone *et al.* reported the successful synthesis of poly(*tert*-butyl acrylate)-*b*-poly(*N*, *N*-diethylacrylamide) in THF at −78 °C. For that purpose, *t*BA was first initiated by an organocesium initiator (Ph_2CHCs) in the presence of Me_2Zn, and DEAAm was then initiated by the poly(*tert*-butyl acrylate)-Cs macroinitiator leading to a well-defined block copolymer ($M_w/M_n = 1.17$) [174].

André *et al.* performed kinetic studies on the polymerization of DEAAm in THF in the presence of triethylaluminum at −78 °C [358]. The kinetics of this process is very complex. It involves two equilibria: activation of monomer and deactivation of chain ends by Et_3Al. These two effects are in a delicate balance that depends on the ratio of the concentrations of Et_3Al, monomer, and chain ends. However, the initiator or blocking efficiencies of these systems remained low ($f < 0.70$). Quantum-chemical calculations on up to trimeric models confirm the various equilibria involved [359]. Et_3Al-coordinated, solvated unimers are the most stable species in the presence of Et_3Al, whereas unimers and dimers coexist in the absence of ligand.

Only one example was reported recently by Kitayama *et al.* for the polymerization of DMAAm in toluene. Living character was observed using a system based on *tert*-butyllithium/bis(2,6-di-*tert*-butylphenoxy)ethylaluminum in toluene at 0 °C [360]. Well-defined block copolymers PDMAAm-*b*-PMMA could be obtained in good yield, but no kinetic studies were performed.

Owing to their acidic proton, the direct anionic polymerization of *N*-monoalkylacrylamides such as *N*-isopropylacrylamide (NIPAAm) is not possible. By using *N*-methoxymethyl-substituted NIPAAm, Ishizone *et al.* synthesized well-defined polymers using organopotassium initiator in the presence of Et_2Zn, but no living character was described [361]. Kitayama *et al.* used *N*-trimethylsilyl-substituted NIPAAm to obtain highly isotactic polymers, but no MWDs were shown due to the poor solubility of the resulting polymers in common solvents [321]. However, these promising methods have opened new synthetic strategies to polymerize *N*-mono-substituted acrylamides with the advantages of anionic polymerization.

1.6
Some Applications of Anionic Polymerization

The application of anionic polymerization to synthesize macromolecular architectures, in particular polymers with various topologies has been reviewed in several reviews and books [16, 145, 362–365]. The polymerization of butadiene by alkali metals had been historically known since the early twentieth century. Synthetic rubberlike product called *Buna* (from the names of the chemicals used in its synthesis: butadiene and Natrium) was made in Germany and in the USSR during World War II using this process [366, 367]. In the 1950s, it was found that the use of lithium in hydrocarbon solvents for the polymerization of butadiene produces high content of *cis*-1,4 microstructure exhibiting better performance [368]. Since then, the anionic homo- and copolymerization of dienes has gained enormous importance in the manufacture of tires and other rubber products.

There is no doubt that the polymer industries and the fields of polymer physics and physical chemistry have benefited immensely from the development of special functional and block copolymers through anionic polymerization. Here, we would like to give some of the important and recent industrial applications of anionic polymerization. More details can be found in the textbook of Hsieh and Quirk [16] and in Chapter 10 of this book.

Various block copolymers consisting of incompatible block segments have been made available commercially by several companies. For example, ABA triblock copolymers of polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) and polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) were made by sequential addition of the monomers to butyllithium in hydrocarbon solvent [369]. These block copolymers and their hydrogenated analogs were sold by Shell under the trade name *Kraton*® and are now sold by Kraton Co. and others. Since the blocks are incompatible, they form microphase-separated structures, where the high-T_g outer polystyrene (PS) blocks form spherical or cylindrical domains in a matrix of the inner low-T_g diene blocks. This material is a thermoplastic elastomer, having rubberlike properties at room temperature, but being processable like a thermoplastic above the T_g of polystyrene. Hydrogenation of the diene block leads to structures resembling polyethylene (PE) or poly(ethylene-*alt*-propylene), which are more stable toward light and oxygen. These thermoplastic elastomers were originally designed to be used in the tire industry, but first applications came in footwear and later in other compounding applications, including automotive, wire and cable, medical, soft touch overmolding, cushions, as well as thermoplastic vulcanizates, lubricants, gels, coatings, adhesives, or in flexographic printing and road marking. Chapter 10 gives an exhaustive review on these materials.

BASF is marketing a variety of polystyrene-*b*-polybutadiene (PS–PB) star-block and star-tapered copolymers made by coupling four living PS–PB chains [370, 371]. With low PB content (*Styrolux*®), this material is used as a high-impact thermoplastic, with high PB content (*Styroflex*®) it is a highly

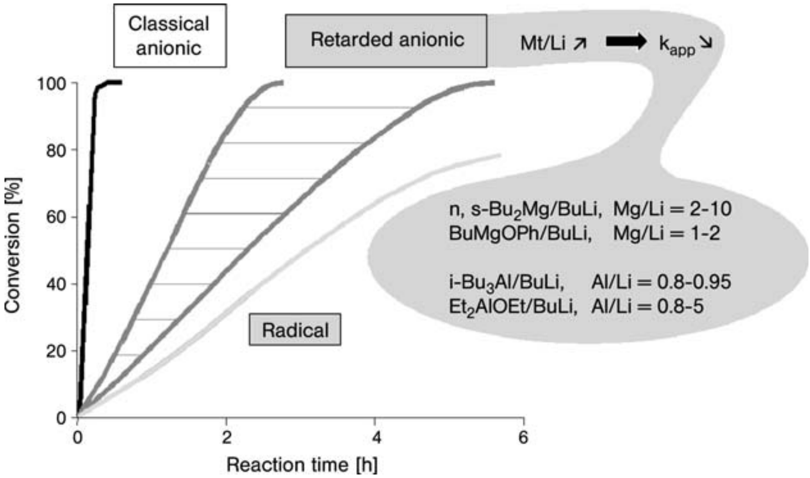


Figure 1.14 Time-conversion plots for a classical anionic (BuLi), retarded anionic and free-radical styrene polymerization: 15% ethylbenzene, $M_W = 450\,000$, $T_{start} = 120\,°C$ (Mt/Li range to reach an appropriate reactivity control) [373]. (Reprinted with permission from Wiley-VCH.)

flexible, transparent wrapping material. Similarly, a polystyrene-*b*-polyisoprene (PS–PI) star-block copolymer is produced by Phillips under the trade name *Solprene*®.

Several intermediate products are prepared by anionic polymerization and used in commercial formulations. For example, low *cis*-polybutadiene rubber is prepared by anionic polymerization (Dow, Mitsubishi, and other companies) and used for manufacturing high-impact polystyrene (HIPS). Recently, Dow has developed a new pentablock copolymer, consisting of hydrogenated PS and PB. Hydrogenation transforms the pentablock copolymer into a new polycyclohexylethylene (PCHE)–PE pentablock copolymer with glassy PCHE as hard blocks and ductile PE as soft blocks (PCHE–PE–PCHE–PE–PCHE). The copolymer has superior mechanical properties with low birefringence, moisture sensitivity, and heat distortion, and is undergoing market testing for optical applications [372].

The ''retarded anionic polymerization'' of styrene, initiated by lithium alkyls or even hydrides in the presence of aluminum and magnesium compounds (Section 1.4.3.2), patented by BASF, for the first time enables a commercial bulk polymerization of styrene at elevated temperatures above the glass transition temperature, T_g, of polystyrene, which might compete with the present radical process. In these bulk polymerizations, the rate is controlled by the ratio of aluminum or magnesium compounds to lithium (Figure 1.14).

Kuraray offers the ABA triblock copolymer PMMA-*b*-P*n*BA-*b*-PMMA as ''LA Polymer''. This is synthesized in the presence of diphenoxyalkylaluminum/Lewis acid combination described in Section 1.5.4.1. It is a thermoplastic elastomer and pressure-sensitive adhesive with excellent optical properties that is also used in nanostructure blends with polyesters.

Arkema sells the ABC triblock terpolymer SBM under the trade name *Nanostrength*®. This polymer is synthesized by sequential monomer addition in nonpolar solvent, where the PMMA block is made in the presence of an alkoxyalkoxide in a flow-tube reactor (Section 1.5.4.2). The material is used for the nanostructuring of epoxy blends and other commercial applications. Chapter 10 offers more details on the commercial applications of block copolymers.

In general, diblock copolymers and triblock terpolymers form a multitude of morphologies in the bulk. They have found use as compatibilizers for polymer blends [364]. In selective solvents, they can self-organize into spherical or cylindrical micelles, vesicles, and many more self-organized structures [363–365, 374–378]. The solution properties of various amphiphilic block copolymers have been explored in great detail as surfactants for emulsion polymerization [379], dispersants for pigments [291], drug carriers [380–382], or biomineralization agents [383]. Finally, the nanostructuring of surfaces by self-organization of block copolymers has led to a multitude of applications in nanotechnology [347, 364, 384–389]. These syntheses of various structures using different controlled/living techniques are discussed in detail in Chapter 8 and their properties in bulk and solution are discussed in detail in Chapter 9. In addition, anionic polymerization enables the synthesis of a number of polymer structures with nonlinear topologies, which are described in Chapter 7.

1.7
Conclusions and Outlook

Anionic polymerization is the oldest living/controlled polymerization and (maybe with the exception of some ring-opening polymerizations) the only one, which is living *and* controlled, at least for some monomers. The mechanisms of anionic polymerization of nonpolar and polar monomers are now well understood and an increasing number of monomers are available to be used in a living/controlled fashion; for example, primary acrylates, the polymerization of which had eluded control for more than 30 years. A number of important applications exist, but – except for rubber – not for the mass market, thermoplastic elastomers covering at least a niche market. This is partially due to the necessity of intensive purification of all reagents and low temperatures in some cases. Also, the number of accessible monomers is limited. Anyway, the possibility to construct complicated polymer structures in a well-defined way has inspired theoreticians and experimental physicists for more than 50 years now.

The advent of the other living/controlled techniques has challenged anionic polymerization as being the only mechanism for the synthesis of polymers with controlled structures. All mechanisms have their advantages and drawbacks: for example, controlled radical polymerization is easy to use with little effort for purification; a huge number of standard and functional monomers are accessible to homo- and copolymerization. On the other hand, when it comes to very high molecular weights, very low polydispersity and very precise block copolymer composition, in particular for nanotechnology applications, anionic polymerization is still in the lead. Thus, we hope that the various living polymerization mechanisms that have emerged during the last decades will coexist and help the synthetic chemist to construct even more sophisticated structures for future applications.

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2
Carbocationic Polymerization

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2.1
Introduction

The term *controlled polymerization* indicates ''control of a certain kinetic feature of a polymerization or structural aspect of the polymer molecules formed, or both'' [1]. The ultimate goal is to obtain a high degree of control over compositional and structural variables that affect the physical properties of macromolecules, including molecular weight, molecular weight distribution (MWD), end functionality, tacticity, stereochemistry, block sequence, and block topology, where the parameters of molecular characterization are well represented by the ensemble average.

Before the 1970s the elementary steps of carbocationic polymerization, i.e., initiation, propagation, chain transfer, and termination were uncontrolled because traces of moisture initiated the polymerizations, chain transfer to monomer was difficult to avoid, and the chemistry of termination was largely unknown. Controlled initiation and termination were discovered during the 1970s and they provided head- and end-group control and allowed the synthesis of block and graft copolymers and macromonomers. Controlled chain transfer appeared in the late 1970s when it was discovered that chain transfer to monomer could be avoided by employing certain Lewis acid coinitiators or by using proton traps. Another important step toward the total synthesis of tailor-made macromolecules was the development of the *inifer* technique by Kennedy. Controlled chain transfer to the *ini*tiator-trans*fer* agent allowed the preparation of well-defined telechelic polymers, block copolymers, and model networks. The discovery of quasiliving polymerization in 1982, where for the first time reversible termination (activation–deactivation) was postulated, heralded the new era of living cationic polymerization, which arrived a few years later.

Living polymerizations, which proceed in the absence of termination and chain transfer reactions, are the best techniques for the preparation of polymers with well-defined structure, and indeed, most of these polymers have been

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prepared using living polymerization. The resulting model polymers have extensively been used in validation of theories with respect to the properties in solution, melt, and solid states [2]. They have also served as excellent standard materials for systematic studies on structure/property relationships of macromolecules, lending an impetus to the major fields of material science and polymer physics. The foregoing activities are made possible by advances in modern synthetic methodologies, combined with state-of-the-art characterization techniques in material science.

The experimental criteria for living polymerizations have been critically reviewed [3]. In general, diagnostic proof for the absence of chain transfer and termination can be obtained from both linear semilogarithmic kinetic plot ($\ln([M]_0/[M])$ vs. time) and linear dependence of number average molecular weight (M_n) vs. monomer conversion (M_n vs. conversion). There are no absolute living systems and the careful control of the experimental conditions (counterion, temperature, and solvent) is necessary to obtain sufficient livingness to prepare well-defined polymers, especially when high molecular weights are targeted [4]. The original author of the seminal paper introducing the concept of living polymers concludes that "we shall refer to polymers as living if their end groups retain the propensity of growth for at least as long a period as needed for the completion of an intended synthesis, or any other desired task" [5]. This view has been adopted in this paper.

2.2
Mechanistic and Kinetic Details of Living Cationic Polymerization

A complete mechanistic understanding of cationic polymerization is fundamental for cationic macromolecular engineering and requires the knowledge of the rate and equilibrium constants involved in the polymerization process. Numerous previous kinetic studies of carbocationic polymerization, however, have generally failed to yield reliable rate constants for propagation (k_p). This is attributed to uncertainties involved in the accurate determination of the active center concentration, a consequence of our incomplete knowledge of the mechanism due to the multiplicity of possible chain carriers (free ions, ion pairs, and different solvated species) and the complexity of carbocationic reaction paths. Recently, new methods have been developed for the determination of rate and equilibrium constants in carbocationic polymerizations [6, 7]. These methods have been utilized to determine the rate constant of propagation (k_p), the rate (k_i), and equilibrium constants of ionization (K_i) and deactivation (k_{-i}) for isobutylene (IB) [8], styrene (St) [9] and ring-substituted styrenes [10–13]. The results show that previously accepted propagation rate constants [14] are underestimated in some cases by as much as four to six orders of magnitude. The k_i values for IB and St have also been determined independently by Storey *et al.* [15–17] from the average number of monomer units added during one initiation–termination cycle (run number). The reported values agreed remarkably well with those published earlier.

The above studies confirmed the results of prior kinetic investigations with model compounds, according to which the propagation rate constant is independent of the nature of Lewis acid and increases moderately with increasing solvent polarity. In agreement with findings of Mayr that fast bimolecular reactions (i.e., ${k_p}^{\pm} > 10^7\ \mathrm{l\,mol^{-1}\,s^{-1}}$) do not have an enthalpic barrier, [18] ${k_p}^{\pm}$ is independent of temperature for IB, *p*-chlorostyrene (*p*-ClSt), St, and *p*-methylstyrene (*p*-MeSt). Although most kinetic investigations have been conducted under conditions where propagation takes place on ion pairs, the propagation rate constant for free ions, ${k_p}^{+}$ for IB is reportedly similar to ${k_p}^{\pm}$ suggesting that free and paired cations possess similar reactivity, and therefore differentiation between free ions and ion pairs is unnecessary [19].

It is apparent that, as a result of the extremely rapid propagation, if all chain ends were ionized and grew simultaneously, monomer would disappear at such a high rate that the polymerization would be uncontrollable. In living cationic polymerization, therefore, a dynamic equilibrium must exist between a very small amount of active ionic and a large pool of inactive dormant species. The expression of ''controlled polymerization'' is sometimes used to describe, perhaps questionably, such polymerizations with reversible deactivation of the chain carriers.

From the k_i, k_{-i}, and k_p values, the sequence of events for an average polymer chain could be ascertained. Using typical concentrations of $[\mathrm{TiCl_4}] = 3.6 \times 10^{-2}\ \mathrm{mol\,l^{-1}}$ and $[\mathrm{IB}] = 1\ \mathrm{mol\,l^{-1}}$ in hexanes/$\mathrm{CH_3Cl}$ 60/40, v/v at −80 °C the following time intervals (τ) between two consecutive events have been calculated.

$$\tau_i = \frac{1}{k_i}[\mathrm{TiCl_4}]^2 = 49\ \mathrm{s}$$

$$\tau_{-i} = \frac{1}{k_{-i}} = 2.9 \times 10^{-8}\ \mathrm{s} = 29\ \mathrm{ns}$$

$$\tau_p = \frac{1}{k_p}[\mathrm{IB}] = 1.4 \times 10^{-9}\ \mathrm{s} = 1.4\ \mathrm{ns}$$

Thus, the time interval between two ionizations (activation) is relatively long (49 s). The ionized chain ends stay active for a very short time, only 29 ns, before reversible termination (deactivation) takes place and the polymer end goes back to a dormant, inactive state. Propagation is 20 times faster than deactivation, however, and thus monomer incorporates on average every 1.4 ns and 20 monomer units are added during one active cycle. This results in a relatively high polydispersity index (PDI) at the beginning of the polymerization, which progressively decreases to the theoretical value at complete conversion [20]:

$$\frac{M_\mathrm{w}}{M_\mathrm{n}} = 1 + [I]_0 k_\mathrm{p}/k_{-\mathrm{i}}$$

The above equation, where $[I_0]$ is the total concentration of (active and dormant) chain ends, is valid for unimolecular deactivation (ion pairs); for bimolecular deactivation the deactivation rate constant should be multiplied by the concentration of the deactivator. The starting [IB] may be decreased to decrease the number of monomer units incorporated during one active cycle and this yields polyisobutylene (PIB) with a lower PDI. For instance, at $[\mathrm{IB}] = 0.1\ \mathrm{mol\ l^{-1}}$, two monomer units are incorporated during one active cycle even at the onset of the polymerization. At $[\mathrm{TiCl_4}] = 3.6 \times 10^{-2}\ \mathrm{mol\ l^{-1}}$ and $[\mathrm{IB}] = 1\ \mathrm{mol\ l^{-1}}$, about 4 and 40 min would be necessary for the formation of a PIB with a number average degree of polymerization ($\mathrm{DP_n}$)= 100 and 1000, respectively. For St under similar conditions propagation is 60 times faster than deactivation, which results in much higher polydispersities and the complete loss of molecular weight control below $\mathrm{DP}_n \sim 60$. Control for low molecular weights can be regained by selecting a weaker Lewis acid (e.g., $\mathrm{SnCl_4}$) compared to $\mathrm{TiCl_4}$.

As indicated in the above examples, for a specific monomer the rate of exchange as well as the position of the equilibrium and, to some extent, the zero-order monomer transfer constants depend on the nature of the counter anion, in addition to temperature and solvent polarity. Therefore, initiator/coinitiator systems that bring about controlled and living polymerization under a certain set of experimental conditions are largely determined by monomer reactivity.

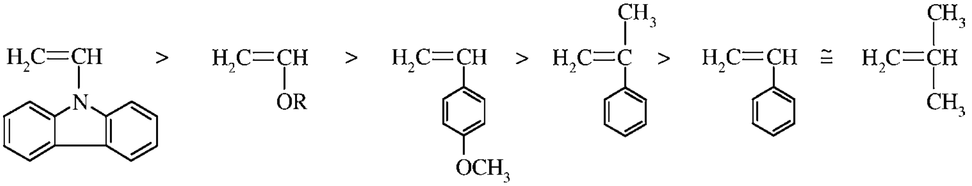
It is important to note that living polymerization does not require the assumption of special growing species such as stretched covalent bonds or stabilized carbocations, as pointed out by Matyjaszewski and Sigwalt [21]. In line with this reasoning, identical propagation rate constants were observed in living and nonliving polymerization indicating that propagation proceeds on identical active centers [8].

2.3
Living Cationic Polymerization

Since the first reports of living cationic polymerization of vinyl ethers [22] and IB [23, 24] in the 1980s, the scope of living cationic polymerization of vinyl monomers has been expanding rapidly in terms of monomers and initiating systems. Compared to anionic polymerization, living cationic polymerization can proceed under much less rigorous and much more flexible experimental conditions. The high vacuum technique is not indispensable, since alternative routes can consume adventitious moisture without terminating the living chains. Nonetheless, rigorous purification of reagents is still required for the best control.

2.3.1
Monomers and Initiating Systems

Initiation and propagation take place by electrophilic addition of the monomers to the active cationic sites. Therefore, the monomer must be nucleophilic and its substituents should be able to stabilize the resulting positive charge. As a result, the reactivity of monomers is roughly proportional to the electron-donating ability of their substituents, as can be seen below.



In addition to these monomers, the total number of monomers for living cationic polymerization was estimated to be around one hundred in 1994 and it appears that this process has a much broader choice of monomers than the living anionic counterpart [25].

With a few exceptions [26, 27], living cationic polymerization is initiated by the initiator/coinitiator (Lewis acid) binary system. Selection of an initiating system for a given monomer is of crucial importance, as there are no universal initiators such as organolithiums in anionic polymerization. For example, while weak Lewis acids such as zinc halides may be necessary to effect living polymerization of the more reactive vinyl ethers, they are not effective for the living polymerization of the less reactive monomers, such as IB and St. Detailed inventories of initiating systems for various monomers are well described in recent publications [25, 28, 29].

2.3.2
Additives in Living Cationic Polymerization

Three main categories of additives have been introduced and extensively utilized in the living cationic polymerization of vinyl monomers: (i) Lewis base [30] (also called *electron donors* (*EDs*) [31] or *nucleophiles* [32]), (ii) proton traps [33], and (iii) salts [34]. As the different names of the first categories of additives imply, the actual roles of these basic adjuvants and the true mechanisms of enhanced livingness have been long-standing controversies. Higashimura and Sawamoto proposed the theory of carbocation stabilization by nucleophilic additives through weak nucleophilic interaction [35]. Similar opinion was also expressed by Kennedy *et al.* [28]. In contrast to this view, Matyjaszewski [32] discussed that these bases only decrease the concentration of active species by reversible formation of onium ions, which do not propagate, or by complexing with Lewis acids. It has also been proposed by Penczek [36] that these bases may enhance the dynamics of equilibrium between dormant and active species via onium ion formation, which provides a thermodynamically more favorable pathway from covalent species to cation and vice versa. Unfortunately, no direct evidence for either nucleophilic interaction or onium ion formation has been provided.

Faust *et al.* demonstrated the living polymerization of IB and styrene coinitiated with $TiCl_4$ or BCl_3 in the *absence* of nucleophilic additives but in the presence of the proton trap (2,6-di-*tert*-butylpyridine), a nonnucleophilic weak base [34, 37]. The addition of nucleophilic additives had no effect on polymerization rates, molecular weights, or MWDs. Thus, it was suggested that the major role of added bases, as well as the sole role of the proton trap, is to scavenge protogenic impurities in the polymerization system. Although supporting view is emerging [38], combination of the first and the second additives in one category is still under discussion.

Common ion salts are considered to suppress the ionic dissociation of covalent species and ion pairs to free ions, which are believed to result in nonliving polymerization [34]. In the light of recent results, which confirmed similar reactivity of free ions and ion pairs, this view may require revision. In addition to the common ion effect, addition of salts can also change the nucleophilicity of counterions by modifying either the coordination geometry [39] or aggregation degree [40] of Lewis acids or their complex counterions. The former is the case with $SnCl_4$ and the latter is the case with $TiCl_4$ in the presence of tetra-butylammonium chloride ($n\mathrm{Bu}_4\mathrm{NCl}$). In both cases, more nucleophilic counterions ($SnCl_6$ vs. $SnCl_5^-$ or $TiCl_5^-$ vs. $Ti_2Cl_9^-$) are generated and these are reported to mediate the living cationic polymerizations of styrenic monomers [39, 41] and isobutyl vinyl ether (IBVE) [40].

2.3.3
Living Cationic Polymerization: Isobutylene (IB)

IB is the most studied monomer that can only polymerize by a cationic mechanism. The living carbocationic polymerization of IB was first discovered by Faust and Kennedy using organic acetate/BCl_3 initiating system in CH_3Cl or CH_2Cl_2 solvents at -50 to $-10\,^{\circ}C$ [23, 24]. Living carbocationic polymerizations of IB to date are based on BCl_3, $TiCl_4$ and organoaluminum halide coinitiators. The activity of the BCl_3-based system is greatly solvent dependent, i.e., sufficient activity occurs only in polar solvent. In less polar solvents, the solvation of the counter anion does not promote ion generation and the binary ionogenic equilibrium is strongly shifted to the left. Therefore, the concentration of growing cations is extremely small, resulting in negligible polymerization rates. However, as PIB is poorly soluble in polar solvents at low temperatures, the molecular weights are limited with the BCl_3-based initiating systems.

A wide variety of initiators, organic esters, halides, ethers, and alcohols, have been used to initiate living polymerization of IB at temperatures up to $-10\,^\circ C$. The true initiating entity with ethers and alcohols is the chloro derivative arising by fast chlorination. The polymerization involving the BCl_4^- counter anion is very slow, measured in hours, compared to the fast polymerization by protic impurities, and in the absence of proton scavenger, the monomer is consumed mainly by this process. In the presence of proton trap or EDs, similar rates, controlled molecular weights, and narrow MWDs (PDI ~1.2) have been reported [37]. According to kinetic studies the polymerization is first order in respect to both monomer and BCl_3 [37]. The absence of common ion salt effect in polymerizations involving the BCl_4^- counter anion suggests that propagation is mainly via the ion pairs, and the contribution of free ions, if any, is negligible [42].

Organic esters, halides, and ethers have been used to initiate living polymerization of IB at temperatures from -90 up to $-40\,^\circ C$. In conjunction with $TiCl_4$, ethers are converted to the corresponding chlorides almost instantaneously, while the conversion of esters is somewhat slow [34]. According to Chen *et al.* alcohols are inactive with $TiCl_4$ alone but have been used in conjunction with BCl_3 and $TiCl_4$ [43]. The BCl_3 converts the alcohols to the active chloride, which is activated by $TiCl_4$. In contrast to Chen *et al.*, Puskas and Grassmuller reported chlorination of alcohols and initiation by $TiCl_4$ alone [44].

Under well-dried conditions, PIBs with controlled M_ns up to ~60 000 and narrow MWDs could be prepared in the absence of any additives in nonpolar solvent mixtures and at low temperatures [33]. PIBs with M_ns up to 150 000 and M_w/M_ns as low as 1.02 have been obtained in the presence of proton trap or Lewis bases. The polymerization is first order in monomer but second order in $TiCl_4$, due to dimeric counter anions [33], although first-order dependency was reported at $[TiCl_4] < [\text{initiator}, I_0]$ [45]. The consequence of the second-order rate dependence is that although excess of $TiCl_4$ over the initiator halide is not required to induce polymerization, at low initiator concentrations high M_n, are obtained at acceptable rates only when high $TiCl_4$ concentrations (16–36 times $[I]_0$) are used. Living polymerization of IB was also reported with the $TiCl_4/TiBr_4$ mixed [46] coinitiator that yields mixed $Ti_2Cl_{n+1}Br_{8-n}^-$ counter anions. By the stepwise replacement of Cl with Br, however, the Lewis acidity decreases, which results in a decreased ionization rate constant and therefore decreasing overall rates of polymerization with decreasing $TiCl_4/TiBr_4$ ratio.

Organoaluminum compounds have also been employed for the living cationic polymerization of IB using 1,4-bis(1-azido-1-methylethyl)benzene/Et_2AlCl/CH_2Cl_2 at $-50\,^\circ C$ to produce a living polymerization of IB for $M_n < 50\,000$ where the presence of an ED like dimethylsulfoxide (DMSO) is not necessary [47]. Another polymerization system based on Et_2AlCl and tertiary alkyl halide initiators has been reported but requires the use of an 80/20 (v/v) nonpolar/polar solvent mixture [48]. The first example of Me_2AlCl catalyzed living polymerizations of IB was presented using conventional tertiary alkyl chloride initiators and 60/40 (v/v) nonpolar/polar solvent mixtures. PIBs were prepared with $M_n = 150\,000$ and M_w/M_ns $= 1.2$ [49] even in the absence of additives such as proton traps or EDs. The "living" nature of these polymerizations has been demonstrated at −75 to −80 °C in both 60/40 (v/v) hexane/CH_2Cl_2 and hexane/methyl chloride (MeCl) solvent systems. Recently, the living polymerization of IB was also reported using 2-chloro-2,4,4-trimethylpentane (TMPCl)/2,6-di-tert-butylpyridine (DTBP)/hexanes : MeCl solvent mixtures/−80 °C using Me_2AlCl, $Me_{1.5}AlCl_{1.5}$, or $MeAlCl_2$ [50]. With the latter two coinitiators, the polymerization was extremely fast and completed in seconds and it necessitated special considerations for reaction control.

2.3.4
β-Pinene

The first example of living cationic isomerization polymerization of *β*-pinene was reported with the HCl-2-chloroethyl vinyl ether adduct [$CH_3CH(OCH_2{-}CH_2Cl)Cl$] or 1-phenylethyl chloride/$TiCl_3(O\textit{i}Pr)$ initiating system in the presence of tetra-*n*-butylammonium chloride ($n$$Bu_4NCl$) in CH_2Cl_2 at −40 and −78 °C [51, 52]. The polymerization was rather slow even at relatively high initiator (20 mM) and coinitiator (100 mM) concentrations. The much stronger Lewis acid coinitiator $TiCl_4$ induced an extremely rapid polymerization yielding polymers with controlled molecular weight but with broad MWDs. The ^1H NMR analysis of the polymers showed a *tert*-chloride end group, and isomerized *β*-pinene repeat units with a cyclohexene ring. Copolymerization of *β*-pinene with IB indicated that the two monomers exhibit almost equal reactivity [53].

2.3.5
Styrene (St)

The conventional cationic polymerizations of St suffers from side reactions such as chain transfer by *β*-proton elimination, and inter- and intramolecular Friedel–Crafts alkylations. Thus, control of the cationic polymerization of St has been considered difficult. The living carbocationic polymerization of St was first achieved by the 1-(*p*-methylphenyl)ethyl acetate/BCl_3 initiating system in CH_3Cl at −30 °C [54]. The MWD was broad (∼5–6) most likely because of slow initiation and/or slow exchange between the dormant and active species. Living polymerization of St with controlled molecular weight and narrow MWD were obtained using $SnCl_4$/1-phenylethyl halides as initiating systems in a nonpolar solvent ($CHCl_3$) [55] and solvent mixtures or in a polar CH_2Cl_2 in the presence of $n$$Bu_4NCl$ [56].

Living polymerization was also reported with the TMPCl/$TiCl_4$/methylcyclohexane (MeChx)/MeCl 60/40 (v/v)/−80 °C system in the combined presence of an ED and a proton trap [57]. Later studies indicated that the ED is unnecessary and the living nature of the polymerization is not due to carbocation stabilization [58]. The living cationic polymerization of St has also been achieved with $TiCl_3$(O*i*Pr) as an activator, in conjunction with 1-phenylethyl chloride and $n$$Bu_4NCl$ in CH_2Cl_2 at −40 and −78 °C [59]. The MWDs were narrow throughout the reactions (MWD ~1.1). Living St polymerization was also reported with the *p*-MeSt·HCl adduct [(*p*-MeStCl)/$TiCl_4$/MeChx/MeCl 60/40 (v/v)/−80 °C] in the presence of a proton trap and was found that *p*-MeStCl is a better initiator than TMPCl for St polymerization using $TiCl_4$ in MeChx/MeCl solvent mixture [60]. Recently, living polymerization of St was obtained with the system 1-phenylethyl chloride/TiC1$_4$/Bu_2O in a mixture of 1,2-dichloroethane and hexane (55/45, v/v) at −15 °C [61].

2.3.6
p-Methylstyrene (*p*-MeSt)

Faust and Kennedy [62] reported the living carbocationic polymerization of *p*-MeSt in conjunction with BCl_3 in CH_3Cl and C_2H_5Cl solvents at −30 and −50 °C; however, the MWDs were rather broad (~2–5). The TMPCl/$TiCl_4$ initiated living polymerization of *p*-MeSt in MeChx/MeCl 50/50 (v/v) solvent mixture at −30 °C in the presence of $n$$Bu_4NCl$ and DTBP has been reported by Nagy *et al.* [63]. Kojima *et al.* reported the living cationic polymerization of *p*-MeSt with the HI/$n$$Bu_4NCl$/$ZnX_2$ system in toluene and CH_2Cl_2 and obtained polymers of fairly narrow MWD [64]. Lin and Matyjaszewski have studied the living cationic polymerization of St and *p*-MeSt initiated by 1-phenylethyl trichloroacetate/BCl_3 in CH_2Cl_2 [65]. Stöver *et al.* studied the living cationic polymerization of *p*-MeSt in the molecular range up to $M_n \approx$ 5500, initiated by 1-phenylethyl bromide/$SnCl_4$ initiating system in $CHCl_3$ or in $CHCl_3$/CH_2Cl_2 solvent mixtures at −27 °C [66]. The polymerization was very slow even though very high concentrations of $SnCl_4$ (0.23 mol l^{-1}) and initiator, 1-phenylethyl bromide (0.0215 mol l^{-1}), were used. The M_ns of the obtained poly(*p*-MeSt) were in agreement with the calculated values; however, the PDI was relatively high, PDI ≈ 1.5–1.6. Living carbocationic polymerization of *p*-MeSt was also obtained with 1,1-diphenylethylene (DPE) capped TMPCl/$TiCl_4$: Ti(I*p*O)$_4$ initiating system in the presence of DTBP using hexanes/MeCl or MeChx/MeCl 60/40 (v/v) solvent mixture at −80 °C [67]. Very recently, the living carbocationic polymerization of *p*-MeSt was achieved with 1-chloro-1-phenylethane, 1-chloro-1-(4-methylphenyl)ethane, and 1-chloro-1-(2,4,6-trimethylphenyl)ethane in conjunction with $SnCl_4$ as Lewis acid and DTBP as proton trap in CH_2Cl_2 at −70 to −15 °C [13].

2.3.7
p-Chlorostyrene (*p*-ClSt)

Kennedy *et al.* reported the living carbocationic polymerization of *p*-ClSt initiated by TMPCl/$TiCl_4$ in the presence of dimethylacetamide as ED and DTBP as proton trap in MeCl/MeChx 60/40 (v/v) solvent mixture at −80 °C [63, 68]. Kanaoka *et al.* obtained poly(*p*-ClSt) of a narrow MWD with 1-phenylethyl chloride/$SnCl_4$ initiating system in CH_2Cl_2 at −15 to +25 °C in the presence of $n$$Bu_4NCl$ [69]. The polymerization was somewhat slow. Controlled cationic polymerization of *p*-ClSt was also achieved by the alcohol/BF_3OEt_2 system in the presence of fairly large amount of water [70]. Recently, for the living polymerization of *p*-ClSt, 1-chloro-1-(4-methylphenyl)ethane and *p*-ClSt·HCl adduct was used in conjunction with $TiCl_4$/DTBP in MeCl/MeChx 40/60 (v/v) solvent mixture at −80 °C [10].

2.3.8
2,4,6-Trimethylstyrene (TMeSt)

In the cationic polymerization of St, one of the major side reactions is indanic cyclization [71]. Intra- and intermolecular alkylation are absent in the cationic polymerization of TMeSt, which was recognized in an early report on the living polymerization of TMeSt initiated by the cumyl acetate/BCl_3 initiating system in CH_3Cl at −30 °C [72]. Recently, the living cationic polymerization of TMeSt was initiated by the 1-chloro-1-(2,4,6-trimethylphenyl)ethane, a model propagating end, in CH_2Cl_2 at −70 °C and the living polymerization yielded polymers with theoretical molecular weights and very low polydispersity ($M_w/M_n = 1.02–1.1$) [11].

2.3.9
p-Methoxystyrene (*p*-MeOSt)

The living carbocationic polymerization of *p*-MeOSt was first reported with the HI/ZnI_2 initiating system in toluene at −15 to 25 °C [30, 73]. Living polymerizations were also attained in the more polar solvent, CH_2Cl_2, with the HI/I_2 and HI/ZnI_2 initiating systems in the presence of $n$$Bu_4NX$ (X = Cl, Br, I) [74]. Comparable but less controlled polymerization of *p*-MeOSt has been reported using iodine as an initiator in CCl_4 [75]. This system gives rise to long-lived but not truly living polymerization. More recently, *p*-MeOStCl/$SnBr_4$ initiating system has been used in CH_2Cl_2 at −60 to −20 °C in the presence of DTBP. The obtained M_ns were in good agreement with the calculated ones assuming that one polymer chain forms per initiator. Polymers with M_ns up to 120 000 were obtained with $M_w/M_n \sim 1.1$ [10]. A recent report indicated the controlled cationic polymerization of *p*-MeOSt with controlled molecular weights and relatively narrow MWD (PDI = 1.4) using the *p*-MeOSt·HCl adduct (*p*-MeOStCl)/Yb(OTf)$_3$ initiating system in the presence of 2,6-di-*tert*-butyl-4-methylpyridine [76]. The authors also claimed the controlled albeit very slow cationic polymerization of *p*-MeOSt in aqueous media using the *p*-MeOStCl/Yb(OTf)$_3$ initiating system. Relatively narrow PDIs (~1.4) were observed and the molecular weights increased in proportion to the monomer conversion. Surfactants [77], sulfonic acid-based initiators [78], and various phosphonic acid initiators [79] were also used for the cationic polymerization of *p*-MeOSt in aqueous medium.

2.3.10
α-Methylstyrene (αMeSt)

The living polymerization of αMeSt was first achieved with the vinyl ether-HCl adduct/SnBr$_4$ initiating system in CH$_2$Cl$_2$ at −78 °C [80]. Controlled polymerization of αMeSt was obtained by the cumyl chloride/BCl$_3$/−78 °C system in CH$_2$Cl$_2$/toluene 1/7 (v/v) solvent mixture in the presence of *n*Bu$_4$NCl [81]. The living polymerization of αMeSt was also studied at −60 °C using iodine in liquid SO$_2$/CH$_2$Cl$_2$ or liquid SO$_2$/toluene [82]. The living polymerization of αMeSt has also been established in hexanes/MeCl 60/40 (v/v) at −60 to −80 °C in the presence of DTBP using DPE-capped TMPCl with SnBr$_4$ or SnCl$_4$ [41] and diphenyl alkyl chloride or HCl adduct of αMeSt dimer with BCl$_3$ or SnCl$_4$ coinitiators [83–85]. Initiation with cumyl chloride, however, is slow relative to propagation, due to the absence of back strain. The living polymerization of *p*-chloro-α-methylstyrene was achieved using the 1,3-dimethyl-1,3-diphenyl-1-chlorobutane/BCl$_3$ initiating system in MeChx/MeCl 60/40 (v/v) at −80 °C [86].

2.3.11
Indene

Chain transfer to monomer via indane formation (intramolecular alkylation), the most important side reaction in the polymerization of styrene cannot take place with indene. Therefore, even conventional initiating systems give high molecular weight and negligible transfer at low temperatures. Cumyl methyl ether [87] or cumyl chloride [88] in conjunction with TiCl$_3$OBu or with TiCl$_4$ and dimethyl sulfoxide as an ED [89] initiates living polymerization of indene. Living polymerization is also claimed with the TMPCl/TiCl$_4$ initiating system using hexanes/MeCl 60/40 (v/v) [90] and MeChx/MeCl 60/40 (v/v) [91] mixed solvents at −80 °C. Thus, polyindene of theoretical molecular weight up to at least 13 000 and narrow MWD ($M_w/M_n \sim 1.2$) can be obtained by the cumyl chloride/BCl$_3$ initiating system in MeCl at −80 °C [92].

2.3.12
N-Vinylcarbazol

There are very few reports available on the living cationic polymerization of *N*-vinylcarbazol, one of the most reactive monomers for cationic polymerization. Living polymerization of *N*-vinylcarbazol was reported in toluene or CH_2Cl_2 solvent system using only HI [93] and I_2 as initiator in CH_2Cl_2 and CH_2Cl_2/CCl_4 1/1 (v/v) [94]. Living cationic polymers of *N*-vinylcarbazole were synthesized with I_2 as initiator at −78 °C in CH_2Cl_2 in the presence of $n\mathrm{Bu_4NI}$ [92].

2.3.13
Vinyl Ethers

Alkyl vinyl ethers are among the most reactive vinyl monomers in cationic polymerization. The pendant alkoxy groups provide the growing vinyl ether carbocation with a high stability. Controlled/living cationic polymerization of IBVE was first discovered with the HI/I_2 initiating system [22]. The living cationic polymerization of vinyl ethers [$CH_2{=}CH{-}O{-}R$, where $R = CH_3$, C_2H_5, isopropyl, *n*-butyl, isobutyl, *n*-hexadecyl, 2-chloroethyl, benzyl, cyclohexyl, etc.] was first developed by the HI/I_2 initiating system and has been reviewed extensively. Subsequently other weak Lewis acids, e.g., $ZnCl_2$, $ZnBr_2$, ZnI_2, have also been employed. A recent review is available [95]. The living cationic polymerization of *tert*-butyl vinyl ether was achieved by the $CH_3CH(O\textit{i}Bu)OCOCH_3/Et_{1.5}AlCl_{1.5}$ initiating system in the presence of tetrahydrofuran (THF) as "Lewis base" at −20 °C [96]. However, the polymerization was slow as close to quantitative yield was reached only in 60 h.

Recently, the living cationic polymerization of *tert*-butyl vinyl ether [97] and cyclohexyl vinyl ether (CHVE) [98] was accomplished in hexanes/MeCl solvent mixtures at −88 °C using TMPCl capped with 1,1-ditolylethylene (DTE) as initiator and $TiCl_4/Ti(O\textit{i}P)_4$ as coinitiators. The process involved capping the initiator, TMPCl, with DTE in the presence of $TiCl_4$, followed by fine-tuning of the Lewis acidity with the addition of $Ti(O\textit{i}P)_4$ to match the reactivity of *tert*-butyl vinyl ether or CHVE. Both polymers exhibited T_gs (88 and 61 °C, respectively) well above room temperature. Poly(vinyl ether)s with a T_g as high as 100 °C have been obtained in the living cationic polymerization of vinyl ethers with a bulky tricyclodecane or tricyclodecene unit using $HCl/ZnCl_2$ in toluene at −30 °C [99]. The fast living cationic polymerization of vinyl ethers with $SnCl_4$ combined with $EtAlCl_2$ in the presence of an ester as an added base was reported [100]. The cationic polymerization of vinyl ethers with a urethane group, 4-vinyloxybutyl *n*-butylcarbamate and 4-vinyloxybutyl phenylcarbamate, was studied with the $HCl/ZnCl_2$ initiating system in CH_2Cl_2 solvent at −30 °C [101]. The cationic homopolymerization and copolymerization of five vinyl ethers with silyloxy groups, each with a different spacer length, were examined with a cationogen/$Et_{1.5}AlCl_{1.5}$ initiating system in the presence of an added base. When an appropriate base was added, the living cationic polymerization of Si-containing monomers became feasible, giving polymers with narrow MWD [102]. The cationic polymerization of 2-[4-(methoxycarbonyl)phenoxy] ethyl vinyl ether, a vinyl ether with a benzoate pendant, was reported to proceed with living/long-lived propagating species with an HCl/$ZnCl_2$ initiating system in dichloromethane at −15 °C [103]. The hexa(chloromethyl)-melamine/$ZnCl_2$ was found to be a efficient initiating system for the living cationic polymerization of IBVE in CH_2Cl_2 at −45 °C [104]. Characterization of the polymers by gel permeation chromatography (GPC) and ^1H NMR showed that initiation was rapid and quantitative and that the initiator was hexafunctional, leading to six-armed star-shaped polymers. A series of aromatic acetals from substituted phenols were employed as initiators in conjunction with Lewis acids such as $AlCl_3$, $SnCl_4$, and $SnBr_4$ for the cationic polymerization of IBVE [105].

2.4
Functional Polymers by Living Cationic Polymerization

Functional polymers are of great interest due to their potential applications in many important areas such as surface modification, adhesion, drug delivery, polymeric catalysts, compatibilization of polymer blends, and motor oil additives. In addition to the controlled and uniform size of the polymers, living polymerizations provide the simplest and most convenient method for the preparation of functional polymers. However, there are relatively few end-functionalized polymers (polymers with functional groups selectively positioned at the termini of any given polymeric or oligomeric chain) synthesized by living cationic polymerization of vinyl monomers, although varieties of end-functionalized polymers have successfully been synthesized in anionic polymerization. There are two basic methods to prepare functional polymers by cationic polymerization:

1. initiation from functional initiators;
2. termination by functional terminators.

2.4.1
Functional Initiator Method

This method involves the use of functional initiators with a protected or unprotected functional group. When the functional group is unreactive under the polymerization conditions, protection is not necessary. Functional vinyl ethers have extensively been used in the living cationic polymerizations of vinyl ethers and these functional poly(vinyl ethers) can be derivatized to the desired functionality by simple organic reactions. Vinyl ethers carrying a variety of functional pendant groups, in a general form (Scheme 2.1):

$$H_2C{=}CH{-}OCH_2{-}CH_2{-}R$$

$$\begin{aligned}R = \;& OMe, OEt, OAc, (CH_2CH_2O)\,Et_n \;\; [n = 1, 2, 4]\\ & OSi(Me)_3, OSi(Me)_2iBu, C(CO_2Et)_3, O_2CPh\\ & OCH_2CO_2Et, OC(O)C(CH_3)H{=}CH_2, OC(O)CH{=}CH_2\\ & CH(CH_2CO_2Et)_2, \text{etc.}\end{aligned}$$

Scheme 2.1 Functional vinyl ethers used for living cationic polymerization.

have been polymerized in a living fashion in toluene (or CH_2Cl_2) using HI/I_2 or HI/ZnI_2 systems [106].

Functionalized initiators have been used extensively for styrene and derivatives to obtain end-functionalized polymers by living cationic polymerization. A series of α-end-functionalized polymers of St and *p*-MeSt were synthesized by living cationic polymerizations in CH_2Cl_2 at −15 °C initiated with the HCl adducts of $CH_2{=}CH(OCH_2{-}CH_2X)$ (X = chloride, benzoate, acetate, phthalimide, methacrylate) using $SnCl_4$ in the presence of $n\mathrm{Bu_4NC1}$ [107]. The living cationic polymerization of αMeSt initiated by HCl adduct of 2-chloroethyl vinyl ether/$SnBr_4$ initiating system in CH_2Cl_2 at −78 °C gave terminal functionalities in the products [80]. The living cationic polymerization of *p*-ClSt induced with $CH_3CH(OCH_2CH_2Cl)Cl/SnCl_4/n\mathrm{Bu_4NCl}$ at 0 °C or room temperature gave living polymers with narrow MWDs, which are a kind of end-functionalized polymers. The authors concluded that a variety of vinyl ethers would lead to end-functionalized poly(*p*ClSt) [73]. The $-CH_2CO_2H$, −OH end functionalities have been obtained using the functional initiator method for the living cationic polymerization of *p*-*tert*-butoxystyrene [108]. A series of end-functionalized polymers of *p*-MeOSt were synthesized by the functional initiator method initiated with a functional vinyl ether−HI adduct, ($X{-}CH_2CH_2OCH(CH_3)I$; X = CH_3COO, $(EtOCO)_2CH$, phthalimide)/ZnI_2, in toluene at −15 °C [109].

A few end-functionalized PIBs have been obtained by using functional initiators. The ester functional initiators 3,3,5-trimethyl-5-chloro-1-hexyl isobutyrate and methacrylate have been successfully employed for the living polymerization of IB [110]. Subsequently, the synthesis of α-carboxylic acid functional PIB was also reported by hydrolysis of the product obtained in the living cationic polymerization of IB using a novel aromatic initiator containing the CH_3OCO−moiety [111]. While these ester functionalities form a complex with the Lewis acid coinitiator, quenching the polymerization with CH_3OH yields the original ester quantitatively. Initiators containing a cationically unreactive vinyl functionality, e.g., 5-chloro-3,3,5-trimethyl-1-hexene and 3-chlorocyclopentene, have been used to prepare PIBs with α-olefin head groups. Following the discovery that the chlorosilyl functionality is unreactive toward Lewis acids or carbocations, a series of novel chlorosilyl functional initiators have been employed in conjunction with $TiCl_4$ in hexanes/MeCl 60/40 (v/v) at −80 °C in the living cationic polymerization of IB to synthesize well-defined PIBs carrying mono-, di-, and tri-methoxysilyl head groups, and a *tert*-chloro end group [112]. A class of unique epoxide initiators, e.g., α-methylstyrene epoxide (MSE), 2,4,4-trimethyl-pentyl-epoxide-1,2 (TMPO-1), 2,4,4-trimethyl-pentyl-epoxide-2,3 (TMPO-2), and hexaepoxi squalene (HES) for the living polymerization of IB in conjunction with $TiCl_4$ have been recently described by Puskas *et al.* [113, 114]. Ring cleavage induced by $TiCl_4$ produces a tertiary cation that initiates the living polymerization of IB. Upon quenching the polymerization with methanol, PIB carrying primary hydroxyl head group and *tert*-chloride end group is obtained. During initiation, however, simultaneous side reactions take place. Although these side reactions do not affect the livingness of the polymerization or the functionality of the PIB, they reduce the initiator efficiency to 3% with TMPO-1 and 40% with MSE.

The α-end-functionalized poly(β-pinene) was obtained by living cationic isomerization polymerization in CH_2Cl_2 at −40 °C using $TiCl_3(O\mathit{i}Pr)/\mathit{n}Bu_4NCl$ and HCl adducts of functionalized vinyl ethers [$CH_3CH(OCH_2CH_2X)Cl$; X = chloride, acetate, and methacrylate] as initiators carrying pendant substituents X that serve as terminal functionalities [51].

2.4.2
Functional Terminator Method

The second method involves end quenching of living polymers with appropriate nucleophiles. Although this approach appears to be more attractive than the first one, *in situ* end functionalization of the living ends is limited to nucleophiles that do not react with the Lewis acid coinitiator. Because the ionization equilibrium is shifted to the covalent species, the concentration of the ionic active species is very low. Quantitative functionalization can only be accomplished; therefore, when ionization takes place continuously in the presence of a nucleophile. By quenching the vinyl ether polymerization with the malonate anion [115], certain silyl enol ethers [116] and silyl ketene acetals [117] have been successfully used to synthesize end-functionalized poly(vinyl ethers). Alkyl amines [118], ring-substituted anilines [119], alcohols [120], and water [121] have also been used to quench the vinyl ether polymerization to synthesize end-functionalized poly(vinyl ethers). Functionalizations by the latter nucleophiles, however, most likely do not entail reactions of the living cationic ends but proceed by SN2 reactions involving the halogen terminated chain ends.

In the functionalization of living polymers of hydrocarbon olefins, success remained limited up until recently. Although there are various methods available to modify the resulting chloro chain ends, they usually involve a number of steps and are rather cumbersome.

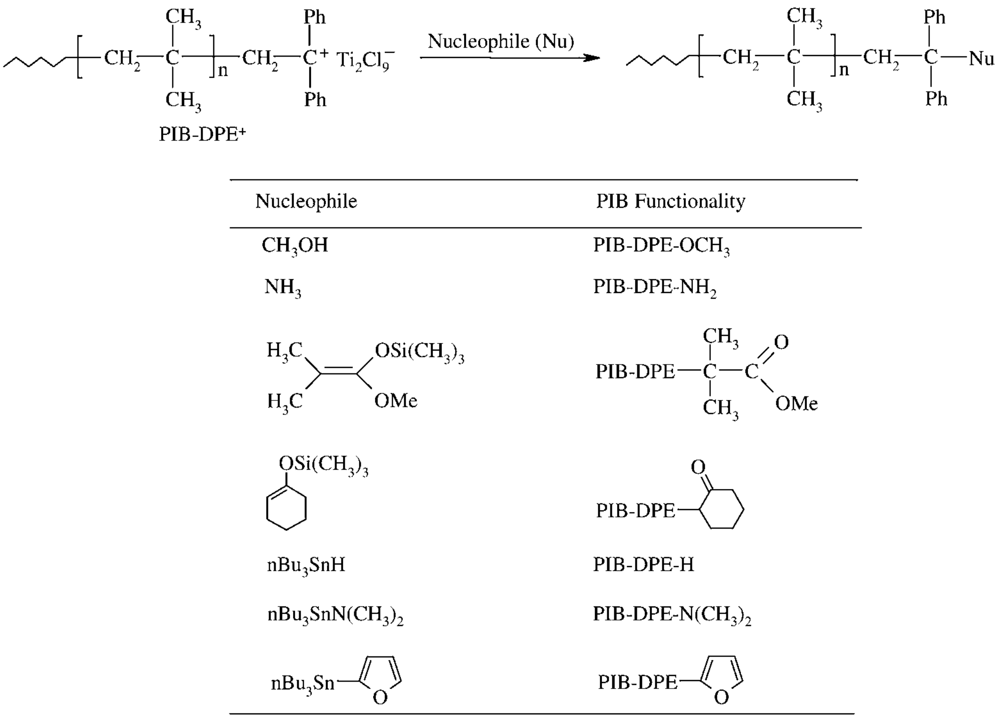
Various nucleophiles, which do not react (or react very slowly) with the Lewis acid, have been used to prepare functional PIBs by *in situ* functionalization of the living ends. As these terminators are mostly π-nucleophiles, multiple additions should be avoided. This can be accomplished by employing π-nucleophiles that do not homopolymerize, yielding a stable ionic product or a covalent uncharged product either by rapidly losing a cationic fragment, e.g., Me_3Si^+ or H^+ or by fast ion collapse. Accordingly, the rapid and quantitative addition of various 2-substituted furans to living PIB^+ has been observed in conjunction with $TiCl_4$ as Lewis acid in hexanes/CH_2Cl_2 or CH_3Cl 60/40 (v/v) at −80 °C and with BCl_3 in CH_3Cl at −40 °C [122]. The formation of the stable allylic cation was confirmed by trapping the resulting cation with tributyltin hydride, which yielded PIB with dihydrofuran functionality. Quenching with methanol resulted in the quantitative formation of 2-alkyl-5-PIB-furan. Furan terminated PIB (2-PIB-Fu) was obtained in quantitative yields in a reaction of PIB^+ with 2-Bu_3-SnFu in hexanes/CH_3Cl 60/40 (v/v) in the presence of $TiCl_4$ at −80 °C. Using unsubstituted furan, coupling of two living chain ends as a side reaction could not be avoided. However, thiophene- and *N*-methylpyrrole-terminated PIB could be obtained by employing unsubstituted thiophene and *N*-methylpyrrole [123], respectively.

Allyl telechelic PIBs have been obtained by end quenching with allyltrimethylsilane (ATMS) [19, 124], methallyltrimethylsilane [19], tetraallyltin, or allyltributyltin (R. Faust, B. Ivan unpublished results). In the functionalization reactions β-proton abstraction should generally be avoided. Quantitative β-proton abstraction with hindered bases reported recently, however, is a valuable method to produce exo-olefin terminated PIB in one pot [125].

A series of end-functionalized polymers of *p*-MeOSt were synthesized by quenching the HI/ZnI_2 initiated living poly(*p*-MeOSt)$^+$ cations with a functional alcohol ($HOCH_2CH_2Z$; $Z = OOCCH_3$, $OOCC(=CH_2)CH_3$, $OOCC(=CH_2)H$ [115].

When all dormant chain ends are converted to active ionic species, as in the capping reaction with diarylethylenes [126], many other nucleophiles, such as NH_3 and CH_3OH, which also quench the Lewis acid, could be used. *In situ* functionalization of the living ends by a variety of nucleophiles was recently realized via capping with non(homo)polymerizable diarylethylenes, or 2-alkyl furans followed by end quenching [127]. The stable and fully ionized diarylcarbenium ion, obtained in the capping of PIBCl or PStCl with DPE, is readily amenable for chain-end functionalization by quenching with appropriate nucleophiles as shown in Scheme 2.2 [128]. Using this strategy, a variety of chain-end functional PIBs, including methoxy, amine, carbonyl, and ester end groups, have been prepared. It is also notable that, when living PIB is capped with DPE, organotin compounds can also be used to introduce new functionalities such as −H, $-N(CH_3)_2$, and furan [129].

Recently, the synthesis of haloallyl functional PIBs (PIB-Allyl-X, where X = Cl or Br) was reported using the capping reaction of living PIB with 1,3-butadiene in hexanes/methyl chloride (MeCl) 60/40 (v/v) solvent mixtures at −80 °C



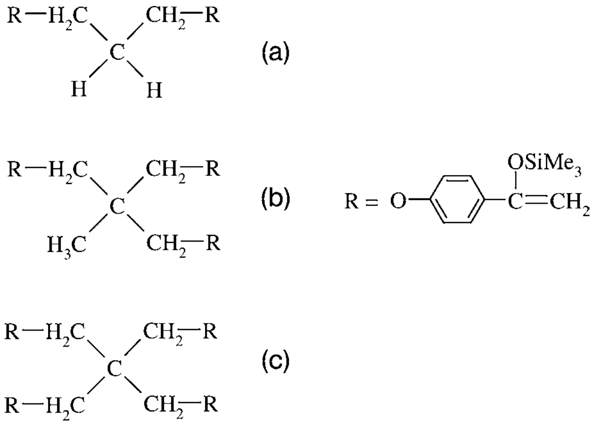
Scheme 2.2 Synthesis of chain-end functionalized PIBs.

[130] with titanium tetrachloride ($TiCl_4$) or methylaluminum sesquibromide ($Me_{1.5}AlBr_{1.5}$) as a Lewis acid.

Monoaddition of 1,3-butadiene followed by instantaneous halide transfer from the counter anion and selective formation of the *trans*-1,4-adduct (PIB-Allyl-X) was observed in hexanes/MeCl 60/40 (v/v) solvent mixtures at $-80\,^{\circ}C$ at [1,3-butadiene] $\leq 0.05\ mol\ l^{-1}$ ([1,3-butadiene]/[chain end] ≤ 12). Simple nucleophilic substitution reactions on these chloro or bromoallyl functional PIBs allowed the syntheses of end functional PIBs including hydroxy, amino, carboxy, azide, propargyl, methoxy, and thymine end groups [131].

2.5
Telechelic Polymers

Telechelic or α,ω-bifunctional and multifunctional polymers carry functional groups at each terminal. Symmetric telechelic or multifunctional polymers can be readily prepared by employing bi- or multifunctional initiators followed by functionalization of the living end as described above [132].

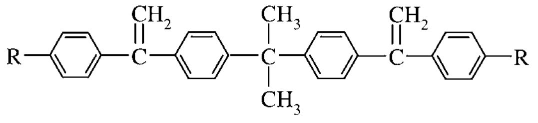


Scheme 2.3 Linking agents living poly(vinyl ethers).

Symmetric telechelic polymers can also be prepared by coupling of α-functional living polymer chains using any of the recently discovered coupling agents. Bifunctional silyl enol ethers, such as 1,3-bis{*p*-[1-[(trimethylsilyl) oxy]vinyl]phenoxy}-propane, 1,4-diethoxy-1,4-bis[(trimethylsilyl)oxy]-1,3-butadiene, and 2,4-bis[(trimethylsilyl)oxyl]-1,3-pentadiene, are efficient bifunctional coupling agents for the living polymers of IBVE initiated with $HCl/ZnC1_2$ at −15 °C in CH_2Cl_2 and toluene solvents [116]. The di- (A), tri- (B), and tetra- (C) functional silyl enol ethers (Scheme 2.3) have extensively been used with vinyl ethers to obtain functional polymers and block copolymers [133]. As an example, telechelic four-arm star polymers were obtained by coupling end-functionalized living poly(isobutyl vinyl ether) with the tetrafunctional silyl enol ethers (A) [134].

Non(homo)polymerizable bis-DPE compounds, such as 2,2-bis[4-(1-phenylethenyl)phenyl]propane (BDPEP) and 2,2-bis[4-(1-tolylethenyl)phenyl]propane (BDTEP) (**1**), have been successfully employed in the living coupling reaction of living PIB [135, 136]. It was demonstrated that living PIB reacts quantitatively with BDPEP or BDTEP to yield stoichiometric amounts of bis(diarylalkylcarbenium) ions, as confirmed by the quantitative formation of diaryl-methoxy functionalities at the junction of the coupled PIB. Kinetic studies indicated that the coupling reaction of living PIB by BDPEP is a consecutive reaction where the second addition is much faster than the first one. As a result, high coupling efficiency was also observed with excess BDPEP.

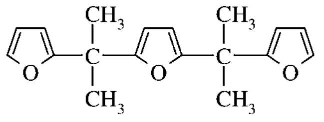
As 2-alkylfurans add rapidly and quantitatively to living PIB yielding stable tertiary allylic cations, the coupling reaction of living PIB was also studied using bis-furanyl compounds [137]. Using 2,5-bis[1-furanyl)-1-methylethyl]-furan (BFPF) (**2**), coupling of living PIB was found to be rapid and quantitative in hexane/MeCl 60/40 or 40/60 (v/v) solvent mixtures at −80 °C in conjunction



1

R = H (BDPEP)
= CH_3 (BDTEP)

with $TiCl_4$, as well as in MeCl at −40 °C with BCl_3 as Lewis acid. For instance, *in situ* coupling of living PIB, prepared by haloboration-initiation using the BCl_3/MeCl/−40 °C system, with BFPF yielded α,ω-telechelic PIB with alkylboron functionality. After oxidation, this telechelic PIB was converted to α,ω-hydroxyl PIB. The synthesis of α,ω-telechelic PIBs with a vinyl functionality was also achieved by the coupling reaction of living PIB, prepared using 3,3,5-trimethyl-5-chloro-1-hexene as an initiator in the presence of $TiCl_4$ [138].



BFPF **2**

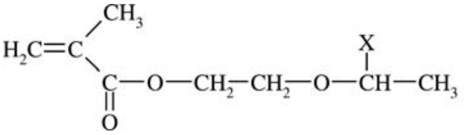
The α,ω-asymmetric polymers are available by the combination of the functional initiator and functional terminator methods. By the rational combination of haloboration-initiation and capping techniques, a series of α,ω-asymmetrically functionalized PIBs have been prepared [139, 140]. Polymers prepared by haloboration-initiation invariably carry an alkylboron head group [42, 141, 142], which can easily be converted into a primary hydroxy [141] or a secondary amine group [139, 140]. To functionalize the ω-living ends, the functionalization strategy shown in Scheme 2.2 is applicable and has been used to incorporate methoxycarbonyl groups as ω-functionality [143].

2.6
Macromonomers

A macromonomer is a macromolecule containing a (co)polymerizable end functional group. Macromonomers have been synthesized by living cationic polymerization using three different techniques: by the functional initiator or functional terminator methods or by chain-end modification.

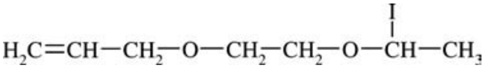
2.6.1
Synthesis Using a Functional Initiator

This technique is the simplest as it generally requires only one step as the polymerizable function is incorporated via the initiator fragment. Most macromonomers have been prepared with a methacrylate end group [144–146] which is unreactive under cationic polymerization conditions. For instance, the synthesis of the poly(vinyl ether) macromonomer was reported by employing initiator **3**, which contains a methacrylate ester group and a function able to initiate the cationic polymerization of vinyl ethers. Other vinyl ethers were also polymerized using initiator **3** under similar conditions [147].



3: X = I
4: X = Cl

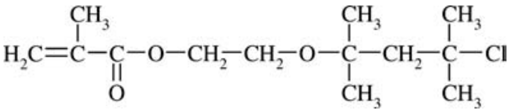
Poly(ethyl vinyl ether) (PEVE) macromonomers were also prepared using initiator **5** bearing an allylic function [148]. This reactive group remained intact during the polymerization and could be transformed into the corresponding oxirane by peracid oxidation.



$H_2C{=}CH{-}CH_2{-}O{-}CH_2{-}CH_2{-}O{-}CH(I){-}CH_3$ **5**

Using functionalized initiator **4**, polystyrene and poly(*p*-methylstyrene) macromonomers bearing a terminal methacrylate group [107] could be prepared by living cationic polymerization in CH_2Cl_2 at −15 °C in the presence of $SnCl_4$ and nBu$_4$NCl. To preserve the α end functionality, mixing of the reagents was carried out at −78 °C. When mixing was performed at −15 °C, the functionality was lower than unity, which was attributed to initiation by protons eliminated following intramolecular alkylation. A similar procedure was also used for the synthesis of methacrylate functional poly(α-methylstyrene) [149].

Methacrylate functional PIB macromonomers have been synthesized by living carbocationic polymerization of IB using the 3,3,5-trimethyl-5-chloro-1-hexyl methacrylate (**6**)/$TiCl_4$ initiating system in hexane/MeCl 60/40 (v/v) [110, 150]. By varying the monomer to initiator ratio, PIBs in the molecular weight range of 2000–40 000 g mol^{-1} were obtained with narrow MWDs and close to theoretical ester functionality.



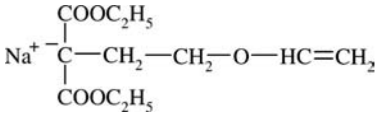
$H_2C{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}CH_2{-}O{-}C(CH_3)_2{-}CH_2{-}C(CH_3)_2{-}Cl$ **6**

The polymerization of β-pinene in conjunction with **4**/$TiCl_3(O\mathit{i}Pr)$ initiating system in the presence of $n Bu_4NCl$ in CH_2Cl_2 at −40 °C yielded poly(β-pinene) macromonomer with a methacrylate function at the α end and a chlorine atom at the ω end [51]. The macromonomers exhibited narrow MWD and the reported functionality was close to unity.

2.6.2
Synthesis Using a Functional Capping Agent

In this method, the polymerizable group is incorporated at the ω-end of the macromolecule by a reaction between a capping agent and the living polymer end.

The sodium salt of malonate carbanions reacts quantitatively with the living ends of poly(vinyl ether)s to give a stable carbon–carbon bond. This reaction was used to functionalize the ends of living poly(isobutyl vinyl ether) or poly(benzyl vinyl ether) with a vinyl ether polymerizable end group supported by a malonate ion (end-capping agent, **7**) [151].



$Na^+\ {}^-C(COOC_2H_5)_2{-}CH_2{-}CH_2{-}O{-}HC{=}CH_2$ **7**

A hydroxy function is also able to quantitatively react with the living end of poly(vinyl ether)s, but the resulting acetal end group has poor stability in acidic media; therefore, a proton trap should be added to scavenge the protons released during the coupling process. Various end-capping agents with a primary alcohol and a polymerizable double bond were used to produce poly(vinyl ether) macromonomers. Most often 2-hydroxyethyl methacrylate (HEMA) [152–155] has been used but other alcohols with an allylic or olefinic group were also employed such as allyl alcohol, 2-[2-(2-allyloxyethoxy)ethoxy] ethanol and 10-undecen-1-ol.

Owing to the lower stability of the growing *p*-alkoxystyrene cations and the possibility of several side reactions, some end-capping agents that were successfully used for poly(vinyl ether)s such as sodiomalonic ester and *tert*-butyl alcohol failed to yield end functional poly(*p*-alkoxystyrene). In contrast, primary and secondary alcohols underwent quantitative reactions to give stable alkoxy terminals. Thus, HEMA and acrylate were used to introduce a polymerizable group at the ω end [108, 109]. Heterotelechelic poly(*p*-MeOS)s were also prepared by the combination of the functional initiator method and the functional end-capping method. This allowed the synthesis of a poly(*p*-MeOSt) macromonomer with one malonate diester at the α end and one methacrylate group at the ω end.

In contrast to vinyl ethers and *p*-alkoxystyrenes, quenching the living cationic polymerization of styrene, in conjunction with $SnCl_4$ in the presence of $n$$Bu_4NCl$, with bases such as methanol, sodium methoxide, benzylamine, or diethyl sodiomalonate, led to the terminal chloride instead of the specific end group. This can be explained by the very low concentration of cationic species compared to that of the dormant C–Cl end group and by the quenching of $SnCl_4$ with the above Lewis bases. This was overcome by using organosilicon compounds such as trimethylsilyl methacrylate and quantitative functionalization was achieved when the quenching reaction was performed at 0 °C for 24 h, in the presence of a large excess of the quencher and low concentration of the Lewis acid [156].

Allyl terminated linear and triarm star PIBs and epoxy and hydroxy telechelics therefrom have been reported by Ivan and Kennedy [124]. Allyl functional PIBs were obtained in a simple one pot procedure involving living IB polymerization using $TiCl_4$ as coinitiator followed by end quenching with ATMS. This method is commercially employed by Kaneka Corp. (Japan) for the synthesis of allyl telechelic PIB, a precursor to moisture curable PIBs. The procedure was based on earlier reports by Wilczek and Kennedy [157, 158] that demonstrated quantitative allylation of PIB–Cl by ATMS in the presence of Et_2AlCl or $TiCl_4$. Quantitative hydroboration followed by oxidation in alkaline THF at room temperature resulted in -OH functional PIBs, which were used to form PIB-based polyurethanes [159]. Quantitative epoxidation of the double bonds was also achieved with *m*-chloroperbenzoic acid in $CHCl_3$ at room temperature, giving rise to macromonomers able to polymerize by ring-opening polymerization.

In a similar development utilizing allylsilanes, the synthesis of α-methylstyryl functional PIB macromonomer was reported by the reaction of 2-phenylallyltrimethylsilane with living PIB [160]. The macromonomer, however, displayed low reactivity in cationic copolymerization with IB, which was ascribed to steric hindrance. In contrast, a reactive and unhindered macromonomer was obtained in the reaction of living PIB with 1-(2-propenyl)-3-[2-(3-trimethylsilyl)-propenyl]benzene, where the reactivity of the allylsilyl function is about 1000 times higher than that of the α-methylstyryl function.

Furan telechelic PIB macromonomers with well-defined M_ns and narrow MWD were synthesized by end quenching living PIB with 2-tributylstannylfuran or 2,2-difurylpropane [137, 161]. Three-arm star, furan functional PIBs were obtained under identical conditions except 1,3,5-tricumyl chloride was used as initiator. The resulting telechelic PIBs could be efficiently photocured by ultraviolet (UV) radiation in the presence of a cationic photoinitiator and a divinyl ether reactive diluent [162]. Owing to the lower reactivity of thiophene compared to furan the reaction of unsubstituted thiophene with living PIB resulted in rapid and quantitative monoaddition and the quantitative formation of 2-polyisobutylenyl-thiophene [163].

Macromonomers with a terminal non(homo)polymerizable vinylidene group, such as DPE, have gained much attention in recent years. One of the most unique and appealing applications of these types of macromonomers is that they can be used as precursor polymers for a variety of block copolymers with controlled architectures such as ABC-type star-block or comb-type graft copolymers. ω-DPE functionalized macromonomers could be prepared by the addition reaction of living cationic polymers to "double" diphenylethylenes such as 1,3-bis(1-phenylethenyl)benzene (*meta*-double diphenylethylene, MDDPE) or 1,4-bis(1-phenylethenyl)benzene (*para*-double diphenylethylene, PDDPE) [164]. The addition reaction of living PIB prepared using the TMPCl/$TiCl_4$/DTBP system in hexane/MeCl 60/40 (v/v) at $-80\,^{\circ}C$ system to 2 equivalent of PDDPE resulted in a rapid and quantitative formation of PIB–DPE macromonomer, as proved by ^1H and ^{13}C NMR spectroscopies, without the formation of the coupled product. With MDDPE larger excess (4 equivalent) was necessary to obtain the monoadduct with negligible amounts of the diadduct.

2.6.2.1 **Chain-End Modification**

In this method, the polymerizable function is incorporated by chemical modification of the α- or ω end group after isolation of the polymer. Although a wide variety of polymerizable groups can be incorporated this way, previously reported methods are generally cumbersome as they involve several steps [165–168]. A new promising avenue for the preparation of PIB macromonomers takes advantage of the high reactivity of primary chloro- or bromo-functional PIBs in nucleophilic substitution reactions as shown above for the synthesis of functional PIBs. Employing these precursors, acrylate [169], methacrylate [169, 170], vinyloxy [169], and epoxy [169] functional PIBs with quantitative functionality have been obtained in one-step reactions utilizing inexpensive reagents.

2.6.2.2 **Block Copolymers**

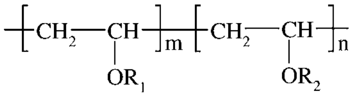
Living polymerization is the most effective and convenient method to prepare block copolymers. Synthetic methodologies, however, need to be carefully selected to prepare block copolymers with high structural integrity. In general, block copolymers can be synthesized by sequential monomer addition or by reactions of living or end-functionalized polymer ends. This second method includes the use of macroinitiator for the polymerization of the second monomer and coupling/linking living and/or end functional polymer ends.

2.7
Linear Diblock Copolymers

Living cationic sequential block copolymerization is one of the simplest and most convenient methods to provide well-defined block copolymers. The successful synthesis of block copolymers via sequential monomer addition relies on the rational selection of polymerization conditions, such as Lewis acid, solvent, additives, and temperature, and on the selection of the appropriate order of monomer addition. For a successful living cationic sequential block copolymerization, the rate of crossover to a second monomer (R_{cr}) must be faster than or at least equal to that of the homopolymerization of a second monomer (R_p). In other words, efficient crossover could be achieved when the two monomers have similar reactivities or when crossover occurs from the more reactive to the less reactive monomer. When crossover is from the less reactive monomer to the more reactive one a mixture of block copolymer and homopolymer is invariably formed because of the unfavorable R_{cr}/R_p ratio. The nucleophilicity parameter (N) reported by Mayr's group might be used as the relative scale of monomer reactivity [171].

When the reactivity of the two monomers is similar and steric factors are absent sequential block copolymerization can be used successfully. Alkyl vinyl ethers have similar reactivity and therefore a large variety of AB or BA type diblock copolymers could be prepared by sequential block copolymerization. A recent review is available [172]. Typical examples are shown [173] in Figure 2.1.

Hydrolysis of the 2-acetoxyethyl vinyl ether or 2-(vinyloxy)diethyl malonate yielded block segments with pendant hydroxyl or carboxyl groups. Most of these syntheses utilized the HI/I_2 or HX/ZnX_2 ($X =$ halogen) initiating systems. Within the vinyl ether family differences in reactivity are relatively small



$$\left[CH_2-\underset{OR_1}{CH}\right]_m\left[CH_2-\underset{OR_2}{CH}\right]_n$$

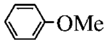
R_1	R_2
$nC_{16}H_{33}$	CH_3, C_2H_5
CH_2CH_2OH	iC_4H_9, nC_4H_9, iC_8H_{17}, $nC_{16}H_{33}$
$CH_2CH_2CH_2COOH$	nC_4H_9, iC_8H_{17}, $nC_{16}H_{33}$
$CH_2CH_2NH_2$	nC_4H_9, $nC_{16}H_{33}$
$CH_2C_6H_5$	iC_4H_9
CH_3 or iC_4H_9	

Figure 2.1 Typical examples of AB or BA type diblock copolymers prepared by sequential block copolymerization.

and could be overcome by increasing the concentration of the Lewis acid for the polymerization of the second, less reactive vinyl ether, for instance in the preparation of poly(isobutyl vinyl ether-*b*-2-acetoxyethyl vinyl ether). Stimuli-responsive diblock copolymers with a thermosensitive segment and a hydrophilic segment have been synthesized via sequential living cationic copolymerization employing $Et_{1.5}AlCl_{1.5}$ as coinitiator in the presence of a Lewis base by Aoshima and coworkers [174]. The block copolymers consisting of a poly(vinyl ether) block segment with oxyethylene pendants exhibiting lower critical solution temperature (LCST)-type phase separation in water and a poly-(hydroxyethyl vinyl ether) segment displayed highly sensitive and reversible thermally induced micelle formation and/or physical gelation. Using essentially the same synthetic method many other vinyl ether-based stimuli-responsive block copolymers (in addition to homo- and random copolymers) have been reported by the same research group. A recent review is available [175].

Similarly block copolymers of vinyl ethers and *p*-alkoxystyrenes could be prepared by a simple sequential monomer addition [74]. In contrast, the synthesis of poly(methyl vinyl ether-*b*-styrene) is more difficult. While methyl vinyl ether smoothly polymerized with the $HCl/SnCl_4$ system in the presence of $n\mathrm{Bu}_4\mathrm{NCl}$ at $-78\,^{\circ}\mathrm{C}$, for the second stage polymerization of the less reactive St additional amount of $SnCl_4$ and increase of temperature to $-15\,^{\circ}\mathrm{C}$ were necessary.

Although structurally different, IB and styrene possess similar reactivity and diblock copolymers poly(IB-*b*-St) [58] as well as the reverse order poly(St-*b*-IB) [60, 176] could be readily prepared via sequential monomer addition. Moreover, identical coinitiator and reaction conditions could be employed for the living cationic polymerization of both monomers. However, while the living PIB chain ends are sufficiently stable under monomer starved conditions, the living PSt chain ends undergo decomposition at close to $\sim$100% conversion of St. [177]. Therefore, IB must be added at $\leq$95% conversion of St to obtain poly(St-*b*-IB) diblock copolymers with negligible homo-polystyrene contamination [60, 178, 179]. The presence of unreacted St monomer, however, complicates the block copolymerization of IB. The first-order plot of IB, which is linear for homopolymerization, is curved downward for block copolymerization, indicating decreasing concentration and/or reactivity of active centers with time. This is attributed to the slow formation of –St–IB–Cl chain ends (because of the reactivity ratios that are both much higher than unity), which are much less reactive than –IB–IB–Cl [60].

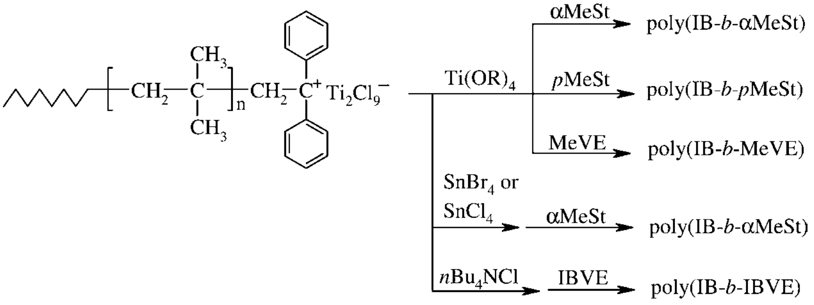
In the synthesis of the reverse sequence, poly(IB-*b*-St), it is important to add St after complete polymerization of IB. When St is added at less than 100% IB conversion the polymerization of St will be slow, which again is due to the formation and low reactivity of –St–IB–Cl chain ends. For instance, when St is added after complete polymerization of IB, St polymerization is complete in 1 h. In contrast, when St is added at 94% IB conversion St conversion reaches only $\sim$50% in 1 h at otherwise identical conditions.

Living cationic sequential block copolymerization from a more reactive monomer to a less reactive one usually requires a change from a weaker Lewis acid to a stronger one. For instance the living cationic polymerization of αMeSt have been reported using the relatively mild Lewis acid, such as $SnBr_4$, $TiCl_n(OR)_{4-n}$, $SnCl_4$, or BCl_3, as a coinitiator [41, 80, 81, 83, 84, 180]. These Lewis acids, however, are too weak to initiate the polymerization of the less reactive IB; therefore, the addition of a stronger Lewis acid, e.g., $TiCl_4$, is necessary to polymerize IB by sequential monomer addition. With $SnBr_4$ or $TiCl_n(OR)_{4-n}$, however, ligand exchange takes place upon addition of $TiCl_4$, which results in mixed titanium halides that are too weak to initiate the polymerization of IB. Ligand exchange is absent with BCl_3, which also induces living cationic polymerization of αMeSt in MeChx/MeCl 60/40 (v/v) solvent mixture at $-80\,^\circ$C. Thus BCl_3 is suitable for the synthesis of poly(αMeSt-*b*-IB) diblock copolymer. Upon addition of IB to the living poly(αMeSt) (PαMeSt) solution, quantitative crossover takes place followed by instantaneous termination (initiation without propagation) and the selective formation of PαMeSt-IB_1-Cl [85, 181]. The addition of $TiCl_4$ starts the polymerization of IB.

The living cationic polymerization of *p*-chloro-α-methylstyrene (*p*ClαMeSt) can also be accomplished under conditions identical to those used for the synthesis of poly(αMeSt-*b*-IB) copolymer [86, 182]. Using the above method poly(*p*ClαMeSt-*b*-IB) diblock copolymer was also prepared via sequential monomer addition. On the basis of GPC UV traces of the starting P*p*ClαMeSt and the resulting poly(*p*ClαMeSt-*b*-IB) diblock copolymer, the B_{eff} was ~100% and homopolymer contamination was not detected.

Sequential block copolymerization of IB with more reactive monomers such as αMeSt, *p*-MeSt, IBVE, or methyl vinyl ether (MeVE) as a second monomer invariably leads to a mixture of block copolymer and PIB homopolymer. To overcome the difficulty in the crossover step, a general methodology has been developed for the synthesis of block copolymers when the second monomer is more reactive than the first one. It involves the intermediate capping reaction with non(homo)polymerizable monomers such as diarylethylenes and 2-substituted furans.

As shown in Scheme 2.4 [183], this process involves the capping reaction of living PIB with DPE or DTE, followed by tuning of the Lewis acidity to the reactivity of the second monomer. First, the capping reaction yields a stable and fully ionized diarylcarbenium ion ($PIB-DPE^+$) [184, 185], which has been confirmed using spectroscopic methods (NMR and UV/Vis) and conductivity measurements. The capping reaction of living PIB with 1,1-diarylethylenes is an equilibrium reaction, which can be shifted toward completion with decreasing temperature, or with increasing Lewis acidity, solvent polarity, electron-donating ability of *p*-substituents, or concentration of reactants. The purpose of the Lewis acidity tuning, following the capping reaction, is to generate more nucleophilic counterions, which ensure a high $R_{\text{cr}}/R_{\text{p}}$ ratio as well as the living polymerization of a second monomer. This has been carried



Scheme 2.4 Synthesis of block copolymers via capping reaction of living PIB with DPE, followed by Lewis acidity tuning and sequential monomer addition.

out using three different methods: (i) by the addition of titanium(IV) alkoxides ($Ti(OR)_4$), (ii) by the substitution of a strong Lewis acid with a weaker one, or (iii) by the addition of $n\mathrm{Bu}_4\mathrm{NCl}$.

The first and simplest method has been successfully employed in the block copolymerization of IB with *α*MeSt [186], *p*-MeSt [66], MeVE [187, 188]. *t*BuVE [97], *t*-butyldimethylsilyl vinyl ether [189], CHVE [190], and *p*-*tert*-butyldimethylsiloxystyrene (*t*BDMSt) [191].

The substitution of $TiCl_4$ with a weaker Lewis acid ($SnBr_4$ or $SnCl_4$) has also been proven to be an efficient strategy in the synthesis of poly(IB-*b*-*α*MeSt) [41, 180] and poly(IB-*b*-*t*-BuOSt) (R. Faust *et al.*, unpublished work) diblock copolymers.

The block copolymerization of IB with IBVE was achieved by Lewis acidity tuning using $n\mathrm{Bu}_4\mathrm{NCl}$ [40, 192]. The addition of $n\mathrm{Bu}_4\mathrm{NCl}$ reduces the concentration of free and uncomplexed $TiCl_4$ ($[TiCl_4]_{\mathrm{free}}$), and mechanistic studies indicated that, when $[TiCl_4]_{\mathrm{free}}$ < [chain end], the dimeric counterion, $Ti_2Cl_9^-$, is converted to a more nucleophilic monomeric $TiCl_5^-$ counterion suitable for the living polymerization of IBVE.

Block copolymerization of IB with MeVE was also carried out using 2-methylfuran or 2-*tert*-butylfuran as a capping agent [122, 193]. However, the crossover efficiency was only ~66% using 2-*tert*-butylfuran and only slightly higher (~75%) when 2-methylfuran was employed as a capping agent under similar condition.

2.8
Linear Triblock Copolymers

2.8.1
Synthesis Using Difunctional Initiators

As soluble multifunctional initiators are more readily available in cationic polymerization than in the anionic counterpart, ABA type linear triblock copolymers have been almost exclusively prepared using difunctional initiation followed by sequential monomer addition. The preparation and properties of ABA type block copolymer thermoplastic elastomers (TPEs), where the middle segment is PIB, have been reviewed recently [194].

The synthesis of poly(St-*b*-IB-*b*-St) triblock copolymer has been accomplished by many research groups [195–201]. The synthesis invariably involved sequential monomer addition using a difunctional initiator in conjunction with $TiCl_4$ in a moderately polar solvent mixture at low (−70 to −90 °C) temperatures. As already mentioned at the synthesis of poly(IB-*b*-St) it is important to add St at ~100% IB conversion. The selection of the solvent is also critical, coupled product that forms in intermolecular alkylation during St polymerization cannot be avoided when the solvent is a poor solvent (e.g., hexanes/MeCl 60/40 (v/v)) for polystyrene [202]. The formation of coupled product is slower in *n*BuCl or in MeChx/MeCl 60/40 (v/v) solvent mixture; however, to obtain block copolymers essentially free of coupled product it is necessary to stop the polymerization of St before completion. Detailed morphological and physical properties of poly(St-*b*-IB-*b*-St) triblock copolymer have been reported [199, 203–206]. The two step sequential monomer addition method has also been employed to obtain poly(*p*-chlorostyrene-*b*-IB-*b*-*p*-chlorostyrene) [68, 207], poly(indene-*b*-IB-*b*-indene) [208], poly(*p*-*tert*-butylstyrene-*b*-IB-*b*-*p*-*tert*-butylstyrene) [209], poly((indene-*co*-*p*-methylstyrene)-*b*-IB-*b*-(indene-*co*-*p*-methylstyrene)) [210], poly(*p*-MeSt-*b*-IB-*b*-*p*-MeSt) [202], and poly(styryl-POSS-*b*-IB-*b*-styryl-POSS) (POSS=polyhedral oligomeric silsequioxane) [211] copolymers.

When the crossover from the living PIB chain ends is slower than propagation of the second monomer, e.g., αMeSt, *p*-MeSt, and vinyl ethers, the final product is invariably a mixture of triblock and diblock copolymers and possibly homoPIB, which results in low tensile strength and low elongation [212]. This slow crossover can be circumvented by the synthetic strategy shown above utilizing an intermediate capping reaction of the living PIB with diarylethylenes followed by moderating the Lewis acidity before the addition of the second monomer. This method has been successfully employed for the synthesis of poly(αMeSt-*b*-IB-*b*-αMeSt) [213], poly(*p*-MeSt-*b*-IB-*b*-*p*-MeSt) [214], poly(*t*BDMSt-*b*-IB-*b*-*t*BDMSt) and poly(*p*-hydroxystyrene-*b*-IB-*b*-*p*-hydroxystyrene) by subsequent hydrolysis [191], poly(*t*BuVE-*b*-IB-*b*-*t*BuVE) [97] and poly(vinyl alcohol-*b*-IB-*b*-vinyl alcohol) by subsequent hydrolysis [215], and poly(CHVE-*b*-IB-*b*-CHVE) [98]. Tensile strengths of most of these TPEs as well as triblock copolymers reported above were similar to that obtained with Poly(St-*b*-IB-*b*-St) and virtually identical to that of vulcanized butyl rubber, indicating failure in the elastomeric domain.

2.8.2
Synthesis Using Coupling Agents

Although the synthetic strategy using non(homo)polymerizable monomers has been shown to be highly effective for the synthesis of a variety of di- or triblock copolymers, ABA type linear triblock copolymers can also be prepared by coupling of living diblock copolymers, a general and useful method in living anionic polymerization.

Several coupling agents for living poly(vinyl ethers) and PαMeSt have been reported in cationic polymerization [116, 216, 217]. Synthetic utilization of non(homo)polymerizable diolefins has been first shown for the coupling reaction of living PIB [135, 218]. Using BDPEP or 2,2- BDTEP or 2,5-bis[1-(2-furanyl)-1-methylethyl]-furan as coupling agent, a rapid and quantitative coupling reaction of living chain end was achieved, independently of the molecular weight of PIB. Kinetic studies indicated that coupling reaction of living PIB with bis-DPE compounds is a consecutive reaction where the second addition is much faster than the first one. As a result, high coupling efficiency was also observed, even when excess BDPEP was used. This coupling agent is therefore best suited for the synthesis of ABA triblock copolymers by coupling of living AB diblock copolymers, and has been employed to obtain Poly(St-*b*-IB-*b*-St) [60] and Poly(αMeSt-*b*-IB-*b*-αMeSt) [182] triblock copolymers. For the synthesis of Poly(St-*b*-IB-*b*-St) triblock copolymers, however, the two step monomer addition method is superior. As IB must be added at $\leq$95% St conversion to obtain living Poly(St-*b*-IB) with negligible PSt homopolymer contamination, the relatively high concentration of unreactive –St–IB–Cl chain ends causes coupling of living Poly(St-*b*-IB) diblocks to be very slow, incomplete even after 50 h.

2.9
Block Copolymers with Nonlinear Architecture

Cationic synthesis of block copolymers with nonlinear architectures has been reviewed recently [219]. $(AB)_n$ type star-block copolymers, where n represents the number of arms, have been prepared by the living cationic polymerization using three different methods: (i) via multifunctional initiators, (ii) via multifunctional coupling agents, and (iii) via linking agents.

The synthesis using multifunctional initiators has been the most versatile method because of the abundance of well-defined soluble multifunctional initiators for a variety of monomers. Using trifunctional initiators many groups have prepared three-arm star-block copolymers such as poly(IBVE-*b*-2-hydroxyethyl vinyl ether)$_3$ [220], poly(IB-*b*-St)$_3$ [195, 221], and poly(IB-*b*-*p*-MeSt)$_3$ [214] star-block copolymers. The synthesis of eight arm poly(IB-*b*-St)$_8$ star-block copolymers was reported [222] using an octafunctional calix[8]arene-based initiator for the living cationic polymerization of IB followed by sequential addition of St. The synthesis of poly(IB-*b*-*p*-(*p*ClSt))$_8$ star-block copolymer was also accomplished using the previously mentioned method [223]. Recently, multiarm star-block copolymers of poly(IB-*b*-St) [224] and poly(IB-*b*-*p*-*tert*-butylstyrene) [225] copolymers were synthesized by living cationic polymerization using a hexafunctional initiator, HES, which was prepared by a simple epoxidation of squalene.

Novel arborescent block copolymers comprised of rubbery PIB and glassy PSt blocks (arb-PIB-*b*-PSt) are described by Puskas *et al.* [226]. The synthesis was accomplished with the use of arb-PIB macroinitiators, prepared by the use of 4-(2-methoxyisopropyl)styrene inimer, in conjunction with $TiCl_4$. Samples with 11.7–33.8 wt% PSt exhibited TPE properties with 3.6–8.7 MPa tensile strength and 950–1830% elongation.

Linking reaction of living polymers has been employed as an alternative way to prepare star-block copolymers. The synthesis of poly(St-*b*-IB) multiarm star-block copolymers was reported using divinylbenzene (DVB) as a linking agent [179, 227]. The synthesis and mechanical properties of star-block copolymers consisting of 5–21 poly(St-*b*-IB) arms emanating from cyclosiloxane cores have been published [172, 228]. The synthesis involved the sequential living cationic block copolymerization of St and IB, followed by quantitative allylic chain-end functionalization of the living poly(St-*b*-IB), and finally linking of these prearms with SiH-containing cyclosiloxanes (2,4,6,8,10,12-hexamethylcyclohexasiloxane) by hydrosilation. Star-block copolymers of poly(indene-*b*-IB) have been prepared using the previously mentioned method [229].

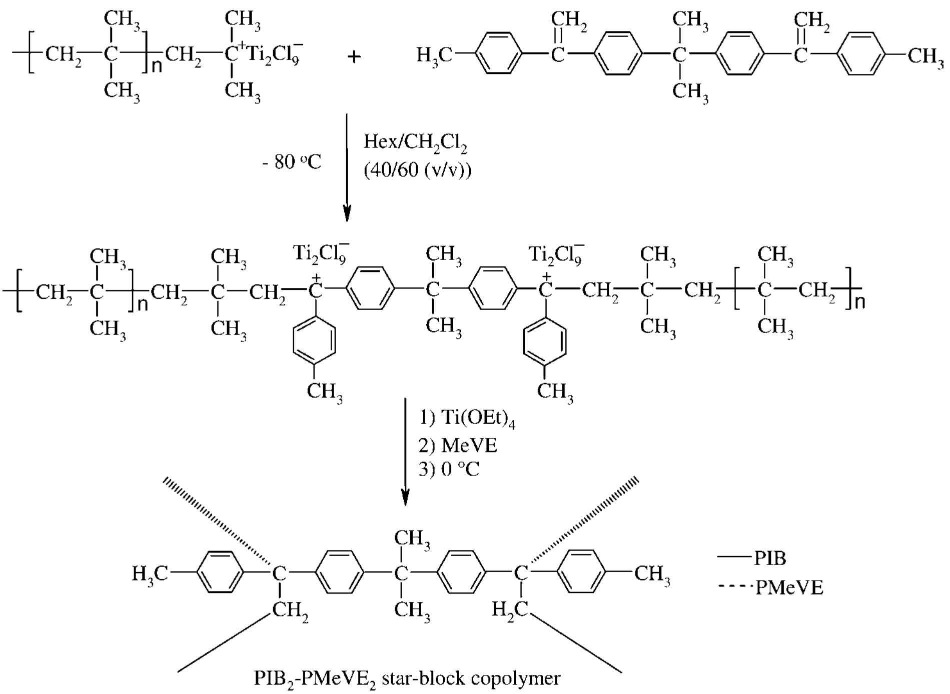
2.9.1

Synthesis of A_nB_n Hetero-Arm Star-Block Copolymers

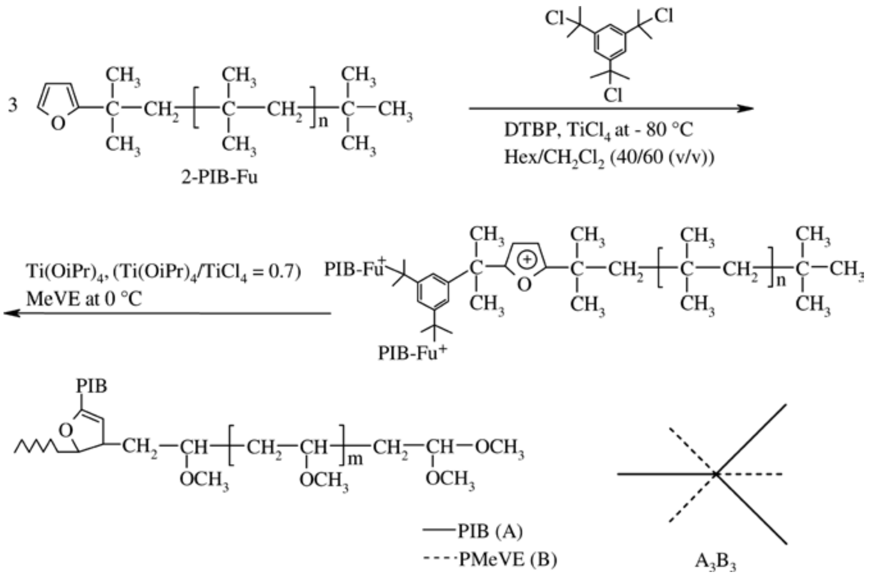
The bis-DPE compounds such as BDPEP or BDTEP, could be useful as “living” coupling agents. It was demonstrated that living PIB reacts quantitatively with these coupling agents to yield stoichiometric amounts of bis(diarylalkylcarbenium) ions. As diarylalkylcarbenium ions have been shown to be successful for the controlled initiation of reactive monomers such as *p*-MeSt, αMeSt, IBVE, and MeVE, A_2B_2 star-block copolymers may be prepared by this reaction.

As a proof of the concept, an amphiphilic A_2B_2 star-block copolymer ($A = PIB$ and $B = PMeVE$) has been prepared by the living coupling reaction of living PIB followed by the chain ramification polymerization of MeVE at the junction of the living coupled PIB as shown in Scheme 2.5 [136].

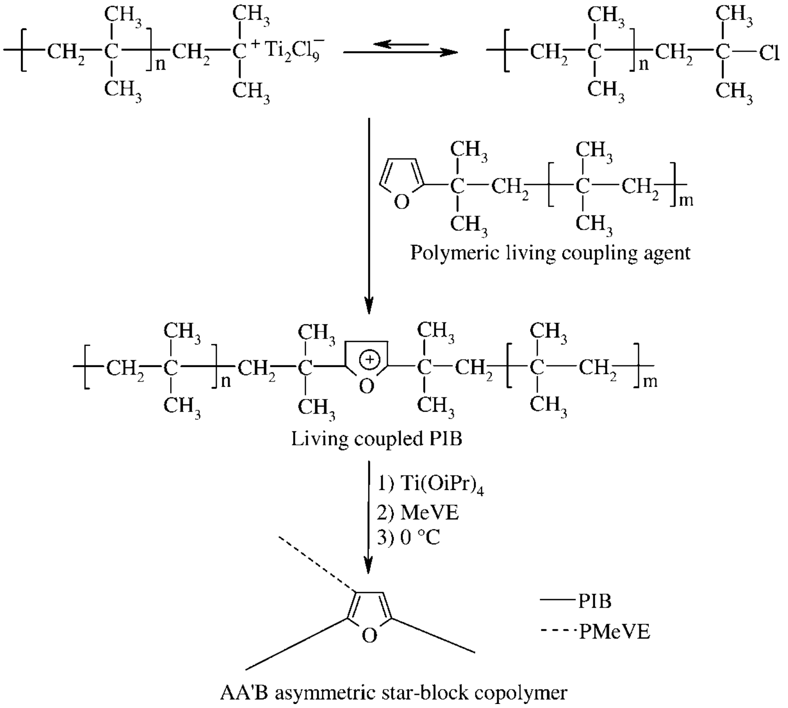
While the concept of coupling with ω-furan functionalized PIB as a polymeric coupling agent has been utilized to obtain AB-type block copolymers, it is also apparent that ω-furan functionalized polymers can be used as living coupling polymeric precursor for the synthesis of hetero-arm star-block copolymers. The synthesis of poly(IB_3-star-$MeVE_3$) is shown in Scheme 2.6. Tricumyl chloride is reacted with 2-PIB-furan and after tuning of the Lewis acidity the living linked 2-PIB-Fu initiated the polymerization of MeVE [230].



Scheme 2.5 Living coupling reaction of living PIB with BDTEP and chain ramification reaction of MeVE for the synthesis of A_2B_2 star-block copolymer.



Scheme 2.6 The synthesis of poly(IB_3-star-$MeVE_3$).



Scheme 2.7 Synthesis of AA″B asymmetric star-block copolymer.

2.9.2
Synthesis of AA′B, ABB′, and ABC Asymmetric Star-Block Copolymers Using Furan Derivatives

The strategy for the synthesis of AA′B-type star-block copolymers, where A = PIB(1), A′ = PIB(2), and B = PMeVE, is illustrated in Scheme 2.7 [161]. First, quantitative addition of ω-furan functionalized PIB (A′), obtained from a simple reaction between living PIB and 2-Bu_3SnFu, to living PIB (A) could be achieved in hexanes/CH_2Cl_2 40/60 (v/v) at −80 °C in conjunction with $TiCl_4$. The resulting living coupled PIB–Fu^+ –PIB′ was successfully employed for the subsequent chain ramification polymerization of MeVE. This technique is unique in the ability to control A and A′ block lengths independently.

2.9.3
Block Copolymers Prepared by the Combination of Different Polymerization Mechanisms

2.9.3.1 Combination of Cationic and Anionic Polymerization

The combination of living cationic and anionic techniques provides a unique approach to block copolymers not available by a single method.

Site transformation and coupling of two homopolymers are convenient and efficient ways to prepare well-defined block copolymers.

Block copolymers of IB and methyl methacrylate (MMA), monomers that are polymerizable only by different mechanisms, can be prepared by several methods. The prerequisite for the coupling reaction is that the reactivities of the end groups have to be matched and a good solvent has to be found for both homopolymers and copolymer to achieve quantitative coupling. Poly(IB-*b*-MMA) block copolymers were synthesized by coupling reaction of two corresponding living homopolymers, obtained by living cationic and group transfer polymerization (GTP), respectively [231].

The synthesis of poly(MMA-*b*-IB-*b*-MMA) triblock copolymers has also been reported using the site-transformation method, where α,ω-dilithiated PIB was used as the macroinitiator [232]. The site-transformation technique provides a useful alternative for the synthesis of block copolymers consisting of two monomers that are polymerized only by two different mechanisms. In this method, the propagating active center is transformed to a different kind of active center and a second monomer is subsequently polymerized by a mechanism different from the preceding one. The key process in this method is the precocious control of α or ω-end functionality, capable of initiating the second monomer. Recently a novel site-transformation reaction, the quantitative metalation of DPE-capped PIB carrying methoxy or olefin functional groups, has been reported [233]. This method has been successfully employed in the synthesis of poly(IB-*b*-tert-butylmethacrylate) (*t*BMA) diblock and poly(MMA-*b*-IB-*b*-MMA) triblock copolymers [234]. In this technique, however, metalation of DPE-capped PIB requires Na/K alloy as organolithium compounds are ineffective.

A new synthetic route for the synthesis poly(IB-*b*-*t*BMA) developed by combining living carbocationic and anionic polymerizations involves metalation of 2-polyisobutylenyl-thiophene with *n*-butyllithium in THF at −40 °C. The resulting stable macrocarbanion (PIB−T−, Li^+) was successfully used to initiate living anionic polymerization of *t*BMA yielding poly(IB-*b*-*t*BMA) block copolymers [235].

The preparation of poly(IB-*b*-methyl methacrylate or hydroxyethyl methacrylate) block copolymers has also been accomplished by the combination of living cationic and anionic polymerization. First DPE end-functionalized PIB (PIB−DPE) was prepared from the reaction of living PIB and 1,4-bis(1-phenylethenyl)benzene (PDDPE), followed by the methylation of the resulting diphenyl carbenium ion with dimethylzinc. PIB−DPE was quantitatively metalated with *n*-butyllithium in THF at room temperature and the resulting macroinitiator could efficiently initiate the living polymerization of methacrylate monomers at −78 °C yielding block copolymers with high block efficiency [236].

2.9.3.2 Combination of Living Cationic and Anionic Ring-Opening Polymerization

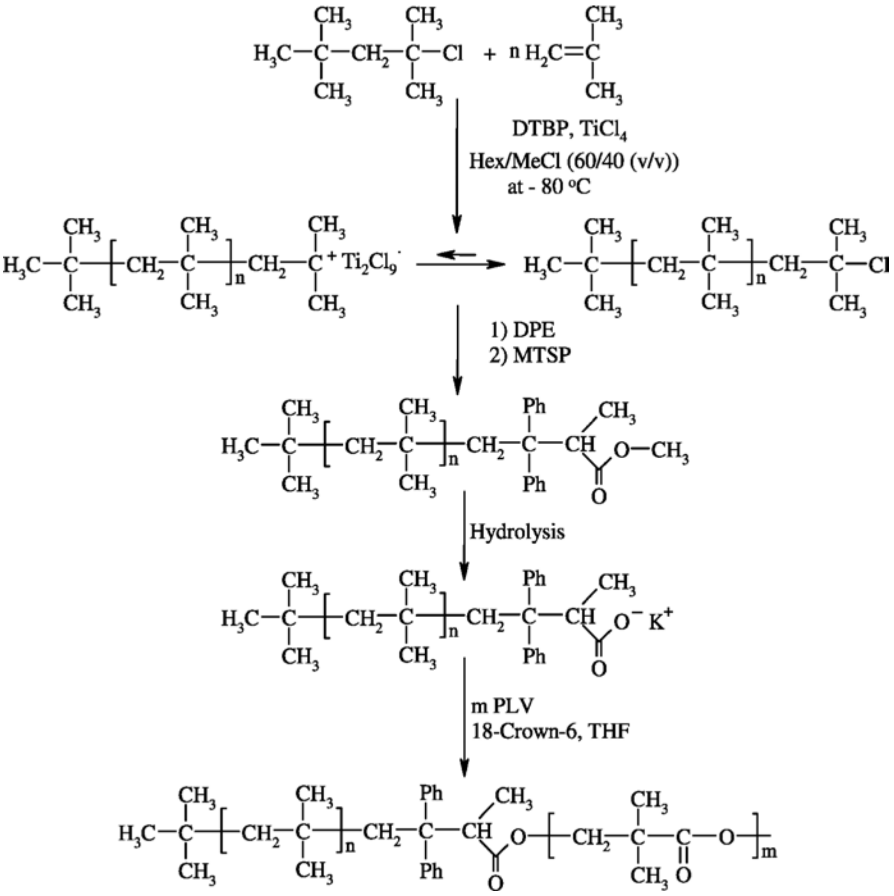
Block copolymers containing crystallizable blocks have been studied not only as alternative TPEs with improved properties but also as novel nanostructured materials with much more intricate architectures compared to those produced by the simple amorphous blocks. As the interplay of crystallization and microphase segregation of crystalline/amorphous block copolymers greatly influences the final equilibrium ordered states and results in a diverse morphological complexity, there has been a continued high level of interest in the synthesis and characterization of these materials.

Owing to the lack of vinyl monomers giving rise to crystalline segment by cationic polymerization, amorphous/crystalline block copolymers have not been prepared by living cationic sequential block copolymerization. Although site transformation has been utilized extensively for the synthesis of block copolymers, only a few PIB/crystalline block copolymers, such as poly(L-lactide-*b*-IB-*b*-L-lactide) [237], poly(IB-*b*-ε-caprolactone (ε-CL)) [238] diblock, and poly(ε-CL-*b*-IB-*b*-ε-CL) [239] triblock copolymers have been reported.

The synthesis of poly(IB-*b*-pivalolactone (PVL)) diblock copolymers was also recently accomplished by site transformation of living cationic polymerization of IB to anionic ring-opening polymerization (AROP) of PVL, as shown in Scheme 2.8 [240–242]. First, PIB with ω-carboxylate potassium salt was prepared by capping living PIB with DPE followed by quenching with 1-methoxy-1-trimethylsiloxy-propene (MTSP), and hydrolysis of ω-methoxycarbonyl end groups. The ω-carboxylate potassium salt was successfully used as a macroinitiator for the AROP of PVL in THF, leading to poly(IB-*b*-PVL) copolymers. The same methodology as mentioned above was applied for the synthesis of poly(PVL-*b*-IB-*b*-PVL) triblock copolymers, except that a difunctional initiator, 5-*tert*-butyl-1,3-bis-(1-chloro-1-methylethyl)-benzene (*t*BuDiCumCl), was used for the polymerization of IB in the first step.

The preparation of novel glassy(A)-*b*-rubbery(B)-*b*-crystalline(C) linear triblock copolymers have been reported where A block is PαMeSt, B block is rubbery PIB, and C block is crystalline PPVL. The synthesis was accomplished by living cationic sequential block copolymerization to yield living poly(αMeSt-*b*-IB) followed by site transformation to polymerize PVL [243]. In the first synthetic step, the GPC traces of poly(αMeSt-*b*-IB) copolymers with ω-methoxycarbonyl functional group exhibited bimodal distribution in both refractive index and UV traces, and the small hump at higher elution volume was attributed to PαMeSt homopolymer. This product was fractionated repeatedly using hexanes/ethyl acetate to remove homo PαMeSt and the pure poly(αMeSt-*b*-IB) macroinitiator was then utilized to initiate AROP of PVL to give rise to poly(αMeSt-*b*-IB-*b*-PVL) copolymer.

Complete crossover from living PαMeSt to IB, could be achieved by modifying the living PαMeSt chain end with a small amount of *p*ClαMeSt after complete conversion of αMeSt. The poly(αMeSt-*b*-IB) copolymer carrying ω-carboxylate group, obtained from hydrolysis of ω-methoxycarbonyl group of



Scheme 2.8 Synthesis of poly(IB-*b*-PVL) copolymer by site transformation.

the block copolymer, was used to initiate AROP of PVL in conjunction with 18-crown-6 in THF at 60 °C, to give rise to poly(αMeSt-*b*-*p*ClαMeSt-*b*-IB-*b*-PVL) copolymer [244].

Recently the synthesis of poly(IB-*b*-ethylene oxide) diblock copolymer has been reported [245]. In the first step, HO-functional PIB was prepared by hydroboration/oxidation of allyl functional PIB, obtained in the reaction of living PIB and ATMS. The ring-opening polymerization of ethylene oxide was initiated by the PIB alkoxide anion in conjunction with the bulky phospazene *t*-BuP$_4$.

2.9.3.3 Combination of Living Cationic and Radical Polymerization

The scope of block copolymer synthesis by the combination of two different polymerization techniques has been rapidly expanded with the advent of living/controlled radical polymerization. Although block copolymers such as poly(St-*b*-IB-*b*-St) could also be prepared by the combination of cationic and atom transfer radical polymerization (ATRP) [246, 247], the more interesting examples involve monomers that do not undergo cationic polymerization. For instance the synthesis of poly(IB-*b*-methacrylic acid) diblocks, poly(methacrylic acid-*b*-IB-*b*-methacrylic acid) triblocks, and three-arm star-block copolymers have been reported by Fang and Kennedy [248], by hydrolysis of the corresponding *t*-BuMA block copolymers. The hydroxyl functional PIBs, obtained by hydroboration/oxidation of allyl functional PIBs, were reacted with 2-bromoisobutyryl bromide to yield a PIB macroinitiator for the ATRP. Radical polymerization of *t*-BuMA followed by hydrolysis gave the targeted block copolymers.

Block copolymers containing PMeVE and poly(*tert*-Bu acrylate), poly(acrylic acid), poly(Me acrylate) or polystyrene, have been prepared by Du Prez *et al.* [249] by the use of a novel dual initiator 2-bromo-(3,3-diethoxy-propyl)-2-methylpropanoate. In the first step, the living cationic homopolymerization of MeVE is performed with the acetal end group of the dual initiator as initiating site or by the ATRP homopolymerization of *tert*-butyl acrylate (*t*BA) from the bromoisobutyrate group of the dual initiator. In the second step in the preparation of block copolymers well-defined PMeVE-Br and poly*p*-*t*BA-acetal homopolymers were employed as macroinitiators, in the ATRP of several monomers and cationic polymerization of MeVE, respectively.

2.10
Branched and Hyperbranched Polymers

The synthesis of branched polymers by cationic polymerization of vinyl monomers has been reviewed recently [219]; therefore, these will be briefly considered here. Star-shaped or multiarm star (co)polymers can be prepared by three general methods:

1. multifunctional initiator method;
2. multifunctional terminator method;
3. polymer linking method.

In the first case, the arms are grown from a single core with a given number of potentially active sites or a well-defined multifunctional initiator. In contrast to anionic multifunctional initiators, well-defined soluble multifunctional cationic initiators are readily available. These multifunctional initiators with 3–8 initiating sites have been successfully applied for the synthesis of 3–8 arm star homo- and block copolymers of vinyl ethers, styrene and styrene derivatives, and IB. For example, six-arm star polystyrenes were prepared using initiator with six phenylethylchloride-type functions emanating from a central hexa-substituted benzene ring [250]. By subsequent end functionalization, a variety of end-functionalized A_n or $(AB)_n$ (see above) star-shaped structures can also be obtained.

In the second and third case, first the arms are synthesized and then linked together using either a well-defined multifunctional terminator or a difunctional monomer leading to a cross-linked core. Well-defined star-branched polymers have been obtained by utilizing multifunctional coupling agents with the nucleophilic functions well separated to avoid steric hindrance. For example, high yields were reported in the synthesis of a three- or four-arm star polymers by reacting short poly(isobutyl vinyl ether) living polymers with a tri- or tetrafunctional silyl enol ether as multifunctional terminator [133].

Difunctional monomers such as DVB or divinyl ether have been found to be efficient in the synthesis of star (co)polymers having a cross-linked core from which homopolymer or block copolymer arms radiate outwards. However, so far only "core last" method has been reported in cationic polymerization. This method is particularly suited to prepare stars with many arms. The average number of arms per molecule is a function of several experimental and structural parameters.

Graft copolymers by cationic polymerization may be obtained by the "grafting from", and "grafting onto" methods and by (co)polymerization of macromonomers. For example, PIB with pendant functionalities could be prepared by copolymerization of IB with a functional monomer such as bromomethylstyrene or chloromethylstyrene in CH_2Cl_2 at $-80\,^\circ C$ with BCl_3. An alternate method to obtain initiating sites along a PIB backbone involves the copolymerization with *p*-MeS followed by selective halogenation [251]. In subsequent initiation of 2-methyl-2-oxazoline, water soluble amphiphilic graft copolymers have been obtained [252].

Highly branched, so called "hyperbranched" macromolecules have recently attracted interest, because of their interesting properties, which closely resemble those of dendrimers. Vinyl monomers with pendant initiating moieties, for example, 3-(1-chloroethyl)-ethenylbenzene, have been reported to give rise to hyperbranched polymers in a process termed *self-condensing vinyl polymerization* [253]. Hyperbranched PIBs have been synthesized by cationic copolymerization of 4-(2-methoxyisopropyl)styrene and IB [254]. Using a similar approach the preparation of arborescent block copolymers of IB and St (arb-PIB-*b*-PSt) has also been reported (see above) [226].

2.11
Surface Initiated Polymerization – Polymer Brushes

Polymer brushes can be generated by reacting by the "grafting to" or "grafting from" techniques. The "grafting to" technique, where a living polymer or a suitable end-functionalized polymer is reacted with a reactive substrate, yields limited surface grafting density because of steric hindrance. In contrast, surface initiated polymerization from a self-assembled initiator on the surface results in high grafting density and film thickness that increases linearly with molecular weight. PSt brushes were prepared on flat silicate substrates by cationic polymerization by Zhao and Brittain [255]. The polymerization of St was initiated from self-assembled monolayers (SAMs) of the cationic initiator, 2-(4-(11-triethoxysilylundecyl)phenyl)-2-methoxypropane in conjunction with $TiCl_4$. PIB brushes could also be obtained on flat silica surfaces by a similar method employing SAMs of 3-(1-chlorodimethyl-silylmethyl)ethyl-1-(1-chloro-1-methyl)ethylbenzene [256]. Initiation from macroscopic surfaces requires the addition of a sacrificial soluble initiator to control the molecular weight of the polymer brush; however, it results in a large amount of unbound polymer. A sacrificial initiator is not necessary when initiation is from nanoparticles with a large surface area as demonstrated for the surface initiated polymerization of IB from SAMs on ~20 nm silica nanoparticles [257]. Owing to the high surface area and grafting density (3.3 chains/nm) approximately 4000 polymer chains of $M_n = 65\,000$ were linked to each nanoparticle resulting in ~220 nm total particle diameter.

2.12
Conclusions

Cationic polymerization is of great theoretical and practical importance. Worldwide production of polymers by cationic vinyl polymerization is estimated at ~2.5 million metric tons per year [258]. Since the discovery of living cationic systems, cationic polymerization has progressed to a new stage where the synthesis of designed materials is now possible.

Practical importance of cationic macromolecular engineering is wide ranging. Commercialization of new technologies based on living cationic polymerization has already begun. Allyl-telechelic curable PIB elastomers (Epion) and poly(styrene-*b*-isobutylene-*b*-styrene) triblock copolymer thermoplastic elastomers (Sibstar) are produced by Kaneka Corporation (Japan). Boston Scientific Corp. also commercialized the synthesis of poly(styrene-*b*-isobutylene-*b*-styrene) (Translute), which it employs as a polymer drug carrier for Paclitaxel-Eluting Coronary Stent system. Due to recent accomplishments in the simple and economic synthesis of functional PIBs further industrial developments may be realized in the field of segmented multiblock copolymers (e.g., thermoplastic polyurethanes) especially in applications where trasparent, flexible, thermally, chemically and oxidatively stable, biocompatible and biostable coatings and adhesives are important.

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3
Radical Polymerization

Krzysztof Matyjaszewski

3.1
Introduction

Approximately 50% of all synthetic polymers are currently made via radical polymerization (RP) processes. The commercial success of RP can be attributed to the large range of radically polymerizable monomers, their facile copolymerization, the convenient reaction conditions employed (typically room temperature to 100 °C, ambient pressure), and very minimal requirements for purification of monomers and solvents. RP is not affected by water and protic impurities and can be carried out in bulk, solution, aqueous suspension, emulsion, dispersion, etc. The range of monomers is larger for RP than for any other chain polymerization because radicals are tolerant to many functionalities, including acidic, hydroxy, and amino groups. In conventional RP, high molecular weight (MW) polymers are formed at the early stages of the polymerization, and neither long reaction times nor high conversions are required, in sharp contrast to step-growth polymerization.

However, RP has some limitations, especially in comparison with ionic processes that provide facile routes to living polymers. For a polymerization to be considered ''living,'' the contribution of chain breaking reactions such as termination and transfer should be negligible. While transfer is not a major issue in RP when the appropriate conditions are applied, termination is much less avoidable and is a major limitation of RP. In contrast to ionic reactions, in which cations or anions do not react via bimolecular termination, radicals terminate with a diffusion controlled rate. To form high MW polymers, the relative probability of such termination must be minimized. This is accomplished by running RP at very low concentrations (from ppb to ppm) of propagating radicals. The concentrations of growing species are thus much lower in RP than in carbanionic or ring-opening polymerizations. In RP, a steady concentration of radicals is established by balancing the rate of termination with that of initiation. The rate of propagation is much faster than the rate of initiation/termination (as required to keep radical concentration low). Therefore,

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chains are continuously generated and it is not possible to prepare (co)polymers with controlled architecture in conventional RP. In RP, a propagating radical reacts with monomer every $\approx$1 ms, and chains typically terminate after $\approx$1 s, during which time a high MW polymer is formed (degree of polymerization (DP) $\approx$ 1000). At any given moment of the polymerization, the number of growing chains, which can be functionalized or chain extended, is very small (i.e., $<$0.1%), unlike in ionic living polymerization, which is essentially carried out with instantaneous initiation and without chain breaking reactions.

Thus, it has not been possible to prepare well-defined (co)polymers via conventional RP. However, new approaches that exploit equilibria between growing radicals and dormant species were recently developed to minimize the proportion of terminated chains in RP. Such controlled radical polymerizations (CRPs) with reversible deactivation (IUPAC recommends a term *controlled reversible-deactivation radical polymerization*) are mechanistically similar to conventional RP methods and proceed through the same intermediates. However, the proportion of terminated chains in CRP is dramatically reduced from $>$99.9% to below about 10% and sometimes even below 1%. As termination cannot be entirely avoided in CRP, these systems are never living at a level of anionic polymerization. However, the degree of control is often sufficient to attain many desirable material properties.

In this chapter, the fundamentals of RP are first briefly summarized and are followed by the most recent developments in stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation transfer (RAFT) as an example of degenerative transfer (DT) processes. These CRP systems enable the synthesis of many well-defined copolymers with novel architectures, compositions, and functionalities. The possible applications of these materials are also highlighted herein.

3.2
Typical Features of Radical Polymerization

In this section, the major features of conventional RP, which are also typical for CRP, are first presented [1–7]. They include some fundamental properties of organic radicals and their typical kinetic features, the range of polymerizable monomers, initiators, additives, and typical reaction conditions.

3.2.1
Kinetics

Organic radicals (also known as *free radicals*) are typically sp^2 hybridized intermediates with a very short lifetime. They terminate with diffusion controlled rate through disproportionation and coupling reactions. As organic radicals have low stereoselectivities (they are sp^2 hybridized), polymers formed by RP are usually atactic. Radicals show high regioselectivities and add to the less substituted carbon in alkenes. Therefore, polymers formed by RP have head-to-tail structures. Radicals have sufficient chemoselectivity (ratio of rates of propagation to transfer), as evidenced by the formation of high MW polymers. At the same time, many vinyl monomers can be easily copolymerized to form statistical copolymers.

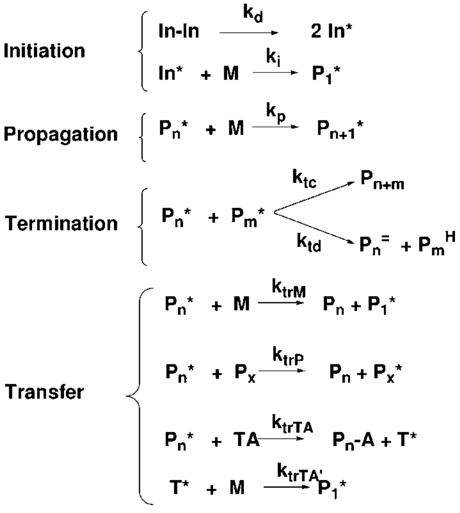
RP comprises four elementary steps: initiation, propagation, termination, and transfer. They involve four different chemical reactions.

Initiation consists of two reactions: the generation of primary initiating radicals (In*), and the reaction of these radicals with monomer (M) (Scheme 3.1). Typically, the former reaction is much slower than the latter and is the rate determining with representative values of $k_d \approx 10^{-5}$ s^{-1} and $k_i > 10^4$ M^{-1} s^{-1}.

Propagation occurs by the repetitive addition of the growing radical to the double bond. Rate constants of propagation have a weak chain length dependence beyond DP ~ 10, with typical values of $k_p \approx 10^{3\pm1}$ M^{-1} s^{-1}.

Termination of two growing radicals occurs by either coupling (k_{tc}) or disproportionation (k_{td}) with rate constants approaching the diffusion controlled limit, $k_t \approx 10^{8\pm1}$ M^{-1} s^{-1}. Termination rate coefficients are strongly chain length and conversion dependent. Coupling is preferred for radicals with small steric effects (i.e., most monosubstituted radicals). In styrene polymerization, for example, the proportion of coupling approaches 95%. Disproportionation becomes more important for disubstituted radicals, such as those derived from methyl methacrylate (MMA).

Transfer can occur to monomer, to polymer, or to some transfer agents (TAs). Transfer to polymer results in branching or even cross-linking. If reinitiation ($k_{trTA'}$) is fast, transfer has no effect on kinetics, but only on MWs. If reinitiation is slow, retardation/inhibition is observed.



Scheme 3.1

Typically, overall rate of RP obeys first order kinetics with respect to monomer and 1/2 order with respect to initiator (Eq. 3.1). Internal first order kinetics in monomer results from the steady concentration of radicals because of equal rates of initiation and termination. The overall rate (R_p) depends on the efficiency of initiation (f) and the rate constants of initiation (k_d), propagation (k_p), and termination (k_t) according to Eq. (3.1). Both rate and MW therefore depend on the $k_p/(k_t)^{1/2}$ ratio. For termination occurring by coupling, MW is defined by Eq. (3.2). When polymerization proceeds faster (at higher temperatures or with more initiator), more radicals are produced and they terminate faster, reducing MW.

$$R_p = k_p[M](fk_d[I]_0/k_t)^{1/2} \tag{3.1}$$

$$DP_n = k_p[M](fk_d[I]_0k_t)^{-1/2} \tag{3.2}$$

The absolute values of the rate constants k_p and k_t can be determined by pulsed laser photolysis (PLP) techniques. A short compilation of the PLP data in Table 3.1 indicates that alkyl substituents in the corresponding (meth)acrylate esters have only a minor effect on k_p. Disubstituted alkenes polymerize slower than monosubstituted. The reactivities of monomers correlate reciprocally with the reactivities of the derived radicals. The order of rate constants follows the radicals' structure, meaning that less reactive monomers polymerize faster because they generate more reactive radicals (i.e., $k_{p(\text{butadiene})} < k_{p(\text{styrene})} < k_{p(\text{methacrylate})} < k_{p(\text{acrylate})}$). On the other hand, the rate constants of termination are more affected by steric contribution from alkyl substituents than by the radical stabilization. They are similar for dodecyl acrylate and dodecyl methacrylate and both are more than an order of magnitude smaller than that for methyl acrylate (MA) or MMA. As rate

Table 3.1 Kinetic parameters for selected monomers obtained by PLP measurements [8, 9].

Monomer[a]	E_p (kJ mol^{-1})	A_p (l mol^{-1} s^{-1})	k_p (M^{-1}s^{-1})	k_t (M^{-1}s^{-1})[c]	References
Dodecyl acrylate	17.0	1.79×10^7	26 100	6.6×10^6	k_p [10], k_t [11]
n-Butyl acrylate	17.9	2.24×10^7	23 100	5.5×10^7	k_p [12], k_t [13]
Methyl acrylate	17.7	1.66×10^7	18 500	2.6×10^8	k_p [10], k_t [11]
Dodecyl methacrylate	21.0	2.50×10^6	786	1.7×10^6[b]	k_p [14], k_t [15]
n-Butyl methacrylate	22.9	3.78×10^6	573	5.0×10^6[b]	k_p [14], k_t [15]
Methyl methacrylate	22.4	2.67×10^6	490	2.5×10^7[b]	k_p [16], k_t [17]
Styrene	32.5	4.27×10^7	162	9.6×10^7	k_p [18], k_t [19]
Butadiene[c]	35.7	8.05×10^7	89	–	k_p [20]

[a] Measurements in bulk at 40 °C and ambient pressure, unless otherwise stated.

[b] k_t reported at 1000 bar.

[c] Solvent = chlorobenzene.

E_p and A_p represent the Arrhenius activation energy for propagation and frequency factor for propagation, respectively.

coefficients of termination depend on chain length and conversion (viscosity), the values in Table 3.1 are given for low conversion and DP $\approx$ 100.

3.2.2
Copolymerization

Facile statistical copolymerization is one of the main advantages of RP. In contrast to ionic polymerization, the reactivities of many monomers are relatively similar, which makes them easy to copolymerize statistically. For monomers with opposite polarities, there is a tendency for alternation ($r_A r_B < 1$, where $r_A = k_{AA}/k_{AB}$ and $r_B = k_{BB}/k_{BA}$). Electrophilic radicals (i.e., those with –CN, –C(O)OR, or Cl groups) prefer to react with electron rich monomers (such as styrene, dienes or vinyl acetate), whereas nucleophilic radicals prefer to react with alkenes containing electron withdrawing substituents.

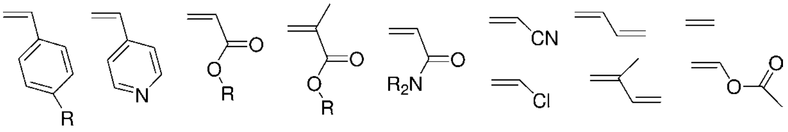
3.2.3
Monomers

Essentially any alkene can be (co)polymerized by radical means. However, formation of high MW polymer requires sufficient stability of the propagating radical, sufficient reactivity of the monomer, and small contribution from transfer. Radicals are typically stabilized by resonance, and to a smaller extend by polar and steric effects. Therefore, styrenes (including vinyl pyridines), various substituted methacrylates, acrylates, acrylamides, acrylonitrile, dienes, and vinyl chloride are well suited for RP (Scheme 3.2). Although polymerization of less reactive alkenes such as ethylene is more challenging, high MW polyethylene is formed commercially in large quantities under high pressure and high temperature (higher k_p/k_t ratio).

Monomers which cannot be successfully homopolymerized radically to high MW polymers include simple α-olefins, isobutylene, and those monomers with easily abstractable H atoms (e.g., thiols, allylic derivatives). They have low reactivity and participate in extensive transfer.

3.2.4
Initiators and Additives

The initiators for RP include peroxides, diazenes, and various redox systems, as well as high energy sources such as ultraviolet (UV) light, γ-rays and



Scheme 3.2

elevated temperatures. Produced radicals initiate new chains, but also may terminate before escaping the solvent cage and form inactive products. Thus, radical initiation has a fractional efficiency ($0 < f < 1$). Value of f usually decreases with conversion as $[M]$ becomes lower and viscosity becomes higher.

Some compounds can affect the rate of RP or the MW of the resulting polymers. Some reagents inhibit or retard RP. Oxygen is a classic inhibitor which forms relatively stable and unreactive peroxy radicals. Other efficient inhibitors include quinones and phenols (in the presence of oxygen), nitro compounds, and some transition metal compounds such as $CuCl_2$ or $FeBr_3$. In fact, the latter species become very efficient moderators for ATRP in the presence of appropriate ligands, as will be discussed later.

Thiols, disulfides and polyhalogenated compounds do not affect rate but they strongly influence MW via transfer processes. Some TAs react with growing radicals faster than monomers do. If a TA carries some additional functionality, it may result in functional oligomers (telechelics). Some TAs may also act as inhibitors and stop RP by degradative transfer.

3.2.5
Typical Conditions

RP can be conducted in bulk, organic or aqueous homogeneous solutions, as well as in dispersed media such as suspension, emulsion, miniemulsion, microemulsion, inverse emulsion, and also precipitation polymerization. Polymerization can also proceed in the gas phase and from surfaces. Typically RP is carried out between 50 and 100 °C, but can be also run at room temperature, at −100 °C, or even at 250 °C (ethylene). The basic prerequisite for RP is deoxygenation of all components; most reactions are run under nitrogen. Inhibitors may be removed by passing the monomer through an alumina column or can be consumed by excess initiator. Polymerization is often exothermic and temperature control is important. At high conversion in bulk polymerizations, autoacceleration may occur (known as the *Trommsdorff effect*) because of a decrease of the termination rate constant, as the system becomes more viscous. The evolution of additional heat that ensues leads to faster initiator decomposition which additionally increases the polymerization rate and may ultimately lead to an explosion.

3.2.6
Commercially Important Polymers by RP

The largest volume polymers produced by RP include polyethylene, polystyrene (PS), and poly(vinyl chloride) (PVC), Because propagation in ethylene polymerization is very slow, to successfully compete with termination, high temperatures (>200 °C) and pressures >20 000 psi (>1.5 kbar) are used. Under these conditions, transfer becomes more significant. A resulting highly branched polyethylene has properties very different from the linear analogue made by coordination polymerization. The low density polyethylene (LDPE) ($T_g \approx -120\,°C$, $T_m \approx 100\,°C$) is flexible, solvent resistant, and has good flow properties and good impact resistance. Nearly 6 million tons of LDPE were produced in Europe in 2007.

PS is a rigid plastic, with good optical clarity (it is amorphous) and resistance to acids and bases. It can be processed at moderate temperatures ($T_g \approx 100\,°C$), and is a good electrical insulator. About 4 million tons of PS were produced in Europe in 2007. Poor solvent resistance and brittleness of PS can be improved by copolymerization with a variety of other monomers. SAN, a copolymer of styrene with acrylonitrile (≈40% AN) provides good solvent resistance to the polymer and increases its tensile strength. Elastomeric copolymers of styrene and 1,3-butadiene (SBR) contain low amounts of styrene (≈25%) and have similar properties to natural rubber. Copolymers with higher contents of styrene are used in paints. The solvent resistance of SAN and flexibility of SBR are combined in copolymers of acrylonitrile and styrene with a rubbery polybutadiene (ABS). ABS has excellent solvent and abrasion resistance and finds application in houseware, construction, electronic housings, automotive parts, and in recreation. In 2007, over 7 million tons of PS copolymers were produced in Europe.

PVC is generally produced by suspension polymerization. Nine million tons of PVC was produced in Europe in 2007. Performance of PVC is greatly improved with the use of additives (i.e., plasticizers and stabilizers). PVC is widely used in construction, packaging, wire insulation, and biomedical applications.

A variety of other commercial polymers are prepared by RP in smaller quantities. Poly(meth)acrylates are primarily used in coatings (automotive, structural, and home) and paints. Acrylic paints are generally prepared as emulsions. In 2007, over 4 million tons of acrylic polymers were produced in Europe and European paint industry sold over 8 billion euro worth of acrylic-based paints. Acrylic copolymers are also used as adhesives, oil additives, and caulks/sealants. Poly(methyl methacrylate) (PMMA) has excellent optical clarity and finds application as safety glass, in light fixtures, skylights, lenses, fiber optics, dentures, fillings, and in contact lenses. Polyacrylamides and poly(vinyl alcohol) (PVA) are used as thickeners, in biomedical applications, and in health and beauty products. PVA is prepared by hydrolysis of poly(vinyl acetate) (PVAc). Polyacrylonitrile is used for the production of fibers. After graphitization, carbon fibers are formed. Poly(vinylidene chloride) is used as self-shrinking film, brominated polymers can serve as flame retardants, and fluoropolymers find application as low surface energy materials. In 2007, worldwide sales of fluorinated polymers exceeded $2 billion.

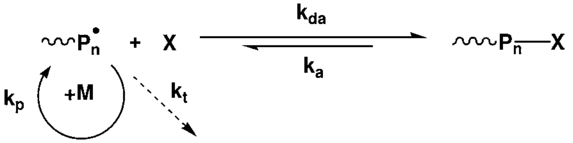
3.3
Controlled Reversible-Deactivation Radical Polymerization

3.3.1
General Concepts

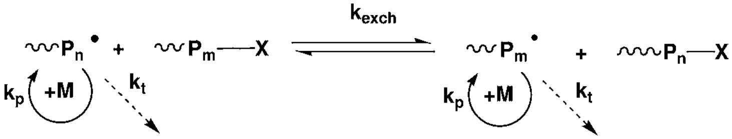
Controlled synthesis of polymeric materials requires minimization of chain breaking reactions and simultaneous growth of all chains. A prerequisite of fast initiation and very slow termination seems to disagree with the fundamental principles of RP, in which steady state of radicals concentration is achieved by balancing the rate of initiation with that of termination. However, such a scenario was realized by the development of controlled/"living" systems in which the active propagating radicals are intermittently formed. This concept, originally applied to cationic ring-opening polymerization [21], was successfully extended to carbocationic systems [22] and later to anionic and other polymerizations where growing centers are in equilibrium with various dormant species [23].

Central to all CRP systems is a dynamic equilibrium between propagating radicals and various dormant species [24, 25]. There are two types of equilibria. Radicals may be reversibly trapped in a deactivation/activation process, according to Scheme 3.3 or they can be involved in a degenerative exchange process (Scheme 3.4).

The first approach is more widely used and relies on the persistent radical effect (PRE) [26, 27]. In systems obeying the PRE, newly generated radicals are rapidly trapped in a deactivation process (with a rate constant of deactivation, k_{da}) by species X (which is typically a stable radical such as a nitroxide [28, 29] or an organometallic species such as a cobalt porphyrine [30, 31]). The dormant species are activated (with a rate constant k_a) either spontaneously/thermally, in the presence of light, or with an appropriate catalyst (as in ATRP) [32, 33] to reform the growing centers. Radicals can propagate (k_p) but also terminate (k_t).



Scheme 3.3



Scheme 3.4

However, persistent radicals (X) cannot terminate with each other but only (reversibly) cross-couple with the growing species (k_{da}). Thus, every act of growing radical termination is accompanied by the irreversible accumulation of X. Its concentration progressively increases with time, following a peculiar 1/3 power law [25–27]. The growing radicals then predominantly react with X, which is present at >1000 times higher concentration, rather than with themselves. As the concentration of X increases with time, the concentration of radicals decreases (as the equilibrium in Scheme 3.3 becomes shifted toward the dormant species) and the probability of termination is diminished.

In systems based on the PRE, a steady state of growing radicals is established through the activation–deactivation process but *not* through initiation–termination. Because initiation is much faster than termination, this essentially gives rise to the simultaneous growth of all chains. By contrast, systems which employ DT are *not* based on the PRE. They follow typical RP kinetics with slow initiation and fast termination. The TA is at much larger concentration than radical initiators and thus plays the role of a dormant species.

Good control over MW, polydispersity, and chain architecture in all CRP systems requires very fast exchange between active and dormant species. Ideally, a growing radical should react with only a few monomer units before it is converted back into a dormant species. Consequently, it would remain active only for a few milliseconds and would return to the dormant state for a few seconds or more. The growth of a polymer chain may consist (for example) of ~1000 periods of ~1 ms activity, interrupted by ~1000 periods of ~1 min dormant states. The lifetime in the active state is thus comparable to the lifetime of a propagating chain in conventional RP (≈1000 ms, i.e., ≈1 s). However, because the whole propagation process in CRP may take ≈1000 min or ≈ one day, the opportunity exists to carry out various synthetic procedures, such as functionalization or chain extension [34].

3.3.2
Similarities and Differences Between RP and CRP

As RP and CRP proceed via the same radical mechanism, they exhibit similar chemo-, regio-, and stereoselectivities and can polymerize a similar range of monomers. If RP and CRP are carried out with the same rate, the absolute amounts of terminated chains are similar, because concentrations of radicals are similar. However, in RP essentially all chains are dead but in CRP dead chains form only a small fraction (<10% of all chains) because of a large amount of dormant species. Nevertheless, several important differences between CRP and RP exist and are summarized below.

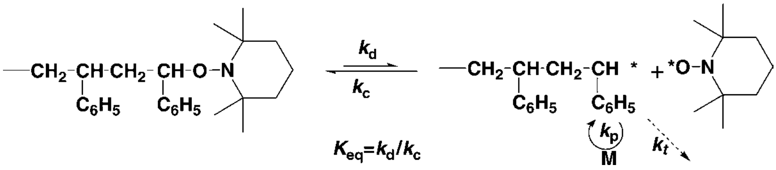
1. The lifetime of growing chains is extended from ≈1 s in RP to more than 1 h in CRP. This is done by participation of dormant species and intermittent reversible activation.

2. In RP, a steady state radical concentration is established with similar rates of initiation and termination, whereas in CRP systems based on the PRE (ATRP, SFRP), a steady radical concentration is reached by balancing the rates of activation and deactivation.
3. In conventional RP, initiation is slow and some free radical initiator is often left unconsumed at the end of the polymerization. In most CRP systems, initiation is fast and all chains start growing at essentially the same time, ultimately enabling control over chain architecture.
4. In RP, nearly all chains are dead, whereas in CRP the proportion of dead chains is usually $<10\%$.
5. Polymerization in CRP is often slower than in RP but this does not necessarily have to be the case. Rates may be comparable, if the targeted MW in CRP is relatively smaller.
6. In conventional RP, termination usually occurs between long chains and constantly generated new chains. In CRP systems based on the PRE (ATRP and SFRP), at the early stages all chains are short (most probable termination); but as they become much longer, the termination rate significantly decreases. In DT processes (e.g., RAFT), new chains are constantly generated by a small amount of conventional initiator and therefore termination is more likely.

3.4
SFRP: NMP and OMRP Systems – Examples and Peculiarities

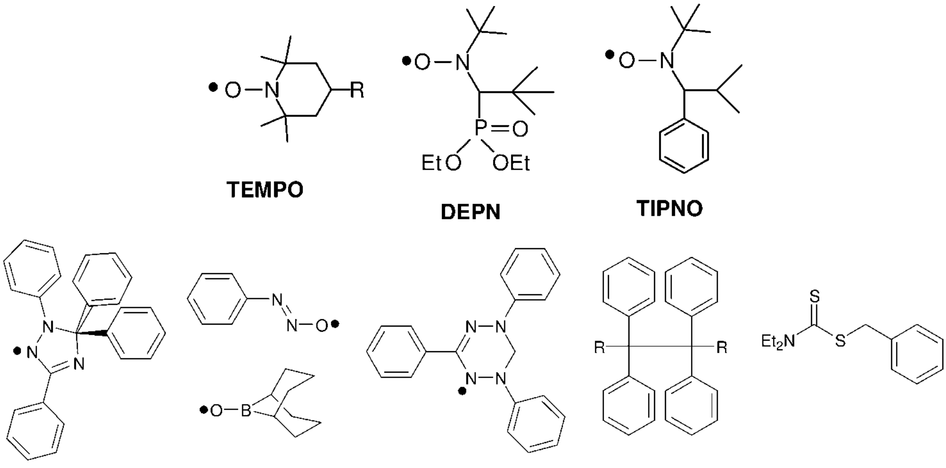
SFRP and, more specifically, nitroxide-mediated polymerization [28, 29] (NMP, IUPAC recommends the term aminoxyl-mediated polymerization) or organometallic-mediated radical polymerization (OMRP) [30, 31] systems rely on the reversible homolytic cleavage of a relatively weak bond in a covalent species to generate a growing radical and a less reactive species (usually the persistent radical, but can be also species with an even number of electrons) [31, 35]. This species should react reversibly only with growing radicals and should *not* react amongst themselves or with monomers to initiate the growth of new chains, and they should *not* participate in side reactions such as the abstraction of β-H atoms.

Nitroxides (aminoxyl radicals) were originally employed as stable free radicals in the polymerization of (meth)acrylates [36]. The field of NMP gained momentum after the seminal paper by Georges who used TEMPO as a mediator in styrene polymerization (Schemes 3.5 and 3.6) [28]. TEMPO and substituted TEMPO derivatives form relatively strong covalent bonds in alkoxyamines that have very low equilibrium constants in NMP (ratio of rate constants of dissociation (activation) and coupling (deactivation), $k_d/k_c = K_{eq} = 2.0\ 10^{-11}$ M at 120 °C for PS) [25] and therefore require high polymerization temperatures.

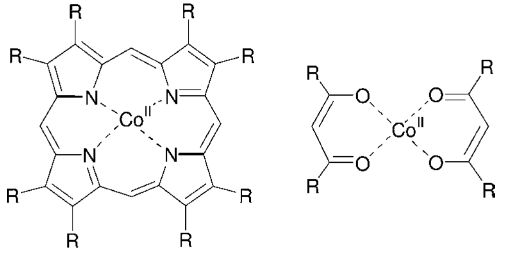


Scheme 3.5

Subsequently, other nitroxides were synthesized which provide a range of C–O bond strengths [29, 37, 38]. DEPN [39] (also known as *SG-1*) and TIPNO [40] in Scheme 3.6 contain a H atom at the α-C. Such nitroxides were originally predicted to be unstable and were expected to quickly decompose. However, the stability of both DEPN and TIPNO is sufficient to control the polymerization of many monomers and a slow decomposition may reduce their accumulation. Steric and electronic effects stabilize these radicals. $K_{eq} = 6.0 \times 10^{-9}$ M for DEPN with PS was determined at 120 °C [39], i.e., several hundred times higher than the TEMPO system. A decrease in the bond dissociation energy (BDE) of these alkoxyamines enables lower polymerization temperatures [37]. Polymerization can be also accelerated in NMP systems by a constant radical flux, for example, by using slowly decomposing free radical initiators [41]. Other systems employing this concept were developed utilizing triazolinyl radicals [42], boronyloxy radicals [43], and bulky organic radicals such as thermolabile al*kan*es [44], (Scheme 3.6). Alkyl dithiocarbamates, originally used by Otsu, undergo homolytic cleavage when irradiated by UV light and can mediate polymerization following an SFRP mechanism. These dithiocarbamyl radicals not only cross-couple but also dimerize and initiate polymerization [45, 46].



Scheme 3.6



3a **3b**

Scheme 3.7

3.4.1
OMRP Systems

The OMRP of MA with Co porphyrines [30], one of the most successful CRP systems, leads to well-defined high MW polyacrylates and has been recently extended to PVAc [47]. However, similar compounds in polymerization of methacrylates act as very efficient catalytic chain TAs [48]. More recently, $Co(acac)_2$ derivatives were used to control the polymerization of vinyl acetate and *N*-vinylpyrrolidone [49, 50]. Other transition metals complexes (of Mo [51], Os [52], Cr [53], and Fe [54, 55]) can act as SFRP moderators (Scheme 3.7). Some of these complexes may also participate in ATRP equilibria (see below) [31].

3.4.2
Monomers and Initiators

The range of polymerizable monomers by NMP includes styrene, various acrylates, acrylamides, dienes, and acrylonitrile. Monomers forming less stable radicals such as vinyl acetate have not yet been successfully polymerized via NMP because of too low values of K_{eq} but they were successfully polymerized by OMRP. Disubstituted alkenes such as methacrylates that form more sterically hindered tertiary radicals show difficulties in control by NMP owing to very slow deactivation and/or disproportionation [56]. Copolymerization with styrene improves the control [57].

Nitroxides in NMP and radical trap in OMRP can be employed together with typical radical initiators and used at nearly stoichiometric amounts. Alternatively, alkoxyamines can be prepared [58]. Sometimes, an excess of nitroxides can actually enhance block copolymerization efficiency [59]. Exchange process in OMRP can involve not only spontaneous homolytic cleavage of dormant species but also a bimolecular exchange by DT process [31].

3.4.3
General Conditions

The BDE of most nitroxides and alkoxyamines in NMP is relatively high, and therefore, high temperatures are required. The polymerization of styrene can be successfully mediated with TIPNO and DEPN at $T > 80\,^\circ\mathrm{C}$, but with TEMPO the temperature exceeds $120\,^\circ\mathrm{C}$. All solvents used in RP can also be employed in NMP. NMP has been successfully used in aqueous systems under homogeneous, emulsion, and miniemulsion conditions [60–62]. Range of temperatures in OMRP is much larger and temperatures are lower than in NMP [31].

3.4.4
Controlled Architectures

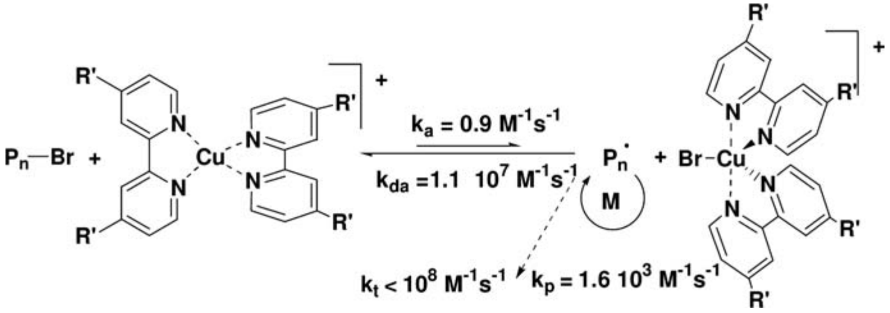
NMP has been applied to the synthesis of various homopolymers, statistical, gradient, block, and graft copolymers. Star, hyperbranched, and dendritic structures have also been prepared [29, 38]. The range of MWs attainable in NMP is quite large, although transfer can limit MWs at elevated temperatures. Also, nitroxides may abstract β-H atoms and lead to elimination and a loss of functionality in some systems. Alkoxyamines can be replaced by halogens at the chain end, but functionalization is not very straightforward. OMRP was mostly used for synthesis of linear homopolymers but there are also examples of more complex architectures.

3.5
ATRP – Examples and Peculiarities

ATRP [32, 33, 63–66] is currently the most widely used CRP technique. This originates from the commercial availability of all necessary ATRP reagents, including transition metal compounds and ligands used as catalysts, as well as alkyl halide initiators, and also from the large range of monomers polymerizable by this technique under a wide range of conditions.

The basic working mechanism of ATRP involves homolytic cleavage of an alkyl halide bond R–X (or macromolecular P_n–X) by a transition metal complex Mt^n/L (such as $\mathrm{CuBr/bpy_2}$). This reaction generates reversibly (with the activation rate constant, k_a) the corresponding higher oxidation state metal halide complex X–Mt^{n+1}/L (such as $\mathrm{CuBr_2/bpy_2}$) and an alkyl radical $\mathrm{R}^\bullet$ (a representative example of this process is illustrated in Scheme 3.8) [33, 67]. $\mathrm{R}^\bullet$ can then propagate with a vinyl monomer (k_p), terminate by coupling and/or disproportionation (k_t), or can be reversibly deactivated by X–Mt^{n+1}/L (k_{da}). Radical termination is diminished as a result of the PRE [26, 27] that ultimately shifts the equilibrium toward the dormant species (activation rate constant << deactivation rate constant). The values of the rate constants in Scheme 3.8 refer to styrene polymerization at $110\,^\circ\mathrm{C}$ [68–71].

One important difference between SFRP and ATRP is that kinetics and control in ATRP depends not only on the concentration of persistent radical (X–Mt^{n+1}/L) but also on that of the activator (Mt^n/L). MWs are defined by the



Scheme 3.8

$\Delta[M]/[RX]_0$ ratio and are not affected by the concentration of the transition metal species. The polymerization rate increases with initiator concentration (P–X) and is proportional to the ratio of concentrations of activator and deactivator, Eq. (3.3).

$$R_p = -d[M]/dt = k_p[M][P^*] = k_p[M](k_a[P\text{–}X][Mt^n/L])/(k_{da}[X\text{–}Mt^{n+1}/L]) \quad (3.3)$$

The synthesis of polymers with low polydispersities and predetermined MWs requires a sufficient concentration of deactivator. Polydispersities decrease with monomer conversion (p) and concentration of deactivator but increase with the k_p/k_{da} ratio. In the absence of any irreversible chain breaking reactions, polydispersities are also lower for higher targeted MW, i.e., for lower $[RX]_0$ [72, 73].

$$M_w/M_n = 1 + 1/DP_n + [(k_p[RX]_0)/(k_{da}[X\text{–}Mt^{n+1}/L])](2/p - 1) \quad (3.4)$$

ATRP proceeds via an inner sphere electron transfer (ISET) process, i.e., atom transfer. A hypothetical outer sphere electron transfer, OSET (also named as a single electron-transfer living radical polymerization, SET-LRP) [74], i.e., a two-step pathway through radical anions or dissociative OSET was estimated to be $\sim 10^{12}$ times slower than ISET for model bromoacetonitrile and CuBr/TPMA system [75]. However, under certain conditions, a reduction or oxidation of radicals to carbanions or carbocations by transition metal complexes can occur as a side reaction [76, 77]. Other side reactions include the formation of organometallic species (as in OMRP) [51], monomer [78, 79] or solvent coordination to the transition metal catalyst, dissociation of the halide from the deactivator [80], HBr elimination, etc. Therefore, the appropriate selection of an initiator and catalyst will not only depend on the monomer or targeted molecular architecture but should also be made with respect to plausible side reactions. ATRP with alkyl iodides and dithioesters or trithiocarbonates may also proceed by concurrent DT mechanism, depending on catalyst and structure of reagents involved [81–83].

3.5.1
Basic ATRP Components

3.5.1.1 Monomers

The list of monomers successfully homopolymerized by ATRP is quite extensive and includes various substituted styrenes [84], (meth)acrylates [85–87], (meth)acrylamides [88, 89], vinyl pyridine [90], acrylonitrile [91], vinyl acetate [92], vinyl chloride [93], and others [33]. Nitrogen containing monomers as well as certain dienes can present challenges in ATRP as monomer or polymer complexation to the catalyst can render it less active. Some nitrogen containing monomers can also retard polymerization by displacing the terminal halogen of a growing chain or by participating in transfer. Nonpolar monomers such as isobutene [94, 95] and α-olefins [96–98] were successfully copolymerized using ATRP.

ATRP is tolerant to many functional groups such as hydroxy, amino, amido, ether, ester, epoxy, siloxy, and others. All of them have been incorporated into (meth)acrylate monomers and successfully polymerized. One exception is the carboxylic acid group which can protonate amine based ligands; it must therefore be protected. However, the polymerizations of methacrylic acid at high pH [99], styrenesulfonic acid, and acrylamide with sulfonic acid functionality have been successful in the presence of amines [100].

As K_{ATRP} depends very strongly on the structure and reactivity of the monomer and RX, specific catalysts must be used for different monomers. The order of the equilibrium constants in ATRP (acrylonitrile > methacrylates > styrene ~ acrylates > acrylamides > vinyl chloride > vinyl acetate) differs from those in SFRP and RAFT. This order should be followed to efficiently prepare block copolymers, i.e., polyacrylonitrile should be chain extended with poly(meth)acrylate and not vice versa. However, it is possible to alter this order by using a technique known as *halogen exchange* whereby a macromolecular alkyl bromide is extended with a less reactive monomer in the presence of a CuCl catalyst [101–103]. The rational behind "halogen exchange" is that the value of the ATRP equilibrium constant for alkyl chloride-type (macro)initiators is one order of magnitude lower than that for the alkyl bromides with the same structure. These C–Cl bonds are activated more slowly, and therefore, the rate of propagation is decreased with respect to the rate of initiation. This effectively leads to increased initiation efficiency from the added macroinitiator and preparation of a second block with lower polydispersity. In this way, block copolymers were successfully prepared from poly(*n*-butyl acrylate) and extended with polyacrylonitrile or PMMA [104, 105].

3.5.1.2 Transition Metal Complexes as ATRP Catalysts

ATRP has been successfully mediated by a variety of metals, including those from groups 4 (Ti [106]), 6 (Mo [51, 107, 108]), 7 (Re [109]), 8 (Fe [92, 110–114], Ru [63, 115], Os [52, 116]), 9 (Rh [117], Co [118]), 10 (Ni [119, 120], Pd [121]), and 11 (Cu [32, 33]). Cu is by far the most efficient metal as determined by the successful application of its complexes as catalysts in the ATRP of a broad range of monomers in diverse media. The transition metal complex is very often a metal halide, but pseudohalides, carboxylates, and compounds with noncoordinating triflate and hexafluorophosphate anions were also used successfully [122].

Ligands include multidentate alkyl amines [123, 124], pyridines [125, 126], pyridineimines [127], phosphines [110, 128], ethers or half-metallocene species [129]. Ligands serve to adjust the atom transfer equilibrium and to provide appropriate catalyst solubility. As atom transfer proceeds via a reversible expansion of the metal coordination sphere, the system should be flexible enough to ensure a very fast reversible ISET process [130]. The atom transfer process should dominate over aforementioned side reactions. Although some catalysts are suitable for several types of monomers, other systems may require a specific catalyst and specific conditions.

Copper complexes with various polydentate N-containing ligands are most often used as ATRP catalysts [33]. This late transition metal does not complex strongly with polar monomers, it has a low tendency to form organometallic species, and it typically does not favor hydrogen abstraction. Figure 3.1

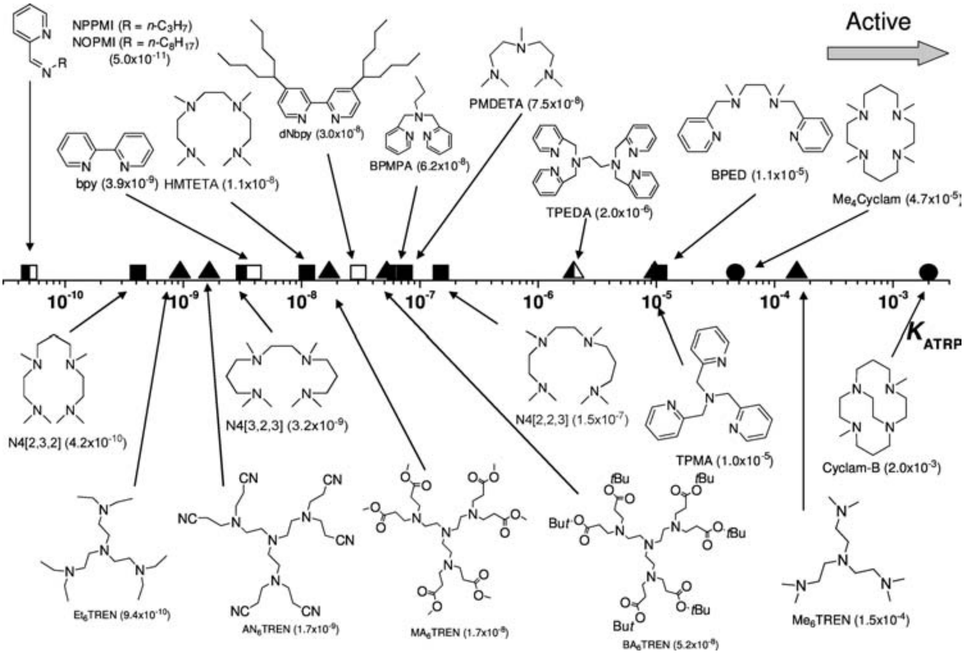


Figure 3.1 ATRP equilibrium constants for various ligands with EtBr*i*B in the presence of Cu^IBr in MeCN at 22 °C. N2: red, N3 and N6: black, N4: blue; amine/imine: solid, pyridine: open, mixed: left-half solid; linear: square, branched: triangle, cyclic: circle [69].

illustrates the order of equilibrium constants for copper complexes with various N-base ligands with EtBr*i*Bu (ethyl 2-bromoisobutyrate) as a standard initiator [69]. There are a few general rules for catalyst activity: (i) activity depends very strongly on the linking unit between the N atoms (C4 << C3 < C2) and/or the coordination angle; (ii) on the topology of the ligand (cyclic ~ linear < branched); (iii) on the nature of the N-ligand (aryl amine < aryl imine < alkyl imine < alkyl amine ~ pyridine); (iv) on steric effects, especially those close to the metal center (i.e., Me$_6$TREN complex is ~100 000 times more active than Et$_6$TREN; 6,6′-diMe-2,2′-bpy is inactive in ATRP in contrast to 2,2′-bpy and 4,4,′-disubstituted 2,2′-bpy) [69, 131].

The redox properties of the catalyst can be adjusted over a very broad range (>500 mV, corresponding to a range of ATRP equilibrium constants spanning eight orders of magnitude) [132–134]. More reducing catalysts are characterized by higher K_{ATRP}. Figure 3.2 presents an excellent linear correlation between K_{ATRP}.and redox potentials of Cu$^{\mathrm{II}}$Br$_2$ complexes with various N-based ligands.

Another parameter which affects equilibrium constants is halidophilicity, i.e., the affinity of halide anions to the transition metal complexes in their higher oxidation state. For example, as Cu(II) species typically do not form strong complexes with iodide anion, alkyl iodides are not efficient initiators in Cu-mediated ATRP [69, 75].

Selection of the catalyst requires attention not only to the appropriate values of K_{eq}, but also to systems with very fast deactivation (k_{da}), as the degree of control over molecular weight distribution in a CRP is defined by the rate of deactivation [69].

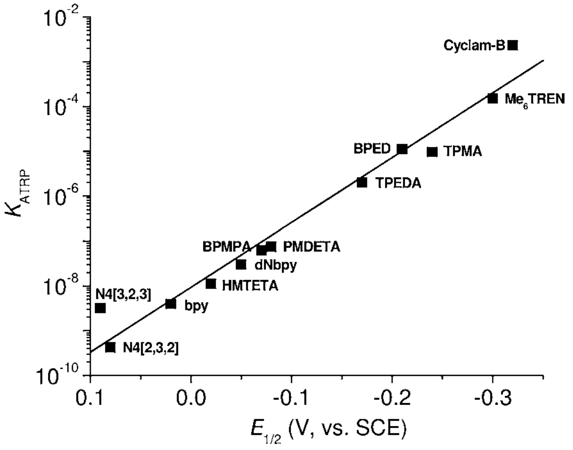


Figure 3.2 Plot of $E_{1/2}$ vs. K_{ATRP} (measured with EtBr*i*B) for 12 Cu$^{\mathrm{II}}$Br$_2$/L complexes in MeCN at 22 °C [69].

3.5.1.3 Initiators

The broad availability of initiators is perhaps the most significant comparative advantage of ATRP. In fact, many alkoxyamines and RAFT reagents are prepared from activated alkyl halides, i.e., ATRP initiators [135, 136]. Essentially all compounds with halogen atoms activated by α-carbonyl, phenyl, vinyl, or cyano groups are efficient initiators. Compounds with a weak halogen–heteroatom bond, such as sulfonyl halides, are also good ATRP initiators [137]. There are many compounds with several activated halogen atoms which were used to initiate multidirectional growth to form star-like polymers, brushes, and related copolymers. Activated halogens can be incorporated at the chain ends of polymers prepared by other techniques such as polycondensation, cationic, anionic, ring-opening metathesis, coordination, and even conventional radical processes to form macroinitiators. Chain extensions via ATRP from such macroinitiators were successfully used to form novel diblock, triblock, and graft copolymers [68, 138, 139]. Inorganic surfaces (wafers, colloids, fibers, and various porous structures) were functionalized with ATRP initiators to grow films of controlled thickness and density [140–142]. Also, several natural products were functionalized with ATRP initiators to prepare novel bioconjugates [143–147].

The reactivity of initiators depends *reciprocally* on the R–X BDE [75, 148]. The equilibrium constants are typically governed by the degree of initiator substitution (primary (black entries) < secondary (blue) < tertiary (red)), by the radical stabilizing groups (–Ph (triangle) ∼–C(O)OR (square) < allyl (star) < –CN (circle)), and by the leaving atom/group (bromo > chloro > iodo). The presence of two stabilizing groups strongly increases activity of alkyl halides, as shown for ethyl bromophenylacetate. The values of the equilibrium constants measured with CuX/TPMA in MeCN at 22 °C are shown in Figure 3.3 [69].

Bond Dissociation Energies and Values of K_{ATRP} Although experimental data on BDEs for alkyl halides relevant for ATRP are limited, enthalpies and free energies of bond dissociation can be accessed computationally using density functional theory (DFT) or *ab initio* procedures [75, 148]. The BDE should correlate well with values of K_{ATRP} as, formally, the ATRP equilibrium can be represented as a combination of two hypothetical reactions, i.e., (i) homolytic cleavage of the C–X bond in the alkyl halide and (ii) formation of the X–Cu^{II} bond in the deactivator from the reaction of Cu^{I} with halogen atom [75].

Atom transfer equilibrium in Scheme 3.9 can be represented as a product of alkyl halide bond homolysis and Cu^{II}–X bond formation (halogenophilicity). The first process, characterized by K_{RX} is the bond dissociation free energy (ΔG). The second process characterized by $K_{Cu,X^\bullet}$ can be defined as the halogenophilicity, i.e., the affinity of the transition metal in the lower oxidation state to the halogen atom. This value can be calculated from the overall ATRP equilibrium constant and bond dissociation free energy, $K_{Cu,X^\bullet} = K_{ATRP}/K_{RX}$.

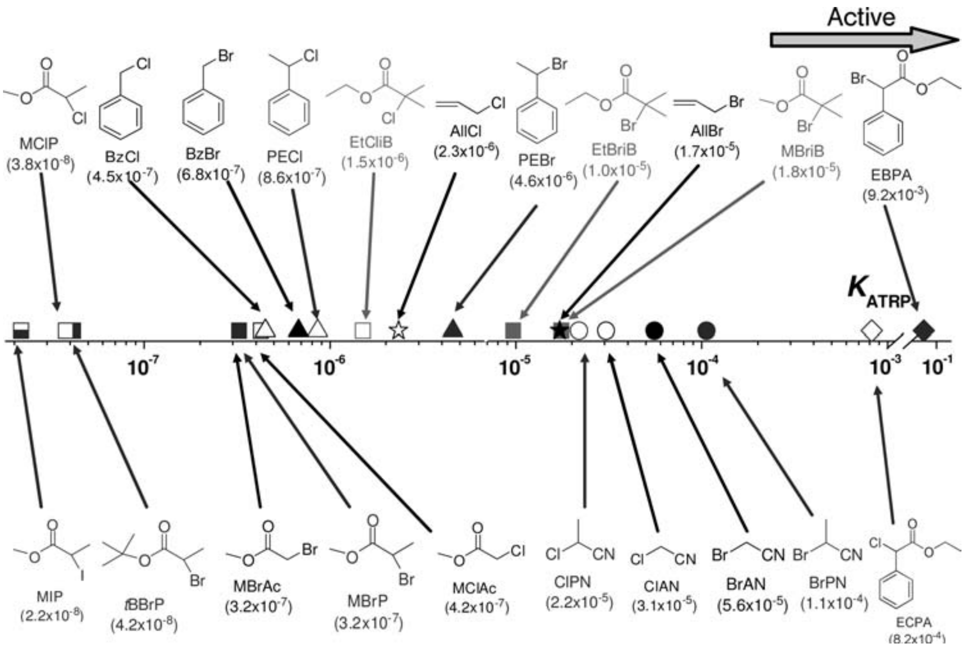


Figure 3.3 ATRP equilibrium constants for various initiators with $\mathrm{Cu^IX}$/TPMA (X = Br or Cl) in MeCN at 22 °C. Tertiary: red, secondary: blue, primary: black; R–Br: solid, R–Cl: open, R–I: bottom-half solid; amide: down-pointing triangle; phenyl: up-pointing triangle; ester: square; nitrile: circle; phenyl-ester: diamond; allyl: star [69].

$$\text{R-X} + \mathrm{Cu^IY/L_n} \underset{k_{\mathrm{deact}}}{\overset{k_{\mathrm{act}}}{\rightleftharpoons}} \mathrm{R^\bullet} + \mathrm{XCu^{II}Y/L_n} \qquad K_{\mathrm{ATRP}}$$

Contributing Reactions

$$\text{(i)} \qquad \text{R-X} \rightleftharpoons \mathrm{R^\bullet} + \mathrm{X^\bullet} \qquad K_{\mathrm{RX}}$$

$$\text{(ii)} \qquad \mathrm{Cu^IY/L_n} + \mathrm{X^\bullet} \rightleftharpoons \text{X-}\mathrm{Cu^{II}Y/L_n} \qquad K_{\mathrm{Cu,X^\bullet}}$$

Scheme 3.9

The value of $K_{\mathrm{Cu,X}}{}^\bullet$ depends on the type of catalyst/ligand ($\mathrm{Cu^IX/L}$) and the type of halogen (X).

Figure 3.4 presents a plot of log K_{ATRP} − log $K_{\mathrm{Cu,X}}{}^\bullet$ versus log K_{RX} where the green line is the line with slope 1, passing through two standards EtBr*i*B and EtCl*i*B. There is an excellent correlation between the equilibrium constants obtained via the calculated BDEs and those obtained experimentally. The scatter is within or close to the expected order of magnitude uncertainty in the theoretical calculations. Figure 3.4 was constructed assuming constant selectivities of initiators and catalysts [69].

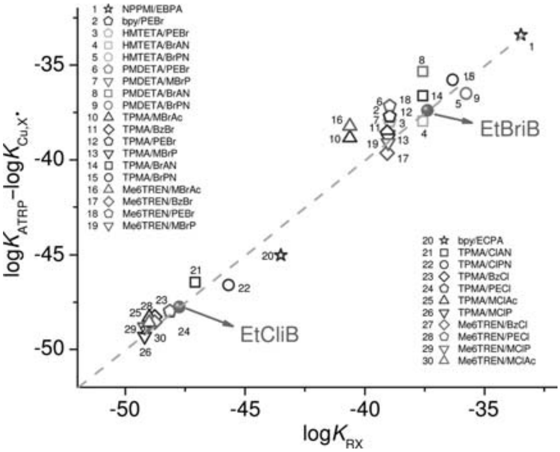


Figure 3.4 Correlation of K_{RX} calculated from the free energy of homolytic bond dissociation of alkyl halides with values calculated from K_{ATRP} using constant halogenophilicities for various complexes. Values of $\log K_{RX}$ correspond to calculated values of ΔG, values of $\log K_{ATRP}$ were experimentally determined, and values of $\log K_{Cu,X}{}^\bullet$ were calculated for each catalyst using EtBr*i*B (and EtCl*i*B) as the reference compound(s) (i.e., $\log K_{Cu,X}{}^\bullet = \log K_{ATRP} - \log K_{RX}$). For precise structure of alkyl halides and ligands, refer to Ref. [69] and Figures 3.1 and 3.3.

Values of $K_{Cu,X}{}^\bullet$ are very large and comparable to the reciprocal values of K_{RX} as their ratio gives a much smaller value of K_{ATRP}. Halogenophilicities are larger for more active catalysts and they are larger for chlorine than for bromine. Values of $\log K_{Cu,Br}{}^\bullet$ range from 27.6 (NPPMI) to 34.1 (Me_6TREN) and values of $\log K_{Cu,Cl}{}^\bullet$ from 38.8 (bpy) to 43.3 (Me_6TREN). Once values of halogenophilicities for various catalysts are known, they can be used together with values of K_{RX} to calculate the unknown values of ATRP equilibrium constants.

Figure 3.5 shows that ATRP equilibrium constants increase because of both the increase in activation and decrease in the deactivation rate constants. The k_{act} contributes to the overall value of K_{ATRP} much more than k_{deact}. Figure 3.5a shows that stronger activators are generally weaker deactivators. Figure 3.5b shows that more active alkyl halides produce more stable radicals that are deactivated slower.

3.5.2
Conditions

ATRP can be conducted over a very broad temperature range: from subzero to >130 °C. Reactions have been successful in bulk, organic solvents, CO_2, water (homogeneous and heterogeneous – emulsion, inverse emulsion,

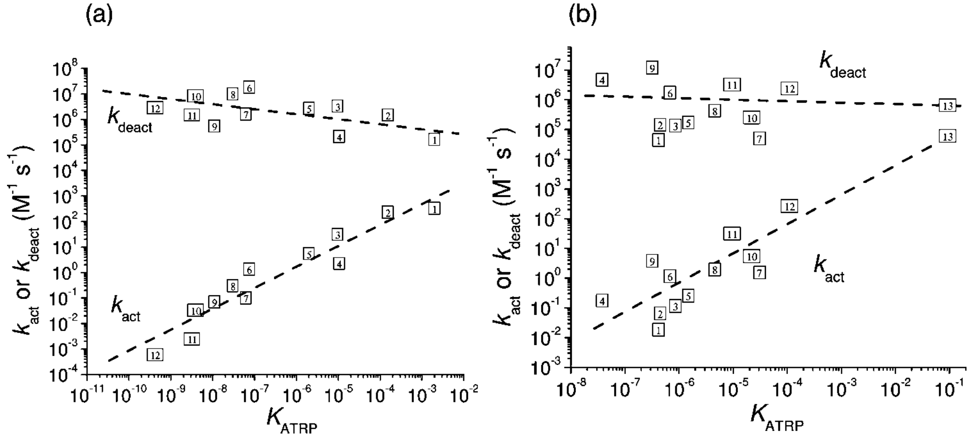


Figure 3.5 Correlation of activation rate constants (k_{act}) and deactivation rate constants (k_{deact}) with equilibrium constants (K_{ATRP}) for various (a) Cu^{I}Br/ligands with EtBr*i*B at 22 °C in MeCN (the broken lines are just to guide readers's eye). The k_{act} values were extrapolated from those at 35 °C [70, 71]. (1) Cyclam-B, (2) Me$_6$TREN, (3) TPMA, (4) BPED, (5) TPEDA, (6) PMDETA, (7) BPMPA, (8) dNbpy, (9) HMTETA, (10) bpy, (11) N4[3,2,3], (12) N4[2,3,2]. (b) For Cu^{I}/TPMA with various initiators at 22 °C in MeCN. The k_{act} values were extrapolated from those at 35 °C [70, 71]. (1) MClAc, (2) BzCl, (3) PECl, (4) MClP, (5) EtCl*i*B, (6) BzBr, (7) ClAN, (8) PEBr, (9) MBrP, (10) ClPN, (11) EtBr*i*B, (12) BrPN, (13) EBPA. For precise structure of alkyl halides and ligands, refer to Ref. [69] and Figures 3.1 and 3.3.

miniemulsion, microemulsion, suspension, precipitation) and even in the gas phase and from solid surfaces.

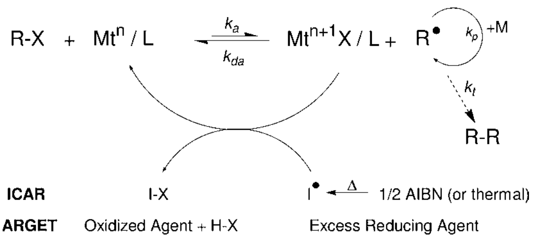
For very reactive and reducing catalysts (which are naturally air sensitive), and for polymerization systems which are difficult to be deoxygenated (water, large vessels), irreversible oxidation of the catalyst by residual oxygen can lead to failed *normal* ATRP. Thus, alternative systems have been developed. *Reverse* ATRP is a convenient method for avoiding such oxidation problems. In this technique, the ATRP initiator and lower oxidation state transition metal activator (Cu^{I}) are generated *in situ* from conventional radical initiators and the higher oxidation state deactivator (Cu^{II}) [149, 150]. The initial polymerization components are less sensitive to oxygen, and yet the same equilibrium between active and dormant species can ultimately be established as in normal ATRP.

However, there are several drawbacks associated with reverse ATRP: (i) because the transferable halogen atom or group is added as a part of the copper salt, the catalyst concentration must be comparable to the concentration of initiator and therefore cannot be independently regulated; (ii) block copolymers cannot be formed; (iii) Cu^{II} complexes are typically less soluble in organic media than the Cu^{I} complexes and often result in a heterogeneous (and poorly controlled) polymerization; (iv) very active catalysts must be used at lower temperatures where the gradual decomposition of thermal initiators results in slow initiation and consequently poor control.

In contrast to reverse ATRP, clean block copolymers can be produced when starting from the higher oxidation state transition metal complex if the *activators* are *generated by electron transfer* (*AGET*). Reducing agents unable to initiate new chains (rather than organic radicals) are employed in this technique. AGET was successful with a number of Cu^{II} complexes using tin(II) 2-ethylhexanoate [151] ascorbic acid [152], amines, sugars [153], metal(0), and other reducing agents, which react with Cu^{II} to generate the Cu^{I} ATRP activator [154–156]. Normal ATRP then proceeds in the presence of alkyl halide initiators or macromonomers. The technique has proven particularly useful in miniemulsion systems [157].

Perhaps the most industrially relevant recent development in ATRP was the realization that *activators* could be *regenerated by electron transfer* (*ARGET*) to decrease the amount of transition metal catalyst necessary to achieve controlled polymerizations (Scheme 3.10) [158, 159]. In principle, the absolute amount of copper catalyst can be reduced under normal ATRP conditions without affecting the polymerization rate. This rate is governed by a ratio of the concentrations of Cu^{I} to Cu^{II} species according to Eq. (3.3).

Because the Cu^{II} deactivator accumulates during ATRP because of radical termination reactions, if the initial amount of copper catalyst does not exceed the concentration of those chains which actually terminate, no Cu^{I} activating species will remain, and polymerization will halt. In ARGET ATRP, the relative concentration of catalyst to initiator can be reduced much lower than under normal ATRP conditions because a reducing agent (such as ascorbic acid, tin(II) 2-ethylhexanoate, or amines [160]) is used in excess to constantly regenerate the Cu^{I} activating species. This technique has effectively reduced the amount of Cu catalyst necessary to achieve control in a polymerization from typical values exceeding 1000 ppm down to below 10 ppm (PS with $M_n > 60\,000\ \mathrm{g\,mol^{-1}}$ and $M_w/M_n < 1.2$ was produced using this technique with only 10 ppm of Cu catalyst [158]). The economical and environmental implications of this development are obvious; additionally, the catalyst and excess reducing agent can effectively work to scavenge and remove dissolved oxygen from the polymerization system, an added benefit of industrial relevance [161].



Scheme 3.10

The role of the reducing agent in ARGET can also be played by radical initiators which can regenerate Cu(I) species. In this system, known as *initiators* for *continuous activator regeneration (ICAR) ATRP* (Scheme 3.10), only very small amounts of radical initiators are used which remain till the very end of the reaction. ICAR very closely resembles RAFT (see below) [162]. The role of dithioester in RAFT is played by an alkyl halide in the presence of ppm amounts of copper catalysts. The small amount of radical initiator is responsible for continuing polymerization. If the radical source disappears, RAFT stops, and ICAR would also stop very quickly.

3.5.3
Mechanistic Features

As ATRP involves transition metal compounds, they could not only reversibly abstract halogen atoms from dormant species or associate with halide anions but also reversibly form organometallic species. They could also form complexes with alkene and alter their reactivity, as well as oxidize growing radicals to carbocations or reduce to carbanions. Contribution of all these reactions in comparison with atom transfer depends on not only the structure, redox properties, and other features of transition metal complexes, but also monomers and reaction conditions. For example, Mo and Os complexes can reversibly form organometallic species but for Os derivatives, control predominantly is associated with atom transfer. Cu(I)/PMDETA complexes with noncoordinating anions form complexes with MA and other vinyl monomers but reactivity of complex monomers is not sufficiently different from that of free monomers to affect copolymer composition.

Radical intermediates in ATRP have the same reactivities and selectivities as those in RP. The radical nature of ATRP is confirmed by the following observations: (i) similar reactivity ratios in conventional RP and ATRP copolymerization; (ii) similar effects of radical scavengers and transfer reagents; (iii) similar tacticity of the polymers generated in RP and ATRP; (iv) the concurrent formation of the higher oxidation state metal species resulting from termination (PRE); (v) similar rates of racemization, exchange, and trapping reactions in RP and ATRP; (vi) indistinguishable ^{13}C kinetic isotope effects between RP and ATRP and (vii) the direct electron spin resonance observation of radicals during ATRP gelation experiments [77, 163–165].

3.5.4
Controlled Architectures

ATRP has been successfully used to control topology (linear, stars, cyclic, comb, brushes, networks, dendritic, and hyperbranched), composition (statistical, blocks, stereoblocks, multi block copolymers, multisegmented block copolymers, graft, periodic, alternating, and gradient copolymers), and functionalities (incorporated into side chains, end groups (homo- and heterotelechelics), and in many arms of stars and hyperbranched materials) [166–168]. In addition, natural products and inorganics were functionalized via ATRP [140, 147]. ARGET and ICAR allow easy access to polymers with designed MWD that lead to materials with novel morphologies such as hexagonally perforated lamellae (HPL) (cf. Figure 3.9) [169].

3.6
Degenerative Transfer Processes and RAFT

Conventional free radical initiators are used in DT processes, and control is assured by the presence of TAs (RX) which exchange a group/atom X between all growing chains. This thermodynamically neutral (degenerative) transfer reaction should be fast in comparison to propagation ($k_{\mathrm{exch}} > k_{\mathrm{p}}$). At any instant, the concentration of dormant species P_n–X is much larger than that of the active species P_n^*. Degrees of polymerization are defined by the ratio of concentrations of consumed monomer to the *sum* of concentrations of the consumed TA and the decomposed initiator.

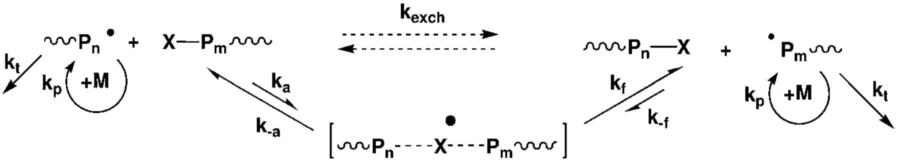
$$\mathrm{DP}_n = \Delta[M]/([\mathrm{TA}] + f\Delta[I]) \tag{3.5}$$

One exception is when DT reagents are activated by a catalyst, such as copper complexes. In such a case, all chains are generated from TA as no radical initiator is used [83].

If transfer is fast and concentration of the decomposed initiator is much smaller than that of the TA, good control can be obtained. Polydispersities decrease with conversion and depend on the ratio of the rate constants of propagation to exchange according to Eq. (3.6) [73].

$$M_{\mathrm{w}}/M_{\mathrm{n}} = 1 + (k_{\mathrm{p}}/k_{\mathrm{exch}})(2/p - 1) \tag{3.6}$$

DT processes do *not* operate via the PRE. A steady state concentration of radicals is established via initiation and termination processes. In some cases, the exchange process may occur via some long-lived intermediates which can either retard polymerization or participate in side reactions such as the trapping of growing radicals (Scheme 3.11).

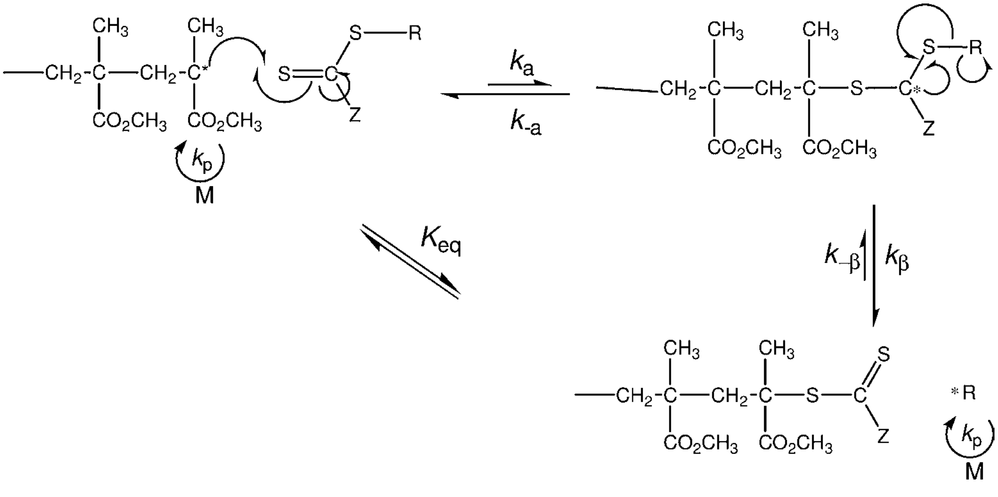


Scheme 3.11

The simplest example of DT occurs in the presence of alkyl iodides [170]. Unfortunately, the rate constants of exchange in these systems are typically < 3 times larger than the rate constants of propagation for most monomers, resulting in polymers with polydispersities greater than 1.3. Exchange is faster in other DT processes employing derivatives of Te, As, or Bi [171–174]; consequently, better control was obtained with these systems.

RAFT polymerization is among the most successful DT processes [135, 175–178]. While addition-fragmentation chemistry was originally applied to the polymerization of unsaturated methacrylate esters (prepared by catalytic chain transfer) [179], RAFT employs various dithioesters, dithiocarbamates, trithiocarbonates, and xanthates as TAs leading to polymers with low polydispersities and various controlled architectures (Scheme 3.12) for a broad range of monomers [180, 181]. The structure of a dithioester has a very strong effect on control. Both R and Z groups must be carefully selected to provide control. Generally, R^* should be more stable than P_n^*, to be formed and to efficiently initiate the polymerization. More precisely, the selection of the R group should also take into account stability of the dormant species and rate of addition of R^* to monomer. The structure of group Z is equally important. Strongly stabilizing Z groups such as Ph are efficient for styrene and methacrylate but they retard polymerization of acrylates and inhibit polymerization of vinyl esters. On the other hand, very weakly stabilizing groups, such as $-NR_2$ in dithiocarbamates or $-OR$ in xanthates, are good for vinyl esters but less efficient for styrene. Thus, the proper choice of the Z substituent can dramatically enhance the reactivity of the thiocarbonylthio compounds [182].

The contribution of termination is slightly different in RAFT than it is in SFRP and ATRP. In the latter two systems all chains are originally short; as



Scheme 3.12

they become long, the probability of termination decreases. However, in DT systems, there will always be a small proportion of continuously generated chains. They will terminate faster than long new chains. This will also make the formation of pure block copolymers via typical DT techniques impossible, as low MW initiators will always generate new homopolymer chains during the polymerization of the second monomer.

3.5.6.1
Monomers and Initiators

DT can be applied to any monomer used in RP unless there is some interference with the TA. For example, dithioesters can be decomposed in the presence of primary amines, and alkyl iodides may react with strong nucleophiles (including amines). RAFT is also suitable to directly polymerize hydrophilic monomers in aqueous media without any protection group chemistry [178, 183].

In principle, there is no limitation for the radical initiators but peroxides may oxidize RAFT reagents [184]. Also, initiator concentrations should be sufficiently small to ensure that large majority of chains originate from the TAs and not from radical initiators.

3.5.6.2
Transfer Agents

As discussed above, TAs should be carefully selected for particular monomers to provide not only sufficiently fast addition but also sufficiently fast fragmentation. Alkyl iodides (and derivatives of Te, Sn, Ge, As, or Bi) should have a leaving group R which provides a more stable radical. Isobutyrates are good for acrylates, but propionates are not efficient in polymerization of methacrylates. This also has implications on the block copolymerization order.

In the RAFT polymerization of MMA with dithiobenzoates (S=C(Ph)SR), the effectiveness of the RAFT agent (i.e., the leaving group ability of R) decreases in the order shown in Figure 3.6. Only the first two R groups are successful in preparing PMMA with low polydispersity ($M_w/M_n \leq 1.2$) and predetermined MW [185, 186].

Groups Z in RAFT should be more radical stabilizing for monomers forming more stable growing radicals. For the RAFT polymerization of styrene, the

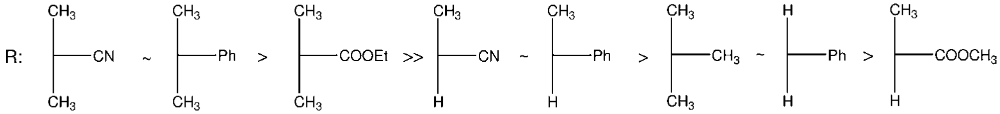


Figure 3.6 Order of R group leaving ability in RAFT.

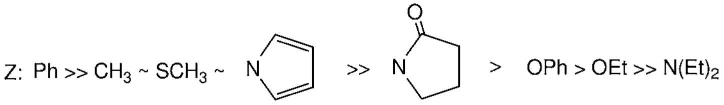


Figure 3.7 Rates of addition decrease and fragmentation increase from left to right for RAFT agents with the Z groups.

chain transfer constants were found to decrease in the series shown in Figure 3.7 [187].

3.6.3
Controlled Architectures

RAFT and other DT systems can be applied to the synthesis of many (co)polymers with controlled architectures. It should be remembered that there will always be some contamination from chains resulting from the radical initiators, unless a concurrent ATRP/RAFT is employed [83].

Multifunctional RAFT reagents are usually prepared from multifunctional activated alkyl bromides. RAFT reagents can be attached to polymer chains or surfaces via either the R or Z group. Attachment via the Z group allows polymer chains to grow (and terminate) in solution. This can reduce cross-linking for multifunctional systems [188].

Statistical, block, stereoblock, alternating/periodic, and gradient copolymers were prepared via RAFT. Many functional monomers were polymerized by RAFT. The dithioester group can be removed by the addition of a large excess of azobisisobutyronitrile (AIBN) [189].

3.7
Relative Advantages and Limitations of SFRP, ATRP, and DT Processes

Each CRP system has some comparative advantages/disadvantages. Recent advances in all three techniques have minimized many of the disadvantages, but others need to be still eliminated.

Advantages of SFRP include:

1. Purely organic system for NMP;
2. Applicable to acidic monomers;
3. No Trommsdorf effect.

Limitations of SFRP include:

1. Relatively expensive moderators must be used in stoichiometric amounts to the chain end;

2. Some limitation for potentially toxic transition metal compounds used in stoichiometric amounts for OMRP;
3. Difficult control for polymerization of disubstituted alkenes such as methacrylates;
4. Difficult to introduce chain-end functionality;
5. Relatively high temperatures required for NMP.

Advantages of ATRP include:

1. Only catalytic amounts of transition metal complexes (commercially available) are necessary;
2. Many commercially available initiators, including multifunctional and hybrid systems; 3. large range of monomers (except unprotected acids);
4. Easy end-functionalization;
5. No Trommsdorff effect;
6. Large range of polymerization temperatures.

Limitations of ATRP include:

1. Transition metal catalyst must often be removed;
2. Acidic monomers require protection.

Advantages of RAFT and other DT processes include:

1. Large range of monomers;
2. Minimal perturbation to RP systems.

Limitations of RAFT and other DT processes include:

1. Commercial availability of various TAs;
2. Dithioester and other end groups should be removed because of color, toxicity and potential odor;
3. Primary and secondary amine containing monomers as well as basic polymerization conditions lead to the decomposition of dithioesters;
4. Range of chain-end functionalities is limited.

However, recently some of the limitations have been overcome and others may be avoided in future:

1. NMP: control of MMA polymerization can be improved in the presence of either new nitroxides or small amounts of styrene, allowing formation of block copolymers [56, 57].
2. ATRP: AGET allows production of clean block copolymers by starting from an oxidatively stable catalyst precursor and employing reducing agents; ARGET and ICAR have lowered the amount of Cu to low ppm amounts and allowed higher MW polymers to be synthesized [159, 162];

new ligands expanded the range of polymerizable monomers to include vinyl acetate and vinyl chloride [92, 93]; simple replacement of a Br end group by azide has opened many possibilities for functionalization via click chemistry [190–192], including new bioconjugates; halogen exchange [101] has allowed the production of some block copolymers with sequences not available via other processes. Kinetically, ICAR resembles RP (like RAFT)

3. In RAFT, dithio end groups could be removed in the presence of large excess of AIBN [189]; with the rational design of RAFT reagents, retardation and side reactions can be avoided [193]; The convergent growth of chains in multifunctional system can prevent macroscopic gelation [188]. Copper catalyst can prevent formation of new chains and allow formation of purer block copolymers [83].
4. In all systems, a better understanding of the processes in dispersed media has allowed the reduction of the amount of necessary surfactant, has increased colloidal stability, and has also resulted in the extension of miniemulsion to true emulsion, microemulsion and inverse miniemulsion systems [60, 62, 152, 167, 178, 194–197]. It has also allowed to form very high MW polymers under high pressure and also with minimal amount of copper [74, 198–202].

3.7.1
Reactivity Orders in Various CRP Systems

The order of reactivity of dormant species dictates the order of segments to be built in block copolymer synthesis. This order generally scales with the stabilities of the resulting radicals, i.e., methacrylates > styrene > acrylates. However, this order also depends on the structure of the capping agent and is specific to each CRP mechanism. The relative rate constants of activation, the equilibrium constants between active and dormant species, and the (cross) propagation rate constants depend on three major factors: radical stability (σ_{RS}), polar effects (σ_υ), and steric effects (υ). These parameters are available in the literature [203]. Dissociation constants for various alkyl bromides, chlorides, iodides, and dithioesters have recently been computed [75, 148]. Dissociation rate constants for various alkoxyamines are also available [203].

Thus, it is possible to correlate values of the corresponding equilibrium (or rate) constants with the three structural parameters of radicals. It appears that polar effects are more important in ATRP than in NMP (RAFT reagents occupy an intermediate position). By contrast, ATRP shows the smallest sensitivity to steric effects, while both alkoxyamines and dithioesters show much larger sensitivity to steric effects [7].

As discussed before, the order of introducing segments in block copolymerization as well as efficiency of R groups in initiator/TAs may depend on the particular mechanism. For example, since RAFT and NMP are more accelerated by steric effects than ATRP, a PMMA block can be extended with polyacrylonitrile. The opposite is true for ATRP which relies more on polar effects [59, 204]. Similarly, *tert*-butyl dithioesters can efficiently control polymerization of acrylates, but *tert*-butyl halides are very inefficient in ATRP [135, 138].

3.7.2
Interrelation and Overlap Between Various CRP Systems

We already presented some evidence showing that new ATRP initiating systems (ARGET and especially ICAR) kinetically resemble RAFT [162]. ATRP can be carried out not only with halogens but also with pseudohalogens, including dithioesters, xanthates, or dithiocarbamates. The resulting control originates in a dual mediating system: activation/deactivation via ATRP and a degenerative exchange via RAFT [83]. Contribution of both processes depends on monomer, structure of RAFT reagent, and catalyst used. So, is it RAFT or ATRP? ATRP with alkyl iodides will also have a mixed DT/ATRP element. OMRP can proceed via SFRP process but some reagents will also have DT component and some species may also participate in ATRP.

Figure 3.8 shows how various CRP systems interrelate and how they conform to a classic SFRP, ATRP, and DT mechanisms illustrated in

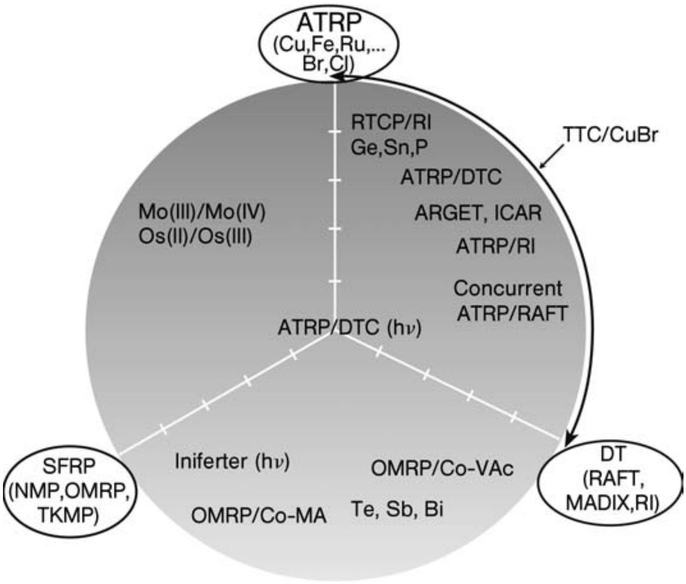


Figure 3.8 Schematic representation of various CRP systems and their relation to classic SFRP, ATRP, and DT mechanisms.

Schemes 3.3.5, 3.8, and 3.11. We already discussed that OMRP of vinyl acetate (VOAc) with Co derivatives proceeds with some contribution of DT [47, 205]. This depends on the use of additives that can promote spontaneous dissociation (SFRP) or rather favor DT process [206]. Some contribution of DT may also happen for MA polymerization. Classic dithiocarbamates as iniferters are poor TAs for styrene and methacrylates but are more efficient for vinyl acetate. Their activation by UV irradiation leads to a homolytic bond cleavage and predominantly SFRP process with methacrylates but a concurrent DT with vinyl acetate [46]. In a similar way Te, Sb, or Bi compounds can cleave homolytically but can also exchange with growing radicals via a degenerative process, depending on their structure and the monomers involved [207].

Alkyl bromides and chlorides in ATRP cannot react directly with growing radicals and do not participate in DT process. However, alkyl iodides can [170]. Contribution of DT will depend on activity of catalyst and kinetics of the activation/deactivation process. ATRP deactivators are usually paramagnetic species and react fast with growing radicals. However, sometimes activators can be paramagnetic. Perhaps the most intriguing is the reversible transfer catalyzed polymerization with GeI_4, SnI_4, or PI_3 deactivators and GeI_3^*, SnI_3^*, and PI_2^* activators [208, 209], reversible transfer controlled radical polymerization, RTCP. ATRP with dithiocarbamates will predominantly occur via activation/deactivation but with xanthates, trithiocarbonates, and dithioesters, contribution of DT process will become progressively larger, but still dependent on monomer, initiator, and catalyst structure. In the presence of light, contribution of SFRP mechanism becomes possible [81–83].

Some Mo, Os, and other organometallic species show not only SFRP but also ATRP activity [31]. This will depend on the nature of halogen, monomer, and ligands. Thus, there are many systems that show a concurrent involvement of spontaneous activation/deactivation (SFRP), a catalyzed process (ATRP), and a degenerative exchange (DT) and their contributions to the overall control depend on not only the structure of reagents but also reactions conditions (concentration, temperature, light, additives, etc.)

3.8
Controlled Polymer Architectures by CRP: Topology

CRP enables preparation of many well-defined (co)polymers with predetermined MW and a narrow, or even designed, MWD. In fact, an independent control of breadth and shape of MWD provides access to materials with new morphologies such as bicontinuous HPL shown in Figure 3.9 [169]. A block copolymer polystyrene–poly(methyl acrylate) $(PS-PMA)_{NB}$ with a narrow MWD PSt and a broad but symmetric MWD poly(methyl acrylate) (PMA) ($M_n = 51\,700$; overall polydispersity index (PDI) $= 1.13$, $\phi_{MA} = 0.35$) phase separates into thermodynamically stable HPL morphology. $PS-PMA_{NN}$ with

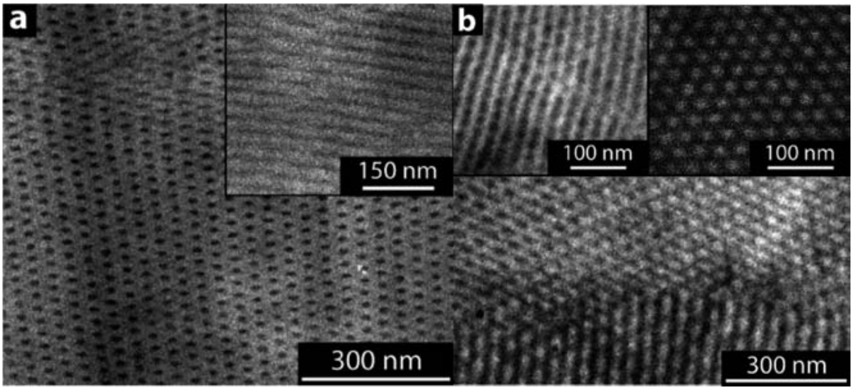


Figure 3.9 Bright field electron micrographs of PS–PMA samples after 72 h of thermal annealing at $T = 120\,^{\circ}\mathrm{C}$ and staining with RuO_4 (PMA is dark domain); (a) $(\mathrm{PS{-}PMA})_{\mathrm{NN}}$: cylindrical microstructure imaged along [001] direction. Inset depicts view along [100] direction. (b) $(\mathrm{PS{-}PMA})_{\mathrm{NB}}$: HPL microstructure imaged at low magnification. The inset on the left depicts the PS perforations within the PMA layers. The inset on the right shows a plane view revealing the hexagonal arrangement of the PS perforations [169].

approximately the same composition but with both blocks having narrow MWD ($M_n = 47\,200$, overall PDI = 1.11, $\phi_{\mathrm{MA}} = 0.29$) arranges into conventional cylindrical morphology. Control of the breadth of MWD is easily accessible via ARGET ATRP by variation of the concentration of copper catalyst. $\mathrm{PMA_N}$ synthesized under identical conditions but using 50 ppm amount of copper catalyst had $M_n = 18\,300$ and PDI = 1.11, and $\mathrm{PMA_B}$ prepared using 5 ppm amount of copper catalyst had $M_n = 18\,500$ and PDI = 1.77.

This example also illustrates that controlled heterogeneity (not only MWD [210] but also composition or topology) may give access to new materials with novel and exciting properties. Not always low PDI, pure block copolymer, and perfectly linear chains are the best for targeted material properties. Specifically designed MWD, gradient in composition along chain length and controlled branching will generate new advanced materials for specific application.

Polymers with controlled topology, composition, and functionality are easily accessible by CRP. Figure 3.10 presents a few examples of polymers with such controlled topology.

3.8.1
Linear Chains

All CRP techniques were successfully used in the synthesis of linear chains. Generally, MWs in CRP are lower than in RP prepared under

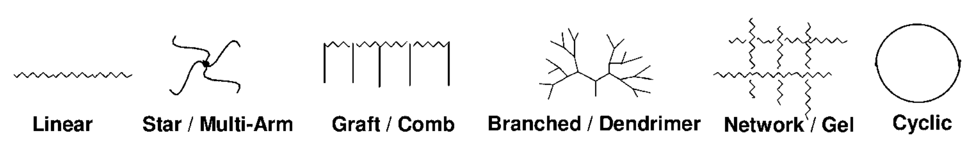


Figure 3.10 Illustration of polymers with controlled topology prepared by CRP.

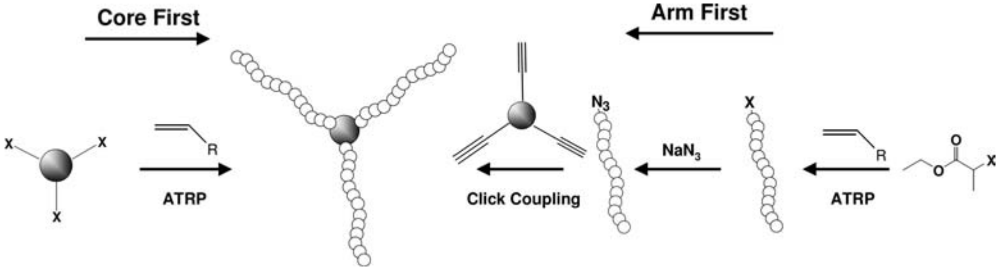
identical conditions. To synthesize polymers with small content of terminated chains, polymerization should be generally slower. Some limitations are associated with concurrent formation of chains from radical initiators (RAFT, ICAR and simultaneous reverse and normal initiation, SR&NI ATRP, and all styrene CRPs carried out at higher temperatures). Generally, it is easier to prepare high MW polymers from rapidly propagating acrylates than methacrylates or styrene. However, higher pressure [199, 200] and compartmentalization/segregation in dispersed media [201, 202] help to reach these goals.

The use of difunctional initiators allowed, for the first time in a radical process, a simultaneous two-directional chain growth. This gives access to both functional telechelic polymers and polymers with MW twice larger than otherwise attainable under similar conditions. There are many initiators and macroinitiators that contain functional group(s) and therefore add value to the obtained products [168, 211]. Several difunctional activated alkyl halides are commercially available. Many others can be prepared by simple esterification of diols and functional alcohols with, for example, 2-bromoisobutyryl bromide.

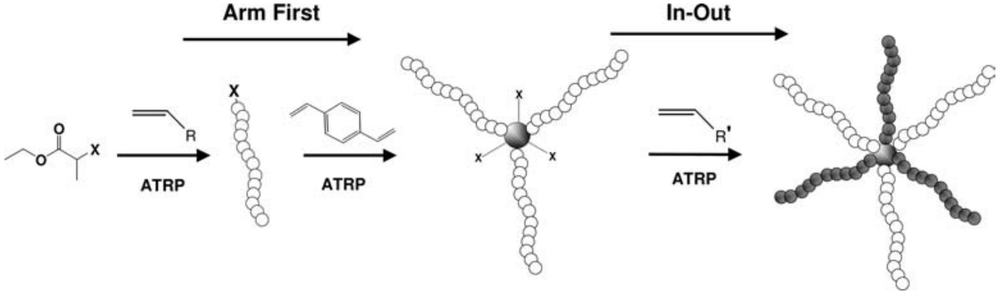
3.8.2
Star-Like Polymers

Star-like polymers have been prepared via four different approaches [212]:

1. Multifunctional initiators were used to simultaneously grow several arms via a core-first approach (left part of Scheme 3.13). ATRP is the most frequently used CRP system for this technique because of the availability of many polyols that have been subsequently converted to the initiating core with 3, 4, 6, 12, or more initiating sites [213–215]. Core can be also prepared by cross-linking the divinyl compound under high dilution [216]. The synthesis of star-like structures by CRP using a core-first method faces the danger of potential cross-linking and gelation because of radical coupling. Thus, a relatively low concentration of radicals and low conversions are often used to minimize star–star coupling.



Scheme 3.13



Scheme 3.14

2. An arm-first approach involves attachment of chains to a functional core (right part of Scheme 3.13). Certain RAFT reagents can be attached to a core via the Z group; therefore, RAFT offers a unique possibility to grow arms in solution [188]. Arms are reversibly attached to the core as a dormant species and therefore cannot terminate. Termination of linear chains in solution does not lead to cross-linking. A similar approach involves growing linear monofunctional Br-terminated chains in solution via ATRP and then converting the end groups to azides. These chains were subsequently ''clicked'' to a core with several acetylene groups [217].
3. Another approach utilizes arms that are cross-linked in the presence of divinyl compounds (Scheme 3.14). In this case, the number of arms in the resulting stars is not precisely controlled. Also, star–star coupling between the cores may occur. This synthetic procedure requires precise manipulation of arm length, the amount of divinyl compound, and the reaction time [218–220]. Cross-linker can be added to isolated arms or at a certain moment during the arm synthesis, allowing for control of the core density. All of these parameters affect the resulting star structure. As an example, the synthesis of stars with ~50 arms in >90% yield will require ~10-fold molar excess of cross-linker (vs. arm end groups) for precursors with DP ~100. Stars in even higher

yield (>98%) and with lower PDI (<1.2) can be prepared by replacing macroinitiators with macromonomers. In that case, in Scheme 3.14, R in monomer is a macromolecular substituent and initiator is used under substoichiometric conditions [221].

4. Stars prepared via the arm-first process (#3) still contain active/dormant species at the core. Thus, they can be used to grow a second generation of arms by the so called *in–out* approach (illustrated for ATRP in Scheme 3.14, but also possible for RAFT and NMP). Such mi*kt*o-arm stars can contain the same monomeric units but can be of different lengths; they can also contain heteroarms. The efficiency of reinitiation is often low because of poor accessibility of the monomer/catalyst to the sterically congested core, but may also result from enhanced termination inside the core. By using degradable cross-linker with an S–S linking unit, it was determined that efficiency of reinitiation is usually ~30% [220, 222]. The vinyl and/or halide residual functionalities were used for further core functionalization [223].

3.8.3
Comb-Like Polymers

Comb-like polymers can be prepared using three techniques which are similar to those described for stars [211, 224]. However, instead of a compact core, a long linear backbone is employed. These three techniques correspond to grafting-from, -onto, and -through.

1. Grafting-from is the most common method and is similar to the core-first approach for stars. It is often used to synthesize graft copolymers with a different composition of the backbone and the side chains; it has (for example) been successfully conducted for grafting-from polyethylene, polypropylene [225–228], PVC [229, 230], and polyisobutylene [231].
2. Grafting-onto is very similar to an arm-first approach. Click chemistry with azides and acetylenes can be used to efficiently attach side chains to a backbone [190, 232].
3. In grafting-through, monofunctional macromonomers are utilized as comonomers together with a low MW monomer, which permits the incorporation of macromonomers prepared by other controlled polymerization processes (such as polyethylene [233, 234], poly(ethylene oxide) [235], polysiloxanes [236], poly(lactic acid) [237], and polycaprolactone [238]) into a backbone of PS or poly(meth)acrylate prepared by CRP. Grafting density depends on the proportion of macromonomer and may not always be uniform. Reactivity ratios in copolymerizations of macromonomers depend not only on true chemical reactivity but also on

viscosity, compatibility, etc. Controlled/living processes have enabled the preparation of combs of different shapes, including tadpole or dumbbell structures [239].

Interesting brush topologies [166] with unique properties can be synthesized using different macromonomers in heterografted brush copolymers [240] or block brush copolymers prepared by a combination of grafting-from and grafting-through [241]. When macromonomers are polymerized by grafting-from a macroinitiator, double grafted brush copolymers can be synthesized where each graft is a brush [242].

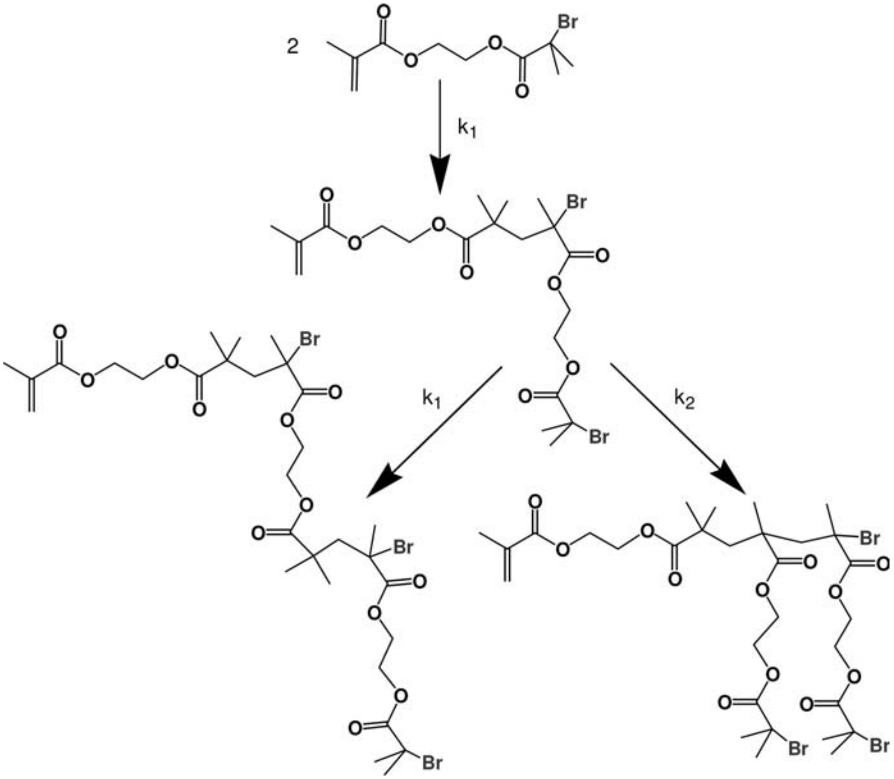
Figure 3.11 presents an atomic force microscopy (AFM) image of molecular brushes consisting of a methacrylate backbone with poly(*n*-butyl acrylate) side chains with a gradient density grafting. These gradient brushes were prepared by copolymerization of MMA with HEMA–TMS using ATRP and a feeding process. Subsequently, trimethylsilyl (TMS) groups were converted to 2-bromopropionate groups to initiate growth of side chains.

3.8.4
Branched and Hyperbranched Polymers

Comb-like polymers can be considered as models for branched polymers. Branching occurs in polymers made by conventional RP as a result of transfer to polymer. It may be due to intramolecular transfer (short branches) or intermolecular transfer which would give long chain branching and ultimately gelation. Branching is favored at higher temperatures and for less stabilized radicals. It becomes a very important reaction at high temperatures in the synthesis of polyethylene (resulting in LDPE). However, CRP is typically run at lower temperatures, and it seems that the contribution of branching is reduced in systems with intermittent activation.

CRP can be also used to prepare hyperbranched polymers [244, 245]. Monomers that also serve as initiators (so called inimers) were successfully used to make such materials (Scheme 3.15). The ratio of reactivities of the initiating site and the active species resulting from the alkene moiety defines the degree of branching (which can approach 50%). It is possible to additionally affect this ratio by varying the concentration of deactivator, as was demonstrated in ATRP. Copolymerization of inimers with regular monomers reduces the degree of branching and increases the branch length [246].

Hyperbranched structures can also be obtained when divinyl monomers are copolymerized in small amounts or in the presence of chain transfer compounds (thiols) [247] or ATRP initiators that favor the formation of branched products [248, 249].



Scheme 3.15

or attached to dendrimers. Single chains were combined with dendrimer structures and dendrons were also functionalized with methacrylate groups and copolymerized to form stiff polymer chains [255–258].

3.8.6
Polymer Networks and Microgels

Most polymer networks have irregular structures. However, CRP can significantly improve network uniformity. When a divinyl compound is copolymerized with a monovinyl compound, the gel point in CRP occurs much later than in RP. This is due to the fact that in CRP, only short chains are formed at the early stages, and the number of pendant double bonds in each chain is much lower than in conventional RP [259]. The gel point depends on the ratio of cross-linker to initiator and generally requires the ratio to exceed unity. However, gel point depends also on the moment of cross-linker addition, initiation efficiency, monomer reactivity, chain polydispersity, and other parameters [248, 260]. Gels prepared by CRP have generally much higher swelling ratio than those made by RP [167, 248, 259].

Additionally, it is possible to prepare well-defined polymers with cross-lin*ka*ble pendant moieties that can subsequently form microgels, even with just a single intramolecularly cross-linked chain. Star polymers with microgel cores have been prepared by ATRP [216, 261, 262]. Water soluble polymeric nanogels were synthesized by xanthate-mediated radical cross-linking copolymerization [263]. Degradable gels were prepared by the copolymerization of styrene or MMA and a disulfide-containing difunctional methacrylate [264, 265]. It is also possible to use cross-linkers which can be reversibly cleaved, which leads to the formation of reversible gels [220, 266].

3.8.7
Cyclic Polymers

CRP has no special advantage in forming cyclic polymers. Rather, anionic and/or cationic polymerizations are much better suited to make cyclics by using complimentary reagents at very low concentrations. However, cyclization has been reported when click chemistry was used in a reaction of azido- and acetylene-terminated chains [267, 268].

3.9
Chain Composition

CRP is very well suited for preparation of copolymers with precisely controlled composition. CRP combines facile crosspropagation with controlled/living character that can be applied to many monomers. Figure 3.12 presents some examples of copolymers with controlled composition.

3.9.1
Statistical Copolymers

Statistical copolymers are formed in RP when comonomers have a similar reactivity. The copolymerization of monomers with different reactivity ratios (e.g., methacrylates and acrylates have reactivity ratios ~3 and

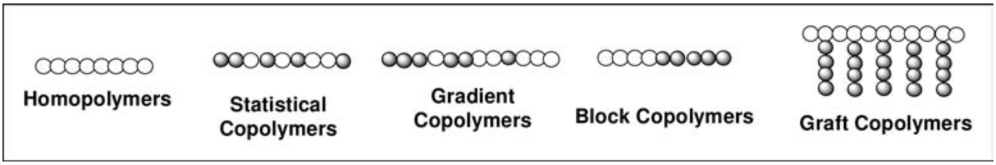


Figure 3.12 Illustration of polymers with controlled composition.

$\sim$0.3, respectively) results in copolymers with a spontaneous gradient (cf. Section 3.9.5) [211, 269]. In general, reactivity ratios in CRP are the same as in RP, although small differences exist which have been ascribed to nonequilibrated systems [270, 271].

3.9.2
Segmented Copolymers (Block, Grafts and Multisegmented Copolymers)

The area of segmented copolymers is perhaps the most prolific in CRP. Because of the tolerance of CRP to many functionalities, essentially an infinite number of possible structures is attainable. The end groups of polymers prepared by other techniques, including cationic, anionic, coordination, and step-growth polymerization, were converted to CRP initiating sites and used as macroinitiators for CRP.

3.9.2.1 Block Copolymers by a Single CRP Method

Efficient block copolymerization requires an appropriate sequence of blocks. This order generally follows radical stabilities and can be correlated with the proportion of active species. This order may be specific for a particular polymerization. In ATRP the order is as follows: acrylonitrile > methacrylates > styrene $\sim$ acrylates > acrylamides. In RAFT, because of steric effects, methacrylates become most reactive. In ATRP, the block order can be altered by using halogen exchange (as discussed before). This way, thermoplastic elastomers of PMMA–PBA–PMMA were successfully obtained by starting from Br–PBA–Br and using CuCl/L to chain extend with MMA [101, 102, 104, 272]. ABC, ABCD, and ABCBA blocks were also prepared by ATRP [273].

3.9.2.2 Block Copolymers by Combination of CRP Methods

ATRP macroinitiators were successfully converted to RAFT and NMP initiators. After site transformation, these macroinitiators served as a starting point for RAFT and NMP mediated block copolymerization [211]. Dual initiators could also be used for a successive ATRP and RAFT polymerization [274].

3.9.2.3 Block Copolymerization by Site Transformation and Dual Initiators

Block copolymers have been successfully prepared by block copolymerization via site transformation or using dual initiators [275, 276].

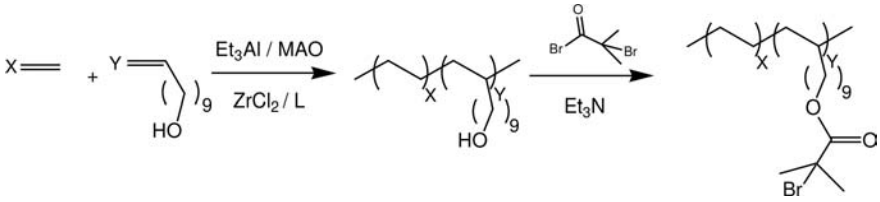
CRP and Living Carbocationic and Carbanionic Polymerization The dormant species in styrene cationic polymerizations and ATRP systems have identical structures. Therefore, Cl-terminated PSs from cationic polymerization could be efficiently extended via ATRP with PS and also with poly(meth)acrylates [138]. ATRP was initiated by acetal end-functionalized alkyl halides which were subsequently used to grow vinyl ethers by living cationic polymerization. The reverse process was also successful because of the high tolerance of cationic polymerization of vinyl ethers to impurities [277]. Living carbanions were quenched by species serving as initiators for NMP and also for ATRP, and subsequently chain extended via CRP [278, 279].

CRP and Ionic Ring-Opening Polymerization Cationic polymerization of tetrahydrofuran (THF) was initiated by 2-bromoisobutyryl bromide and silver triflate. The subsequent addition of ATRP catalyst allowed the controlled polymerization of MMA, butyl acrylate (BA), and styrene from the residual bromoester moiety [280]. In a similar way, oxonium ions at the chain end of living polyTHF were quenched with 4-hydroxyTEMPO and then used to chain extend the polyTHF with styrene via NMP [281]. Bromo end groups in ATRP of styrene were used to directly initiate ring-opening polymerization of oxazolines [282].

Hydroxy end groups in polymers from anionic ring-opening polymerization, AROP of ethylene oxide or lactones were directly esterified to bromoesters and used as ATRP initiators. In this way not only mono but also di- and multifunctional polymers were synthesized. 2-Hydroxyethyl 2′-bromoisobutyrate is a simple dual initiator capable of initiating both AROP and ATRP [283]. Depending on the initiating/catalytic systems, the rates of both processes can be comparable allowing the simultaneous presence of two noninterfering processes [284, 285].

CRP and Coordination Polymerization Unsaturated chain ends in polyethylene and polypropylene were transformed to bromoesters to initiate ATRP of styrene and (meth)acrylates. Hydroxy functional polyethylene obtained in DT polymerization of ethylene was used in a similar way for block copolymerization via ATRP [225, 226, 234, 286]. A similar approach was used to create graft copolymers. Copolymerization of ethylene and 10-undecen-1-ol in the presence of a trialkylaluminum protecting group can be conducted with a metallocene catalyst. The hydroxyl functionality was converted into an α-bromoisobutyrate functionality (Scheme 3.16) and the resulting polyethylene multifunctional macroinitiator was used for a ‘‘grafting-from’’ ATRP procedure. In this way, copolymers such as polyethylene-*g*-PMMA have been produced which act as compatibilizers for otherwise immiscible polymers [225, 287, 288].

Several methods combine CRP with ring-opening metathesis polymerization, ROMP. Molybdenum alkylidene chain ends are destroyed by aldehydes. Thus, aldehydes with activated alkyl bromides were used to terminate ROMP of norbornene and subsequently form block copolymers with styrene and



Scheme 3.16

(meth)acrylates [68]. Another interesting possibility is the simultaneous growth of polymer chains via ROMP on ruthenium alkylidenes which also serve as ATRP catalysts. Interestingly, an excess of phosphines reduces the rate of ROMP but does not affect the rate of ATRP [289–291].

CRP and Polycondensation Polymers End groups from many step-growth polymers are easily transformed to ATRP macroinitiators. Thus, terminal hydroxy groups from polyesters, polycarbonates or polysulfones were esterified to bromoesters and subsequently chain extended with styrene or (meth)acrylates [139, 292, 293].

Polythiophenes are formed by polycondensation, but the mechanism follows a chain growth rather than a step-growth process. It is therefore possible to prepare polythiophenes with low polydispersity. End groups are well controlled and can be converted to ATRP initiators. Block copolymerizations with this technique have been very efficient, and well-defined nanostructured materials have been prepared [294–297].

CRP and RP CRP was also combined with polymers prepared by conventional RP. For example, telechelic polymers prepared by RP can either contain ATRP active sites or can be converted to the corresponding macroinitiators and used for controlled ATRP. In such a way, PVAc was block copolymerized with styrene and acrylates. Conversely, well-defined blocks were used to initiate uncontrolled RP of vinyl acetate to afford another type of block copolymer [298].

3.9.2.4 **Multisegmented Block Copolymers**

Multisegmented block copolymers are typically prepared by polycondensation processes. ATRP can be used to make ABC or ABCBA segments by sequential polymerization. However, chain coupling can afford multisegmented copolymers in a much simpler way. Such coupling can be done with termination by radical coupling; however, yields in these reactions are rather low.

Another approach involves click chemistry. An ATRP initiator with an acetylene functionality (such as propargyl 2-bromoisobutyrate) can be used to synthesize an α-alkyne-ω-bromo-terminated block copolymer which can further be reacted with NaN_3 to generate the corresponding α-alkyne-ω-azido-terminated block copolymer. This functional diblock can then be click coupled in a step-growth process at room temperature in the presence of Cu^I to generate segmented block copolymers (Scheme 3.17) [267, 299].

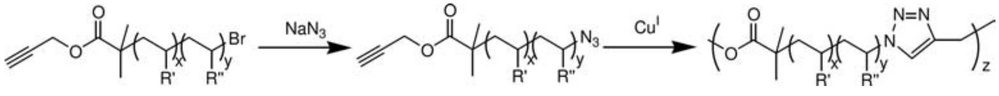
3.9.2.5 **Stereoblock Copolymers**

RP is not stereoselective. However, in the presence of some complexing agents, which strongly interact with the pendent groups of the polymer chain end and/or the monomer, the proportion of syndiotactic or isotactic triads can be significantly increased. This has been demonstrated for the polymerization of acrylamides in the presence of catalytic amounts of $Yb(OTf)_3$ or $Y(OTf)_3$ [300] and also in the polymerization of vinyl esters in fluoroalcohols [301]. CRP offers the special advantage that atactic segments formed without complexing agent can be extended with regular blocks formed in the presence of such agents. In such a way, stereoblock poly(*atactic*-dimethylacrylamide)-*b*-poly(*isotactic*-dimethylacrylamide) was formed [302–304]. (Scheme 3.18). An interesting extension of this approach was applied to prepare stereogradient copolymers [305].

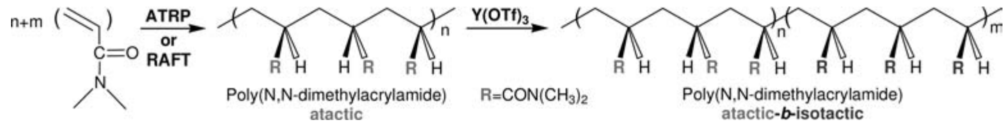
3.9.3
Graft Copolymers

Techniques used for the synthesis of graft copolymers include those applied for the preparation of comb polymers (grafting-from, -onto, and -through) as well as methods known for block copolymerization, including site transformation.

Polymer backbones containing hydroxy functionalities can be easily esterified to form bromoesters with a controlled amount of ATRP initiating sites for use in "grafting-from". In such a way, either very densely grafted molecular brushes or loosely grafted copolymers were prepared. Grafting density can be varied along the chain length (cf. Section 3.9.5). Various types of block/graft copolymers have also been generated, including core–shell cylinders and double grafted structures. "Grafting-onto" is the least explored grafting technique in CRP. Click chemistry of azides, acetylenes and



Scheme 3.17



Scheme 3.18

maleic anhydride/phthalimides with amino-terminated polymers were used for grafting-onto. Several macromonomers were copolymerized by ATRP and other CRP techniques providing graft copolymers with variable density via “grafting-through.” Copolymerization via CRP provides more uniform grafts because the growth of the backbone is slower and macromonomer has enough time to diffuse to the growing chain [306]. Additionally, it is possible to use macroinitiator with the same chemical composition as macromonomers to inherently compatibilize the graft copolymer.

The mechanical properties of graft copolymers prepared by copolymerization of poly(dimethylsiloxane), PDMS macromonomers with MMA using ATRP and RP are dramatically different. Regular graft copolymers with $M_n \approx 100\,000$ and $\approx$50 wt% PDMS ($M_n = 2000$) prepared by ATRP have tensile elongation $\approx$300%, whereas that for irregular grafts is only $\approx$100%. Interestingly, graft copolymers with a gradient composition had tensile elongation only $\approx$30 % (Figure 3.13) [236, 237, 307].

Homopolymerization of macromonomer by CRP is difficult. Only those with relatively “thin” side chains such as poly(ethylene oxide), PEO or polyethylene were homopolymerized to high MW polymers. Macromonomers with “thicker” chains such as poly(n-butyl acrylate), PBA can be polymerized only to relatively low DP. Homopolymerization of macromonomers by CRP may be more difficult than by RP. Rate constants of propagation of macromonomers are smaller than those of regular monomers, but the rate constants of termination are even less. Thus, in RP, an overall rate of homopolymerization may still be sufficient as it scales with the $k_p/k_t^{1/2}$ ratio. In ATRP, polymerization rate is not affected by k_t and consequently it is much slower for macromonomers than for low MW monomers.

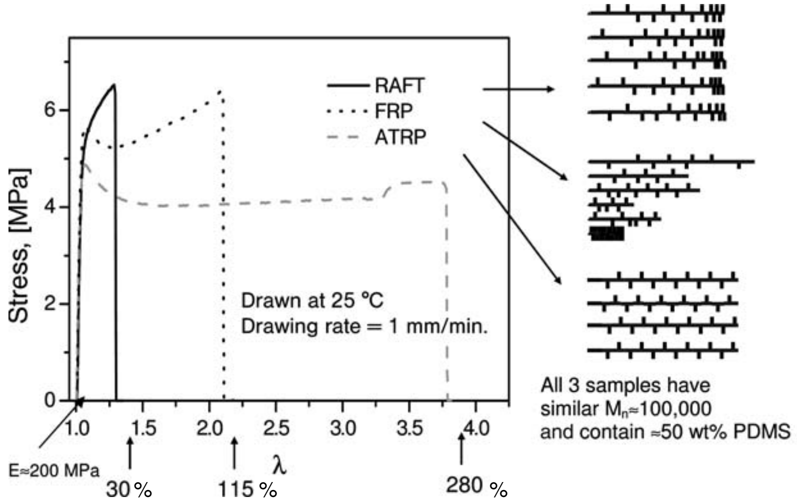


Figure 3.13 Cold drawing of press-molded films of PMMA–PDMS grafts [236].

3.9.4
Periodic Copolymers

Alternating copolymers are the simplest periodic copolymers. There are several comonomer pairs which copolymerize in alternating fashion by RP. They are typically strong electron donors and strong electron acceptors, such as styrene–maleic anhydride or styrene–maleimides [308]. They were successfully copolymerized by all CRP techniques. It is also possible to use one kinetically reactive but thermodynamically nonhomopolymerizable monomer. Maleic anhydride can serve as an example [309]. Another possibility is to use a less reactive monomer in large excess. In such a way nearly alternating copolymers of acrylates with olefins were prepared [94, 97]. The reactivity ratios of monomers can also be affected by complexation. For example, in the presence of strong Lewis acids, MMA tends to form alternating copolymers with styrene [310]. For some inimers with a reactive alkyl halide but unreactive alkene, a polyaddition is possible that generates a new polymer structure with a heteroatom in the main chain [311].

3.9.5
Gradient Copolymers

In contrast to conventional free radical copolymerization, where differences in comonomer reactivity ratios result in a variation in copolymer composition, in CRP this variation in instantaneous incorporation of the monomers into the copolymer results in a tapering in composition along the main chain of the copolymer. Gradient copolymers can be prepared by either simultaneous copolymerization of monomers with different reactivity ratios (spontaneous gradient) or continuous feeding of one monomer (forced gradient) [312, 313]. The shape of the gradient depends on concentration of comonomers, on their reactivity ratios, and on the feeding process. In miniemulsion it also depends on comonomers solubility [314]. Gradients can be linear, V-shaped, and also curved. Gradient uniformity is a very important parameter. The uniformity depends on the frequency of intermittent activation. If only a few monomer units are added during each activation step, then all copolymers should have a similar composition along the chain length. However, if many monomer units are added at each step, chains would contain long sequences formed at a certain conversion and individual chain composition and microstructure would differ from one another. Additionally, gradient copolymerization can be extended to the formation of graft copolymers with a gradient distribution of grafts (Figure 3.10) [239, 243]. Gradient may reflect not only density of grafting or composition but also stereostructure [305]. Macroscopic gradients were generated on surfaces [315].

3.9.6
Molecular Hybrids

Molecular hybrids comprise synthetic polymers attached covalently to inorganic materials and to natural products [140]. The well-defined organic–inorganic hybrids can be formed by grafting-from flat, convex, concave, or irregular surfaces [141, 316]. Surfaces of gold, silicon, silica, iron, and other inorganic substrates were functionalized with bromoesters to initiate growth of PS, poly(meth)acrylates, polyacrylonitrile, or polyacrylamide chains via ATRP [317]. It is possible to vary grafting density and prepare very densely grafted films, with density approaching $\sim 0.5-1$ chain/nm^2 [318, 319]. Grafting density could be continuously varied along the substrate to prepare surfaces with a macroscopic gradient [315]. Very dense grafting is not possible via grafting-onto, as attached polymer chains collapse on the surface and prevent other chains from solution reaching the surface. Nonuniform growth cannot provide high grafting density. Only when polymer chains grow by adding "a few monomer units at a time," is high grafting density possible. The resulting hybrids have many new and unusual properties related to their unique compressibility, lubrication, swelling, or interpenetration [319]. Grafting can be performed by normal ATRP but also by ARGET [161].

It is also possible to graft polymers and block copolymers onto inorganic surfaces. For example, poly(methacrylic acid)-*b*-PMMA-*b*-poly(sodium styrenesulfonate) prepared by ATRP was grafted onto ~ 200 nm diameter iron particles to destroy residual chlorinated solvents [320].

Functional groups in natural products have been converted to ATRP initiators (NH_2 or OH groups converted to bromoamides and bromoesters) [146, 321]. During polymerization the original substrate should not interfere with the ATRP process and the functionality and properties of the natural products should not be destroyed by ATRP. Alternatively, chains prepared by CRP containing functionalities (NH_2 or OH) were used to grow polypeptides or DNA. It is also possible to fuse functionalized natural products and organic polymers together either with click reactions or by biotin–avidin chemistry [144, 145, 147, 322–333].

3.9.7
Templated Systems

Templating with CRP can be more precise than with conventional RP. Slower growth may facilitate better control of templated systems. Mesoporous silica was functionalized with bromoesters and used to grow polyacrylonitrile, PS, or poly(meth)acrylates. Growth of polymer chains was followed by thermogravimetric analysis, TGA, porosity and analysis of detached polymers. Highly uniform growth was achieved not only on the molecular level

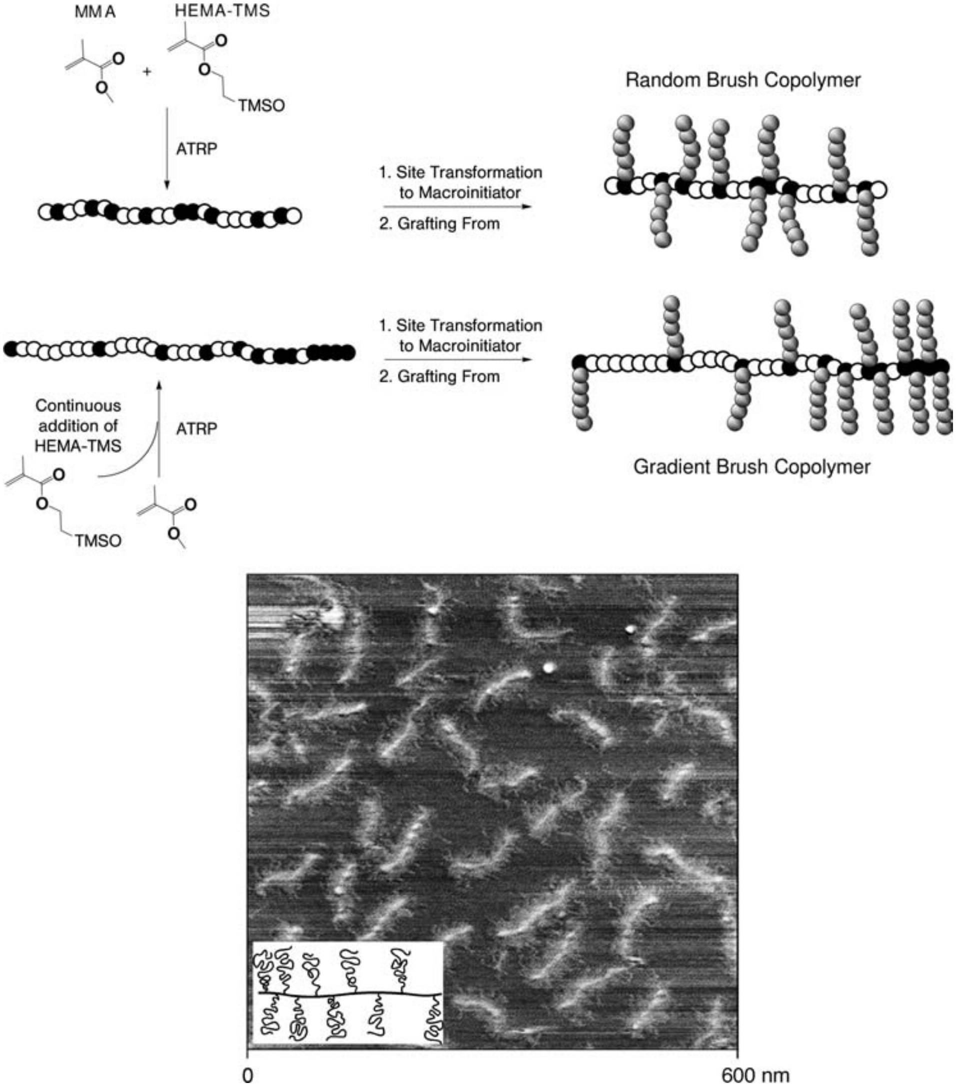


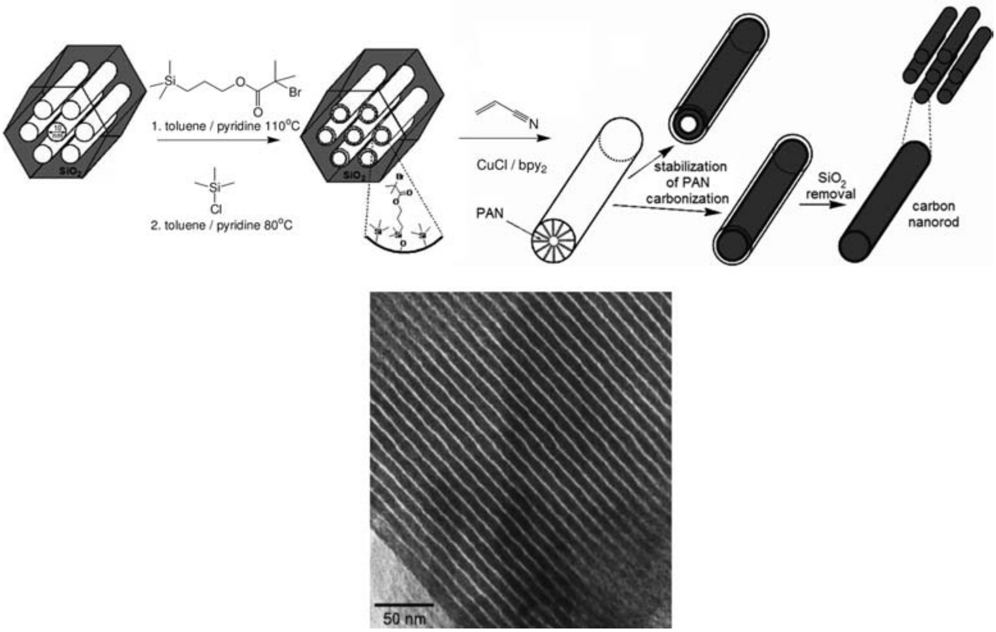
Figure 3.11 Synthetic route to and AFM image of gradient molecular brushes [243].

3.8.5
Dendritic Structures

While hyperbranched systems are irregular, branching is controlled in dendritic structures by the degree of polymerization. Dendritic structures have been prepared by a single CRP method [250, 251] as well as with various combinations of CRP and other controlled living polymerization techniques [252–254]. Polymer chains were grafted from dendrimer surfaces (as evidenced by low polydispersity of detached polymers analyzed by gel permeation chromatography (GPC)) but also macroscopically (overall porosity measurements). The resulting polyacrylonitrile was converted to very regular nanosize carbon filaments ($D \sim 10$ nm, $L > 1$ μm, $S = 840$ m^2 g^{-1}; Scheme 3.19) [316, 334, 335].

3.10
Functional Polymers

RP is tolerant to many polar groups such as –OH, –NH$_2$, or –COOH and can be carried out in water. In CRP, functionalities can be incorporated into specific parts of polymer chains, as shown in Figure 3.14 [168].



Scheme 3.19

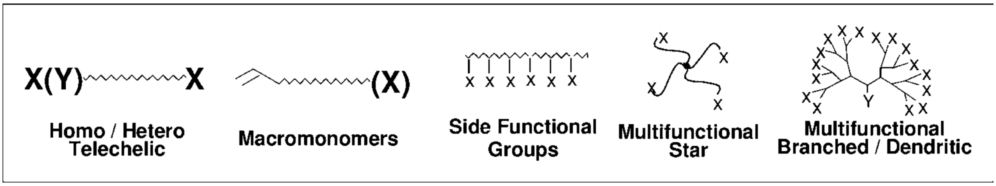


Figure 3.14 Illustration of polymers with controlled functionality prepared by CRP.

3.10.1
Polymers with Side Functional Groups

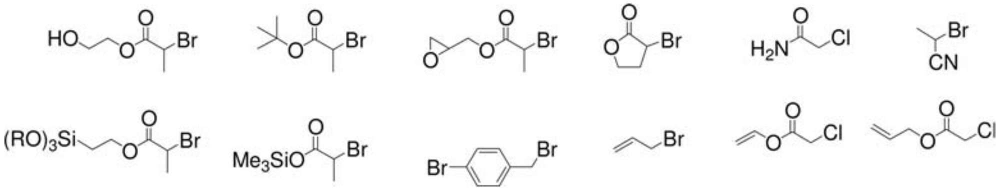
Functional monomers were directly incorporated into polymer backbones as well as incorporated in a protected form. For example, 2-hydroxyethyl (meth)acrylate was homopolymerized and copolymerized by all CRP techniques [336, 337]. Also, TMS derivatives were polymerized and subsequently deprotected. The hydroxy groups were then functionalized with 2-bromopropionate groups and extended to form densely grafted molecular brushes [336, 338].

(Meth)acrylic acid was polymerized directly by RAFT and NMP but less successfully by ATRP [180, 339]. Better results were obtained when the acid functionality was either protected by acetal, a TMS group, *t*-Bu, or benzyl ester, or converted to a Na salt [340, 341].

The side functional groups were subjected to further reactions. In addition to simple deprotection of acetal or ester functionalities, other reactions such as the conversion of cyano groups from acrylonitrile units to tetrazoles and reactions of azides with functional acetylenes were employed [342].

3.10.2
End Group Functionality: Initiators

End groups can be incorporated either by using functional initiators or by converting growing chain ends to another functional group [168]. There is strong interest in di- and multifunctional polymers, but functional initiators allow the introduction of functionality to only one chain end. Various functionalized ATRP initiators were used to prepare hetero-telechelic polymers (Scheme 3.20) [168]. Additionally, atom transfer radical coupling (ATRC) enables the efficient coupling of chains and provides a route to telechelic PSs [343]. ATRC is less efficient for methacrylates (the growing radicals predominantly disproportionate rather than couple) and for acrylates (too low equilibrium constant). However, it is sufficient to add a few styrene units at the acrylate chain end to successfully form polyacrylate telechelics. Multifunctional star polymers were prepared from functional macroinitiators.



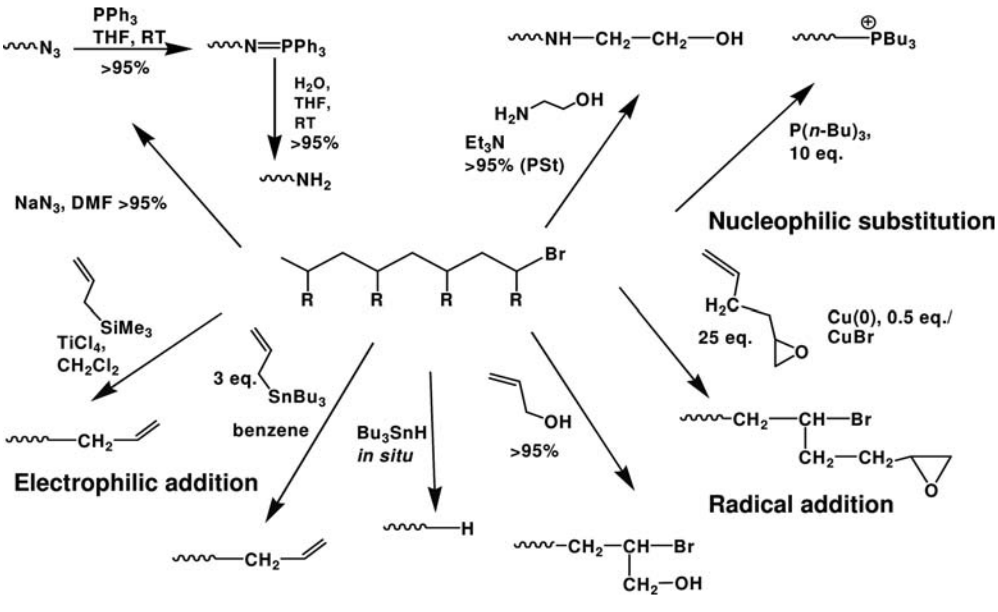
Scheme 3.20 Functional ATRP initiators.

3.10.3
End Group Functionality through Conversion of Dormant Chain End

The dormant chain end in all CRP processes can be further converted to other functional groups by radical or nonradical processes. For example, dithioesters in RAFT were converted to thiols, the alkoxyamines in NMP to alkyl chlorides, and the alkyl halides in ATRP to allyl, hydroxy, amino, azido, and ammonium or phosphonium groups in excellent yields. It is also possible to incorporate one functional monomer at the chain end, if the monomer is much less reactive and forms an unreactive dormant species. Scheme 3.21 presents three types of reactions employed for end-functionalization of ATRP polymers; nucleophilic substitution, electrophilic substitution and radical processes.

The conversion of dormant species in chains growing in two directions leads to telechelics, and in stars to multifunctional polymers. A similar approach was applied to hyperbranched polymers prepared by (co)polymerization of inimers (Section 3.9.4).

Dithioesters from the chain ends of RAFT polymers can be removed in the presence of large access of peroxides or AIBN [189]. Also, it possible to reduce them to thiols with primary amines or other reducing agents [135]. Subsequently thiols can be conjugated with other functional groups via, e.g., thiol-ene chemistry [344].



Scheme 3.21

3.11
Applications of Materials Prepared by CRP

Chapter 10 describes some applications of materials prepared by anionic living polymerization that was discovered over 50 years ago. Nevertheless, although NMP, ATRP, and RAFT were invented in just the last decade, they are already finding application in commercial production. It is anticipated that many more specialty products will be available and successfully commercialized in the future [345]. A few examples are highlighted hereafter.

3.11.1
Polymers with Controlled Compositions

Block copolymers based on acrylates and other polar monomers may find applications as polar thermoplastic elastomers [102] in automotive applications, especially in the presence of hydrocarbons that will not swell. However, they can also be used for much more sophisticated applications such as controlled drug release in cardiovascular stents [346]. Amphiphilic block copolymers with water soluble segments were successfully used as very efficient surfactants [347] and were also used for higher end applications including pigment dispersants [348, 349], various additives, and components of health and beauty products. Segmented copolymers with nanostructured morphologies are promising as microelectronic devices [296].

Graft copolymers have been used as compatibilizers for polymer blends and may be used in many applications described for block copolymers [225, 350]. Gradient copolymers hold great promise in applications ranging from surfactants to noise and vibration dampening materials [95, 312, 351, 352].

3.11.2
Polymers with Controlled Topology

Designed branching allows precise control over melt viscosity and polymer processing. Such polymers (as well as comb and star polymers) can be used as viscosity modifiers and lubricants [353].

An ultimate example of controlled topology might be a macromolecular bottle-brush [166]. Such polymers, when lightly cross-linked, result in supersoft elastomers [354]. Materials were synthesized with moduli ~1 kPa, in the range attainable by hydrogels. However, hydrogels must be swollen 100 times by water to reach such low moduli. Molecular brushes are swollen by their own short side chains that never leach. Thus, applications are foreseen ranging from intraocular lenses and other biomedical applications requiring a soft material that does not leach to surrounding tissue, to electronic applications requiring the protection of delicate components by a soft solid. These materials also show very high ionic conductivities reaching 1 mS cm^{-1} for Li cations at room temperature [355]. Brushes can be also used as a core–shell cylindrical templates to prepare various nanostructured materials [356, 357].

3.11.3
Polymers with Controlled Functionality

CRP offers unprecedented control over chain-end functionality. End functional polyacrylates are excellent components of sealants for outdoor and automotive applications [345, 358]. Multifunctional low MW polymers are desirable components in coatings with a low organic solvent content important for volatile organic compounds, VOC reduction [359]. It is also possible to design systems with two types of functionalities, curable by two independent mechanisms. Incorporation of degradable units into the backbone of vinyl polymers allows controlled cleavage and degradation/recycling of such polymers.

3.11.4
Hybrids

Molecular hybrids with a covalent attachment of well-defined functional polymer to either an inorganic component or a natural product are currently being extensively investigated and should lead to numerous materials with previously unattainable properties. Such hybrids allow better dispersability of inorganic components (pigments, carbon black, carbon nanotubes, nanoparticles), they dramatically enhance the stability of such dispersions, and they allow the formation of molecular nanocomposites. Also, dense polymer layers improve lubrication, prevent corrosion, and facilitate surface patterning. Precise grafting-from chromatographic packing enables enhanced chromatographic resolution of oligopeptides and synthetic prions [360].

Other potential applications include microelectronics, microfluidics, and optoelectronics, as well as biomedical applications such as components of tissue and bone engineering, controlled drug release and drug targeting, antimicrobial surfaces [361], steering enzyme activity [145, 147, 362–364], and many others.

3.12
Outlook

CRP is currently the most rapid developing area of synthetic polymer chemistry. It bridges chemistry with physics and processing/engineering to rationally design and prepare targeted functional materials. Nevertheless, to reach its full potential, more research in this field is required.

3.12.1
Mechanisms

Continuation of mechanistic and kinetic studies of all CRP processes is needed. The deeper understanding of structure–reactivity correlation in NMP may lead to satisfactory control over polymerization of methacrylates. A full understanding of structural effects with ATRP catalysts could lead to the development of even more active complexes used in smaller amounts, which in turn could minimize the environmental impact of this chemistry as well as expand the range of polymerizable monomers to include acrylic acid and α-olefins. This may also lead to complexes that can participate in both ATRP and OMRP and potentially in coordination polymerization. In a similar way, the proper choice of dithioesters will eliminate some retardation effects of RAFT reagents. Model reactions with low MW analogs and oligomers enhance our comprehension of penultimate effects. Various additives that can accelerate polymerization and provide improved microstructural (tacticity and sequence) control should also be evaluated. Better cross-fertilization between synthetic organic chemistry and polymer chemistry is needed. In the past, achievements in organic chemistry were applied to polymer chemistry. Recently, advances made in polymer chemistry also benefit organic chemistry; e.g., new catalysts developed for ATRP are used for atom transfer radical addition and cyclization and new nitroxides developed for NMP are used in organic synthesis [365, 366]. ARGET chemistry has been recently extended to atom transfer radical addition and cyclization processes [367].

It is anticipated that computational chemistry will start playing a progressively more important role. A deeper insight into the reaction intermediates and energetic pathways is possible this way [75]. It can also lead to the development of new mediating systems. However, precise computational evaluation requires a large basis set, as many reaction pathways may become dramatically affected by tiny changes in the structure of the substituents. Thus, continued model studies and their correlation with macromolecular systems are very much needed to better understand and optimize the existing processes.

Although current CRP techniques seem to cover all major mechanistic approaches to equilibria between active and dormant species, it is feasible to imagine more efficient stable free radicals, more active transition metal complexes and better degenerative TAs than currently available. Thus, both a serendipitous and rational search for new mediating agents in CRP should continue.

3.12.2
Molecular Architecture

Previous sections described many elements of controlled molecular architectures attainable by CRP. Further studies are needed to prepare higher MW polymers, important for some commercial applications, polymers with better control of end functionality, copolymers with precisely controlled gradients, materials with hierarchical structural control (such as in molecular brushes or other nano-objects with a core–shell), and other nanostructured morphologies.

Control of heterogeneity of macromolecular structure will open a door to new materials. It is important to prepare systems with designed MWDs, both with symmetrical and asymmetrical distributions. Also, the introduction of imperfections, such as missing functionality or a missing arm in a star may be important for further structure–property evaluation. Some specialty applications will require systems responding reversibly to external stimuli (pH, temperature, light, pressure, and magnetic or electric field). Thus, segmented copolymers with components responding separately to individual stimuli will be needed. Such systems may associate or dissociate under certain conditions and can rearrange, self-repair, and be useful for advanced applications in microelectronics and biomedical areas.

The importance of hybrids was already emphasized, and it is anticipated that with a continued reduction of dimensions for many high-tech applications, the demand for precisely designed multifunctional nanocomposite materials will rapidly grow. The same is anticipated for smart drug delivery systems.

3.12.3
Structure–Property Relationship

Improved synthesis and more complex architectures require more precise characterization techniques to determine quantitatively the level of functionality, detect existing imperfections, and precisely describe composition, topology, and microstructure. This is needed both at a level of macromolecular assembly, as well as for individual molecules. Therefore, various novel scattering techniques, modulated thermomechanical analysis, more sensitive spectroscopic techniques, multidimensional chromatography, and visualization of individual molecules by AFM are just a few examples of techniques needed to characterize the structure of prepared materials.

New polymers with precisely controlled architecture are primarily developed to explore novel properties. Such structure–property correlation is very much needed for many applications. As macromolecular systems are very large and complex, it is difficult to predict all properties by modeling and computational techniques without input from well-defined macromolecules. The detailed correlation of molecular structure with final properties is not yet obvious because many properties depend also on processing conditions, including the solvent used and its removal conditions, mechanical stresses, and thermal history. The incorporation of such parameters into simulation will be very beneficial.

Additionally, evaluation of all imperfections and synthetic errors on properties of prepared polymers is needed. This should include the effect of polydispersities and shape of MWD. Polymers with higher polydispersities can allow more flexible processing regimes. In CRP, it will be much more economical to prepare polymers faster, with more termination, and with more errors. Therefore, it will be important to understand how these imperfections may affect material properties to maximize cost–performance ratio.

Acknowledgments

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4

Living Transition Metal-Catalyzed Alkene Polymerization: Polyolefin Synthesis and New Polymer Architectures

Joseph B. Edson, Gregory J. Domski, Jeffrey M. Rose, Andrew D. Bolig, Maurice Brookhart, and Geoffrey W. Coates

4.1

Introduction

One of the ultimate challenges in polymer chemistry is the development of new synthetic methods for the polymerization of a wide range of monomers with well-defined stereochemistry [1] while controlling molecular weight and molecular weight distribution [2, 3]. A primary goal of synthetic polymer chemistry over the last half century has been the development of chain-growth polymerization methods that enable consecutive enchainment of monomer units without termination. Known as *living polymerizations* [4], these systems allow both precise molecular weight control as well as the synthesis of a wide array of polymer architectures [5]. Living polymerization methods also allow the synthesis of end-functionalized polymers in addition to the creation of virtually limitless types of new materials from a basic set of monomers.

Polyolefins are by far the largest volume class and most important commercial synthetic polymers in use today [6]. Since the initial discoveries of Ziegler *et al.* [7] and Natta *et al.* [8], remarkable advances have been reported concerning the control of comonomer incorporation as well as dramatic improvements in activity. Homogeneous olefin polymerization catalysts now exist that are unparalleled in all of polymer chemistry concerning the detailed control of macromolecular stereochemistry [9]. However, olefin polymerization catalysts have traditionally been inferior to their other chain-growth counterparts in one respect. While extraordinary advances in living/controlled polymerization have been discovered using anionic [10], cationic [11], and radical-based polymerization [12–15], until very recently there existed a comparative lack of living olefin polymerization systems. The main reason for this is that alkene polymerization catalysts often undergo irreversible chain transfer to metal alkyls and β-elimination reactions that result in the initiation of new polymer chains by the catalyst (Scheme 4.1). However, systems are now available that have acceptable rates of propagation

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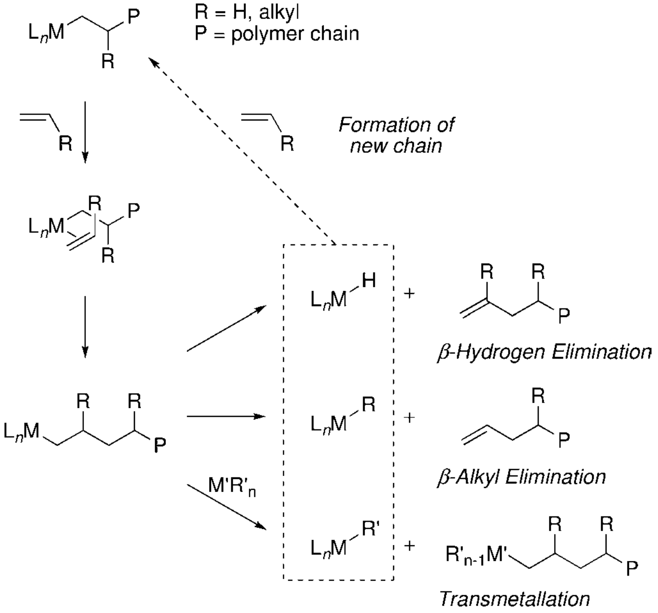


Scheme 4.1 Mechanisms of propagation and chain transfer in transition metal-catalyzed olefin polymerization.

with negligible rates of termination, which allow the truly living polymerization of alkenes such that block copolymer synthesis via sequential monomer addition methods are now possible.

This review is a comprehensive account of living alkene polymerization systems with special attention paid to systems developed in the past couple of years focusing on the polymer types and architectures as in our previous review [3]. This review will primarily focus on living polymerization of terminal alkenes with some coverage of nonconjugated dienes and cyclic olefins. The homopolymerization of the aforementioned alkenes will be initially discussed with an order of early metal- to late metal-catalyzed polymerizations followed by a section discussing new polymer architectures with special emphasis placed to block copolymers. The transition metal-catalyzed polymerization of internal or heavily substituted alkenes is currently limited and will not be covered. Note that in this review, we refer to living species for alkene polymerization as catalysts, not initiators, to emphasize the fundamental catalytic event of monomer enchainment, not polymer chain formation. There are seven generally accepted criteria for a living polymerization: (i) polymerization proceeds to complete monomer conversion, and chain growth continues upon further monomer addition; (ii) number average molecular weight (M_n) of the polymer increases linearly as a function of conversion; (iii) the number of active centers remains constant for the duration of the polymerization; (iv) molecular weight can be precisely controlled through stoichiometry; (v) polymers display narrow molecular weight distributions, described quantitatively by the ratio of the weight average molecular weight to the number average molecular weight ($M_w/M_n \sim 1$); (vi) block copolymers can be prepared by sequential monomer addition; and (vii) end-functionalized polymers can be synthesized [16]. Few polymerization systems, whether ionic, radical, or metal-mediated, which are claimed to proceed by a living mechanism have been shown to meet all of these criteria. This review will therefore include all systems that claim living alkene polymerization, provided that a number of the key criteria have been met.

4.2
Living α-Olefin Polymerization

1-Hexene is the most commonly employed monomer for detailed studies of living olefin polymerization due to the fact that it is an easily handled liquid, and molecular weight determination of its polymers is easily accomplished at or slightly above room temperature employing low-boiling gel permeation chromatography (GPC) eluents (Figure 4.1). However, due to their poor

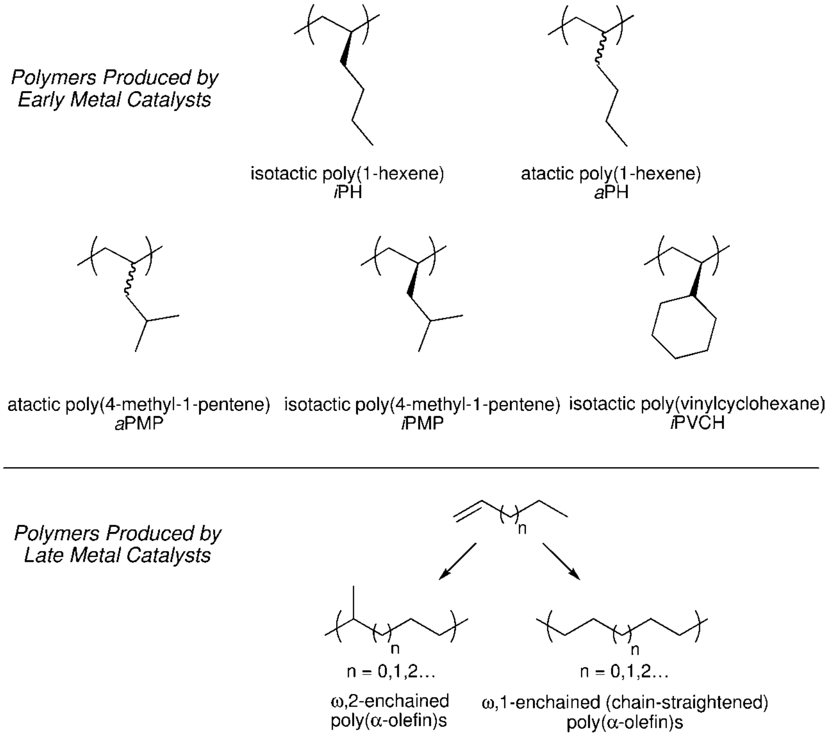


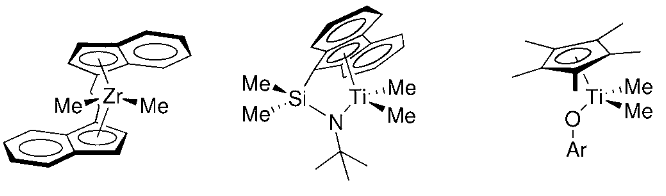
Figure 4.1 Homopolymers of higher 1-alkenes.

mechanical properties, poly(1-hexene) (PH) and homopolymers derived from higher α-olefins (with the exception of poly(4-methyl-1-pentene)) are of little commercial significance. One application of amorphous poly(α-olefin)s is as impact-strength modifiers when blended with polypropylenes (PPs) [6].

4.2.1
Metallocene-Based Catalysts

Since the discovery of their catalytic activity, group 4 metallocene complexes have found extensive use as olefin polymerization catalysts [1]. Because of their high propensity toward termination via chain transfer (e.g., β-H elimination/transfer, transfer to alkylaluminum species), there have been few examples of living olefin polymerization using metallocene-based catalysts. However, several groups have shown that by employing well-defined boron-based activators [17] at low reaction temperatures, these termination pathways can be suppressed. For example, Fukui reported the living polymerization of 1-hexene with a *rac*-(Et)Ind$_2$ZrMe$_2$ (**1**, Figure 4.2) activated with B(C$_6$F$_5$)$_3$ at −78 °C in which Al(*n*Oct)$_3$ was used as a scavenging agent to furnish isotactic poly(1-hexene)s with narrow molecular weight distributions ($M_w/M_n = 1.22–1.29$) [18]. While the molecular weights were relatively low ($M_n \leq 5400\ \text{g mol}^{-1}$), M_n was shown to increase linearly with reaction time. Titanium complexes, bearing a linked monocyclopentadienyl-amido ligand, such as **2** (Figure 4.2), have also been shown to polymerize 1-hexene in a living fashion when activated with B(C$_6$F$_5$)$_3$ in the presence of Al(*n*Oct)$_3$ at −50 °C [19]. The PH formed was syndio enriched ([*rr*] = 0.49) with M_n up to 26 000 g mol^{-1} and $M_w/M_n = 1.07–1.12$. A linear relationship between M_n and polymer yield was also demonstrated. In a subsequent report, **2**/(B(C$_6$F$_5$)$_3$/Al(*n*Oct)$_3$ was also shown to polymerize 1-octene and 1-butene in a living fashion [20].

Nomura and Fudo demonstrated that an unbridged half-metallocene complex bearing a phenoxide donor (**3**, Figure 4.2) was capable of polymerizing 1-hexene in a living fashion [21]. When activated with [Ph$_3$C][B(C$_6$F$_5$)$_4$] in the presence of Al(*i*Bu)$_3$ at −30 °C, **3** furnished PHs with narrow



1 **2** **3** Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

Figure 4.2 Metallocene and monocyclopentadienyl catalyst precursors for living 1-hexene polymerization.

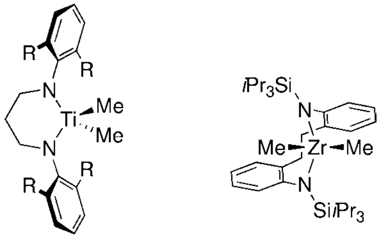
polydispersities ($M_w/M_n = 1.27–1.64$) and high molecular weight (M_n up to 1 865 000 g mol^{-1}). The M_n was shown to increase linearly with turnover number (TON).

4.2.2
Catalysts Bearing Diamido Ligands

While group 4 metallocene-based olefin polymerization catalysts have dominated the field of homogenous olefin polymerization catalysis since the late 1950s [1], the development of complexes bearing non-Cp ligands as potential olefin polymerization catalysts has become a rapidly expanding area over the last 15 years [22, 23]. McConville and Scollard reported that titanium complexes bearing diamide ligands, compounds **4a** and **b** (Figure 4.3), polymerized 1-hexene, 1-octene, and 1-decene to high molecular weight ($M_n = 121\,500–164\,200$ g mol^{-1}) and narrow polydispersity index (PDI) ($M_w/M_n = 1.07$) upon activation with $B(C_6F_3)_3$ at room temperature [24]. Polymerization of 1-hexene by **4b**/$B(C_6F_5)_3$ exhibited a linear increase of M_n with time. Kim and coworkers later reported the living polymerization of 1-hexene catalyzed by a structurally similar zirconium diamide with an ethylene bridging unit [25]. When activated with $B(C_6F_5)_3$ at −10 °C, **5** (Figure 4.3) furnished PHs with $M_n = {\sim}30\,000–175\,000$ g mol^{-1} and $M_w/M_n = 1.18–1.27$. It was also shown that the M_n increased linearly with increasing monomer loading.

4.2.3
Catalysts Bearing Diamido Ligands with Neutral Donors

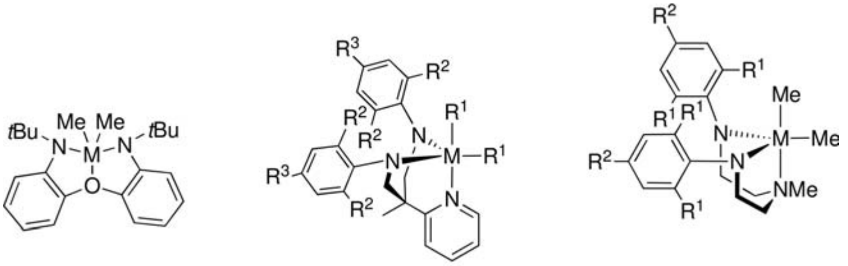
Schrock and coworkers reported on the olefin polymerization behavior of tridentate diamido group IV complexes bearing a central oxygen donor that was postulated to enhance stability of the corresponding cationic alkyl active species [26, 27]. Upon activation with $[PhNMe_2H][B(C_6F_5)_4]$ at 0 °C, the zirconium complex **6a** (Figure 4.4), furnished atactic poly(1-hexene)



4a R = iPr
4b R = Me

5

Figure 4.3 Diamido-ligated catalyst precursors for living alkene polymerization.



6a M = Zr
6b M = Ti
6c M = Hf

	M	R^1	R^2	R^3
7a	Zr	Me	Me	Me
7b	Zr	*i*Bu	Me	Me
8	Hf	*i*Bu	Me	Me
9	Hf	*i*Bu	Cl	H

	M	R^1	R^2
10a	Zr	Me	Me
10b	Zr	Cl	H
10c	Hf	Cl	H

Figure 4.4 Amido–donor–amido ligated catalyst precursors for living olefin polymerization.

(*a*PH) with $M_n = {\sim}4000–40\,000\ \text{g mol}^{-1}$ and $M_w/M_n = 1.02–1.14$. A linear increase in M_n with increasing monomer conversion was exhibited. Upon activation with $[PhNMe_2H][B(C_6F_5)_4]$, the titanium congener (**6b**) decomposed to unidentifiable species which were not active for 1-hexene polymerization. The analogous hafnium complex (**6c**) furnished PH with broadened molecular weight distribution ($M_w/M_n = 1.19–1.53$) and anomalous M_n values when activated with $[PhNMe_2H][B(C_6F_5)_4]$.

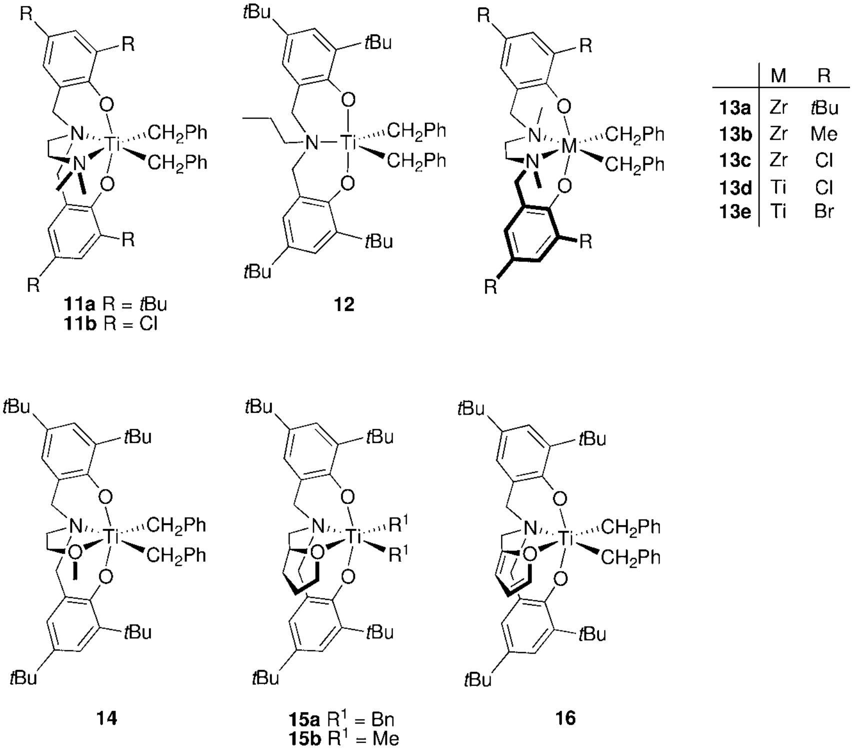
A second class of catalysts developed by Schrock and coworkers bearing diamidopyridine ligands were shown to be effective living olefin polymerization catalysts [28]. The diamidopyridine zirconium complexes **7a** and **b** (Figure 4.4) when activated with $[Ph_3C][B(C_6F_5)_4]$ produce PHs with narrow polydispersities ($M_w/M_n < 1.08$). The identity of the alkyl group bound to zirconium was shown to greatly affect the polymerization behavior. Upon activation, **7a** reacts with 1-hexene to a significant extent by 2,1-insertion into the initial Zr–Me bond to give a 3-heptyl complex that undergoes β-H elimination to yield 2-heptenes; only a fraction that undergoes 1,2-insertion gives a stable propagating species. No 2,1-insertion into the Zr–*i*Bu bond is observed upon activation of **7b**, which gives rise to a relatively well-behaved polymerization system in which M_n values are three times higher than those expected on the basis of the assumption of one polymer chain per metal center (M_n^{theo}). The diisobutyl hafnium analog (**8**) was also shown to polymerize 1-hexene in a living fashion at 0 °C upon activation with $[Ph_3C][B(C_6F_5)_4]$ to furnish PHs with $M_w/M_n = 1.02–1.05$ and $M_n = 10\,000–50\,000\ \text{g mol}^{-1}$ that matches M_n^{theo} [29, 30]. The apparent difference in polymerization behavior is attributed to greater stability toward β-H elimination in this system. Upon replacing the mesityl groups with 2,6-$C_6H_3Cl_2$ within the ligand framework of **8**, Schrock and coworkers found that the living character of 1-hexene polymerization catalyzed by **9**/$[Ph_3C][B(C_6F_3)_4]$ was slightly diminished with evidence of β-H elimination [31]. Despite the fact that β-H elimination was observed, the resultant polymers still displayed narrow polydispersities ($M_w/M_n = 1.01-1.05$) and the M_n values were about 90% of those expected.

A third class of compounds for olefin polymerization introduced by Schrock and coworkers was the diamidoamine complexes of zirconium and hafnium [32–34]. When activated with $[Ph_3C][B(C_6F_5)_4]$, **10a** ($R^1 = R^2 =$ Me, Figure 4.4) was shown to be active for 1-hexene polymerization, furnishing PHs that possessed $M_w/M_n = 1.1-2.1$ and $M_n = 19\,200-45\,000$ g mol^{-1} that deviated from the expected values [32]. Subsequent studies showed that **10a** undergoes deactivation via an intramolecular C–H activation of the *ortho*-Me on the mesityl group upon methide abstraction. Replacing the *ortho*-Me with *ortho*-Cl (**10b**) and subsequent activation with $[PhNMe_2H][B(C_6F_5)_4]$ at 0 °C gives rise to a catalyst that is living for 1-hexene polymerization [33]. The resultant polymer exhibited narrow polydispersity ($M_w/M_n = 1.01-1.04$) and M_n values that were in good agreement with M_n^{theo}. When activated with $[Ph_3C][B(C_6F_5)_4]$ or $B(C_6F_5)_3$, the hafnium analog of **10b** (**10c**) exhibited significant termination via β-H elimination [34].

4.2.4
Amine-Phenolate and Amine-Diol Titanium and Zirconium Catalysts

In 2000, Kol and coworkers reported on the synthesis and olefin polymerization behavior of a titanium complex bearing an amine bis(phenolate) ligand into which was incorporated an additional amino side-arm donor (**11a**, Figure 4.5) [35]. When activated with $B(C_6F_5)_3$ at room temperature, **11a** furnished *a*PHs with narrow molecular distributions ($M_w/M_n = 1.09-1.18$) and the M_n was shown to increase linearly with time. When the amino side-arm donor was omitted (**12**), only low molecular weight PH ($M_n = \sim 2000$ g mol^{-1}) with $M_w/M_n = 1.92-2.43$ was obtained. Replacing the bulky *t*Bu groups with sterically less demanding chlorides (**11b**) allowed the living polymerization of 4-methyl-1-pentene to furnish atactic poly(4-methyl-1-pentene) [36].

In 2000, Kol and coworkers reported on the synthesis and polymerization behavior of the C_2-symmetric, ethylene-bridged zirconium analog of **11a** (**13a**, Figure 4.5) [37]. When activated with $B(C_6F_5)_3$ at room temperature, **13a** furnished highly isotactic poly(1-hexene) and poly(1-octene) (PO). The PHs exhibited narrow polydispersities ($M_w/M_n = 1.11-1.15$) with $M_n = \sim 4000-12\,000$ g mol^{-1}; M_n was shown to increase linearly with monomer consumption. Reducing the substituent size on the phenoxide moiety (**13b**) furnished *a*PH with a broadened molecular weight distribution ($M_w/M_n = 1.57$). In a subsequent report it was shown that replacing the *ortho*- and *para-tert*-butyl substituents of **13a** with chlorides (**13c**) resulted in greatly diminished living behavior [38]. Importantly, the titanium congener (**13d**) and the analogous 2,4-dibromophenol-bearing complex (**13e**) polymerized



11a R = *t*Bu
11b R = Cl

12

	M	R
13a	Zr	*t*Bu
13b	Zr	Me
13c	Zr	Cl
13d	Ti	Cl
13e	Ti	Br

14

15a R^1 = Bn
15b R^1 = Me

16

Figure 4.5 [ONNO], [ONO], and [ONOO] complexes of titanium and zirconium.

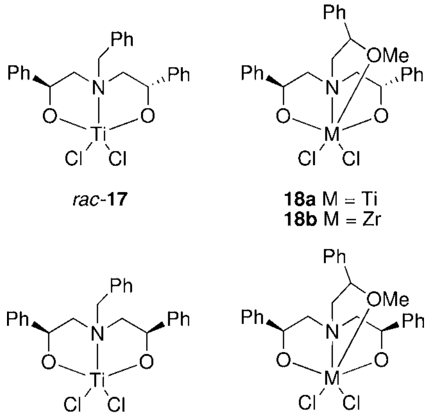
1-hexene in a living manner for a period of 40–75 min when activated with $B(C_6F_5)_3$. The PHs exhibited extremely high molecular weights (M_n up to 1 750 000 g mol^{-1}, $M_w/M_n \leq 1.2$) and moderate degrees of isotacticity (**13d**: [*mm*] = 0.60, **13e**: [*mm*] = 0.80).

In 2001, Kol and coworkers introduced a third class of novel olefin polymerization catalysts featuring [ONOO] group 4 metal complexes bearing a methoxy side-arm donor [39]. Upon activation with $B(C_6F_5)_3$ at room temperature, **14** (Figure 4.5) furnished PHs with narrow polydispersities ($M_w/M_n = 1.07$–1.12) and high molecular weights (M_n up to 445 000 g mol^{-1}). A linear increase in M_n with increasing reaction time was observed for up to 31 h. The living character of the polymerization was maintained upon heating to 65 °C for 1 h as evidenced by the narrow polydispersity of the resultant polymer ($M_w/M_n = 1.30$). Introduction of the 2,4-dimethyl or 2,4-dichloro phenoxide moiety led to a loss of living character [40]. The zirconium and hafnium analogs of **14** also deviated from living behavior ($M_w/M_n = 1.4$–3.0) [41].

The effect of the neutral oxygen donor's identity on the polymerization behavior of the [ONOO] titanium complexes has also been investigated.

Replacing the methoxy donor of **14** with a tetrahydrofuran (THF) moiety (**15a**, Figure 4.5) gave similar results; however, replacing the benzyl ligands with methyl ligands (**15b**) resulted in a dramatic increase in the duration of the living period for up to six days at room temperature upon activation with $B(C_6F_5)_3$. The resultant *a*PH had M_n up to 816 000 g mol^{-1} and $M_w/M_n = 1.04–1.12$ [42]. Introduction of a furan donor (**16**, Figure 4.5) into the ligand framework led to a 10-fold increase in polymerization activity relative to **15a**/$B(C_6F_5)_3$ furnishing PHs of high molecular weight (M_n up to 500 000 g mol^{-1}, $M_w/M_n \leq 1.37$) [43]. The increase in activity of **16**/$B(C_6F_5)_3$ resulted in diminished living character of the 1-hexene polymerization, exhibiting a linear increase in M_n over the course of only 2 h.

The importance of neutral donors in the ligand framework of living olefin polymerization catalysts was also demonstrated recently by Sundararajan *et al.* [44, 45]. In 2002, the authors reported titanium dichloride complexes of tridentate aminodiol ligands (*rac*- and *meso*-**17**, Figure 4.6) treated with methylaluminoxane (MAO) furnished PHs possessing relatively narrow polydispersities ($M_w/M_n = 1.07–2.9$) with a range of tacticities depending on the symmetry of the catalyst precursor [44]. Incorporation of a pendent methoxy donor into the aminodiol ligand framework gave rise to catalysts that were capable of living 1-hexene polymerization [45]. When activated with MAO at temperatures between −10 and 30 °C, both **18a** and **18c** furnished PHs with low polydispersities ($M_w/M_n = 1.06–1.11$) and M_n = 73 000–424 000 g mol^{-1}. The highest degree of isotacticity ([*mmmm*] = 0.85) was obtained for polymer produced by **18a** at −10 °C. At −10 °C a linear dependence of M_n on reaction time was observed. The zirconium congeners of **18a** and **c** (**18b** and **d**, Figure 4.6) have been prepared by Sudhakar and upon activation with MAO gave similar results for 1-hexene polymerization



rac-**17**

18a M = Ti
18b M = Zr

meso-**17**

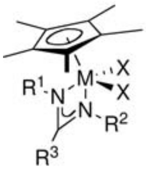
18c M = Ti
18d M = Zr

Figure 4.6 Titanium and zirconium complexes bearing aminodiol ligands.

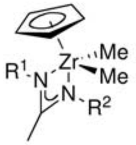
[46]. A linear relationship between M_n and reaction time was observed at 28 °C.

4.2.5
Monocyclopentadienylzirconium Amidinate Catalysts

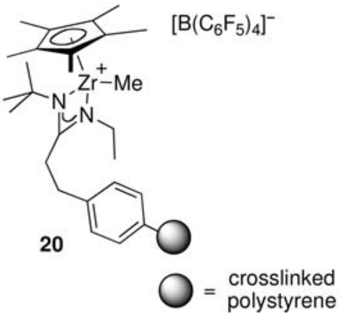
In 2000, Sita and Jayaratne reported monocyclopentadienyl acetamidinate zirconium dimethyl compounds that exhibited living polymerization behavior at temperatures between −10 and 0 °C [47]. Upon activation with $[PhNMe_2H][B(C_6F_5)_4]$ at 0 °C, **19a** (Figure 4.7) formed *a*PH with a narrow polydispersity ($M_w/M_n = 1.10$) and a lack of olefinic resonances in the ^{13}C and ^1H NMR spectra. The C_1-symmetric complex, **19b**, when activated in an identical manner at −10 °C, furnished highly isotactic poly(1-hexene) ([*mmmm*] > 0.95) with a narrow molecular weight distribution ($M_w/M_n = 1.03–1.13$). The molecular weight was shown to increase linearly with conversion. This was the first report of a Ziegler–Natta polymerization catalyst that was both living and highly isospecific for α-olefin polymerization. Covalently attaching **19b** to a cross-linked polystyrene (PS) support was also shown to furnish a living and isoselective 1-hexene polymerization catalyst (**20**, Figure 4.7) [48]. The hafnium congener of **19b** (**21a**, Figure 4.7) and its diisobutyl analog (**21b**) were also shown to be living and isospecific 1-hexene polymerization catalysts albeit with a rate about 60 times slower than **19b** [49].



	M	X	R¹	R²	R³
19a	Zr	Me	Cy	Cy	Me
19b	Zr	Me	*t*Bu	Et	Me
19c	Zr	Me	*t*Bu	Cy	Me
21a	Hf	Me	*t*Bu	Et	Me
21b	Hf	*i*Bu	*t*Bu	Et	Me
23a	Zr	Me	*t*Bu	Et	Ph
23b	Zr	Me	*t*Bu	Et	H
23c	Zr	Me	*t*Bu	Et	*t*Bu



22a $R^1 = R^2 = Cy$
22b $R^1 = R^2 = iPr$
22c $R^1 = tBu$, $R^2 = Cy$



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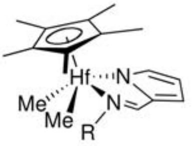


24a $R = 4\text{-}MeOC_6H_4$
24b $R = 4\text{-}MeC_6F_4$
24c $R = Cy$

Figure 4.7 Cp–amidinate and Cp*–iminopyrrolyl complexes.

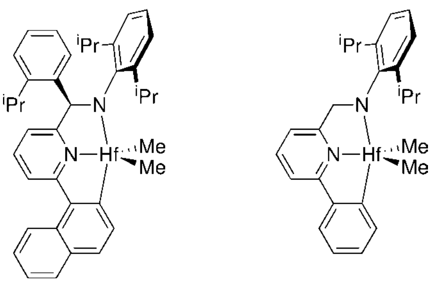
By replacing the Cp* moiety with the less sterically demanding Cp ligand, Sita and coworkers were able to greatly increase the 1-hexene polymerization activity for this class of catalysts [50]. When activated with $[PhNMe_2H][B(C_6F_5)_4]$ at −10 °C, compounds **22a–c** (Figure 4.7) furnished *a*PHs with narrow molecular weight distributions ($M_w/M_n = 1.03–1.10$); however, a decrease in enantiofacial selectivity was also observed. The more open environment of the active site did impart the ability to polymerize the more challenging vinylcyclohexane (VCH). Upon activation with $[PhNMe_2H][B(C_6F_5)_4]$ at −10 °C, **22a** and **b** furnished highly isotactic poly(VCH)s ([*mmmm*] = 0.95) with narrow polydispersities ($M_w/M_n = 1.04–1.10$). The authors postulate that the high degree of isoselectivity displayed is likely the result of chain-end control.

The effect of further structural elaboration of the amidinate ligand framework on polymerization behavior was reported in 2004 [51]. Specifically, altering the identity of the distal R^3 substituent (Figure 4.7) led to dramatic effects on both the living character and stereospecificity of 1-hexene polymerization. Polymerization of 1-hexene by **23a** or **b** (R^3 = Ph or H)/$[PhNMe_2H][B(C_6F_5)_4]$ at −10 °C furnished polymer with a significantly lower degree of isotacticity than the PH produced by **19b**/$[PhNMe_2H][B(C_6F_5)_4]$, and in the case of **23b**, the polymerization is no longer living. Furthermore, **23c** (R^3 = *t*Bu)/$[PhNMe_2H][B(C_6F_5)_4]$ was found to be completely inactive for polymerization. The loss in stereocontrol of **23a** was attributed to a "buttressing effect" by which the *t*Bu and Et groups were "pushed" forward toward the active site leading to a lack of steric discrimination at the metal center for olefin coordination. The decrease in stereoselectivity of **23b** was attributed to a low barrier to metal-centered epimerization relative to **19b.**

Mashima and coworkers recently reported on the synthesis and 1-hexene polymerization behavior of Cp* hafnium dimethyl complexes bearing an iminopyrrolyl ligand [52]. When activated with $[Ph_3C][B(C_6F_5)_4]$ at 0 °C or below, compounds **24a–c** (Figure 4.7) polymerized 1-hexene to furnish polymers with narrow molecular weight distributions ($M_w/M_n = 1.07–1.12$) and $M_n = 9000–36\,100$ g mol^{-1}. The PHs were all significantly iso-enriched with the highest level of isotacticity ([*mmmm*] = 0.90), being obtained from **24b** at −20 °C. The polymerization of 1-hexene with **24a** exhibited a linear dependence of M_n versus time at −20 and 0 °C.

4.2.6
Pyridylamidohafnium Catalysts

One of the more recent classes of catalysts to emerge are the C_1-symmetric pyridylamidohafnium complexes (**25**, Figure 4.8) developed by Dow and Symyx, which furnish high molecular weight and highly isotactic poly(α-olefin)s at high reaction temperatures upon activation [53–55]. Coates and coworkers have shown that the catalyst derived from a C_s-symmetric



25 **26**

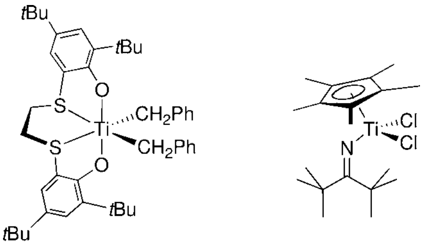
Figure 4.8 Pyridylamidohafnium complexes.

pyridylamidohafnium complex (**26**, Figure 4.8) furnished isotactic poly(1-hexene) in a living fashion when activated with $B(C_6F_5)_3$ [56]. The PHs exhibited narrow polydispersities ($M_w/M_n \leq 1.20$, M_n up to 152 000 g mol^{-1}) and the M_n was shown to increase linearly with monomer conversion. At 50 °C, the PDI of the polymer produced by **26**/$B(C_6F_5)_3$ remains narrow, suggesting that living behavior is maintained at elevated temperatures.

4.2.7
Titanium Catalysts for Styrene Homo- and Copolymerization

As opposed to other homopolymers of higher α-olefins, PS has found extensive use as a commodity material. Recently, Okuda and coworkers have demonstrated for the first time living and isospecific polymerization of styrene with a series of titanium complexes bearing tetradentate [OSSO] bis(phenolate) ligands [57]. When activated with $[PhNMe_2H][B(C_6F_5)_4]$ in the presence of Al(*n*Oct)$_3$ at 25 °C, **27** (Figure 4.9) produced highly isotactic polystyrene (*i*PS) ([*mm*] > 0.95) with narrow molecular weight distributions ($M_w/M_n = 1.08$–1.27) and $M_n = 18\,300$–$106\,100$ g mol^{-1}. The M_n was shown to increase as a linear function of the conversion.

In 2005, Nomura and Zhang reported on the living copolymerization of ethylene and styrene using a cyclopentadienyl(ketimide)titanium(IV) complex (**28**, Figure 4.9) [58]. Upon activation with MAO at 25 °C, **28** furnished



27 **28**

Figure 4.9 Titanium-based precatalysts for styrene homo- and copolymerization.

poly(ethylene-*co*-styrene) with narrow polydispersities ($M_w/M_n = 1.14–1.36$) and $M_n = 53\,000–173\,000\ \text{g mol}^{-1}$. The M_n was shown to increase linearly with time. Interestingly, **28**/MAO exhibited nonliving behavior for styrene and ethylene homopolymerizations.

4.2.8
Tripodal Trisoxazoline Scandium Catalysts

While complexes of group 4 transition metals dominate the field of living olefin polymerization, there are rare examples of group 3 complexes displaying characteristics of living behavior. Recently, Ward *et al.* reported on the synthesis and 1-hexene polymerization behavior of a unique C_3-symmetric scandium complex bearing a tripodal trisoxazoline ligand [59]. When treated with two equivalents of $[Ph_3C][B(C_6F_5)_4]$ at −30 °C in the presence of 1-hexene, **29** (Figure 4.10) produced isotactic poly(1-hexene) ([*mmmm*] = 0.90) with $M_n = 750\,000\ \text{g mol}^{-1}$ and $M_w/M_n = 1.18$. The ^{1}H NMR spectra showed a complete lack of olefinic end groups, further supporting living behavior.

4.2.9
Late Transition Metal Catalysts

In the mid-1990s, Brookhart and coworkers reported the synthesis and olefin polymerization activity of α-diimine complexes of nickel and palladium [60]. These systems were unique among late metal catalysts in their ability to produce high molar mass materials, rather than oligomers, from both ethylene and higher α-olefins. Furthermore, the metal centers were shown to migrate along polymer chains ("chain walking" [61]), allowing access to polyolefins with a wide variety of microstructures simply by varying ligand substitution patterns, temperature, or pressure. Shortly thereafter, conditions were disclosed that allowed the nickel catalysts **30a** and **31** (Figure 4.11) to polymerize 1-hexene and 1-octadecene in a living fashion [62]. Upon activation with MAO or modified methylaluminoxane (MMAO) at −10 °C and low monomer concentrations, **30a** and **31** resulted in living systems furnishing polymers of $M_n = 19\,000–91\,000\ \text{g mol}^{-1}$ and M_w/M_n as low as 1.09. The

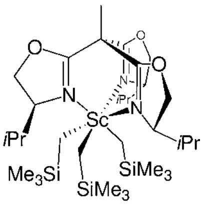


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Figure 4.10 Tripodal trisoxazoline scandium complex for 1-hexene polymerization.

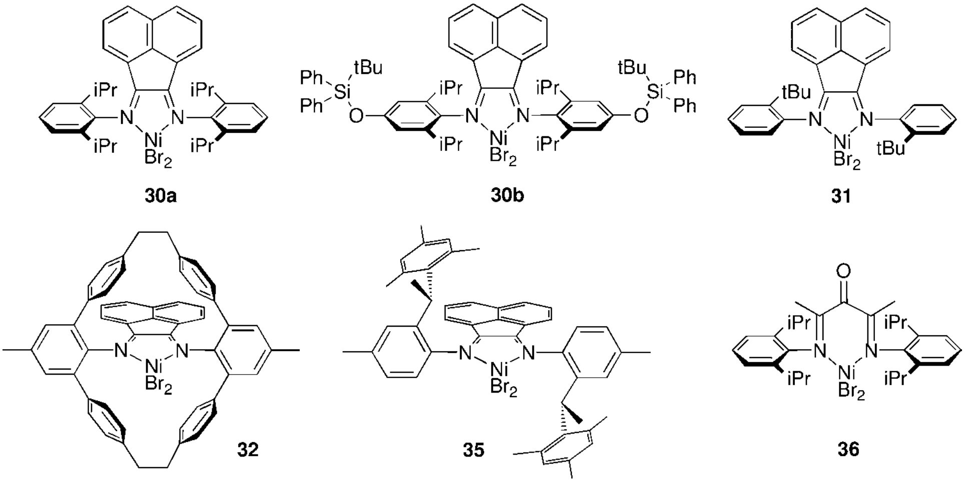
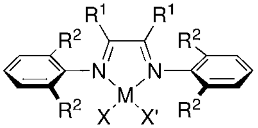


Figure 4.11 Representative nickel diimine complexes for living polymerization of 1-alkenes.

systems exhibited a linear increase in M_n with time. Branching density was less than that calculated for perfect sequential 1,2-insertions as a result of ω,1-enchainment, or "chain straightening" [63]. PH with as few as 118 branches/1000 carbons (vs. 167 expected for perfect 1,2-insertions) and poly(1-octadecene) with as few as 39 branches/1000 carbons (vs. 56 expected) were produced at this temperature. Branching density was controlled by reaction conditions and catalyst structure, with **31** producing more linear polymers than **30a**. In a study of several palladium and nickel complexes, Merna *et al.* [64] reported living-like behavior with **30a**/MAO up to 20 °C. These values are considerably narrower than those reported by Brookhart for similar reactions at 23 °C, although the reason for the improvement is not clear.

Marques *et al.* [65] synthesized a siloxy-substituted analog of **30a** (**30b**, Figure 4.11) and studied its application for the living polymerization of 1-hexene at −11 °C and up to 16 °C. At the higher temperature, the polydispersity increases somewhat ($M_w/M_n = 1.12–1.21$), and the increase in molecular weight is only linear for the first 40 min. In addition, the polymer has a different microstructure, with branching greatly decreased at 16 °C relative to −10 °C (83 vs. 132 branches/1000 carbons, respectively).

Camacho and Guan reported the first living polymerization at elevated temperatures with nickel by using a structural variant of **30a**, utilizing a cyclophane diimine ligand (**32**, Figure 4.11) [66]. When activated with MMAO, **32** furnished PHs with narrow molecular weight distributions ($M_w/M_n = 1.13–1.22$) up to 75 °C and branching densities (52–58 branches/1000 carbons) approximately one-half of those reported for **30a**. The authors attribute the improved behavior to the cyclophane framework which very effectively blocks the axial sites of the nickel center preventing chain transfer.

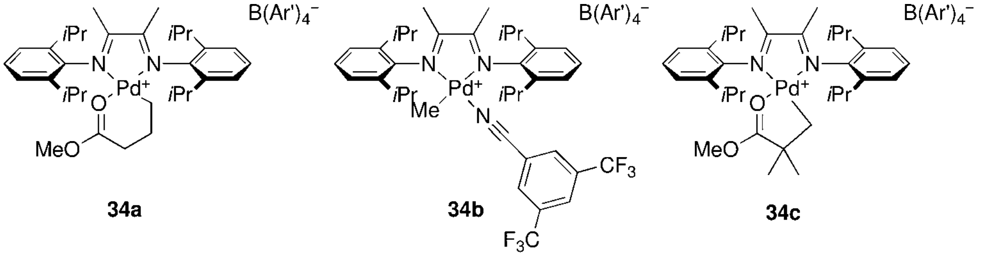


	M	R^1,R^1	R^2	X	X'
33a	Ni	Me,Me	*i*Pr	Br	Br
33b	Ni	Me,Me	Me	Br	Br
33c	Ni	1,8-naphthyl	*i*Pr	Br	Br
33d	Pd	Me,Me	*i*Pr	Cl	Cl
33e	Pd	Me,Me	*i*Pr	Cl	Me

Figure 4.12 Nickel and palladium diimine complexes for 1-hexene polymerization.

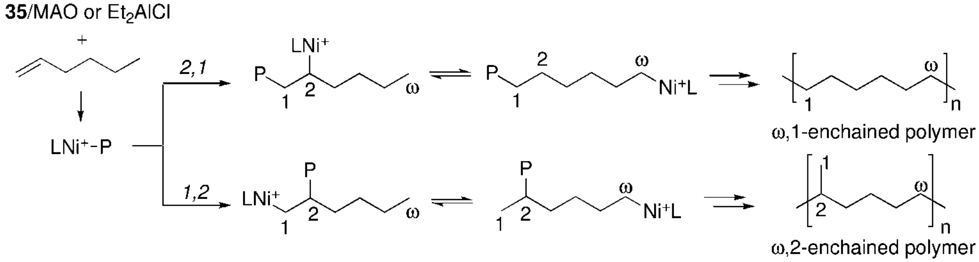
Suzuki *et al.* have explored α-diimine complexes of both nickel and palladium (**33a–e**, Figure 4.12) for the polymerization of 1-hexene at very high pressures (up to 750 MPa) [67]. While nickel catalysts displayed nonliving behavior, the palladium catalysts **33d** and **e** (Figure 4.12) were living for 1-hexene polymerization and polydispersities decreased at higher pressures ($M_w/M_n = 1.27–1.29$ at 0.1 MPa vs. 1.11–1.17 at 500 MPa with **33e**).

Using diimine complexes of palladium, Gottfried and Brookhart have demonstrated conditions that allow for living polymerizations of 1-hexene and 1-octadecene at 0 °C where quenching with Et_3SiH is required to prevent chain coupling [68]. Catalyst **34a** (Figure 4.13) exhibited improved living behavior relative to **34b** for 1-hexene polymerization. This was attributed to the ability of the nitrile donor to compete with 1-hexene for the open coordination site in **34b**. Both **34a** and **b** showed a linear increase in M_n with time over the course of 3 h and furnished PHs with narrow molecular weight distributions ($M_w/M_n = 1.10–1.15$) and branching densities of 75–85 branches/1000 carbons. Catalyst **34b** was likewise applied to the living polymerization of 1-octadecene. Although M_n was observed to increase linearly over the first 3 h at 0 °C, the molecular weight distribution increased as well ($M_w/M_n = 1.34$ after 3 h). This was attributed to precipitation of the polymer at this temperature, which also limits the accessible molecular weights to ~40 000 g mol^{-1}. Sen and coworkers reported on a structurally similar diimine palladium complex to **34a** bearing a five-membered ester chelate arising from 1,2-insertion of methyl methacrylate (MMA) into the cationic palladium precursor (**34c**, Figure 4.13) [69]. Catalyst **34c** displayed "quasiliving" behavior for 1-hexene polymerization, showing an increase in M_n with time over the course of 22 h.



34a **34b** **34c**

Figure 4.13 Palladium α-diimine catalysts for 1-hexene polymerization.



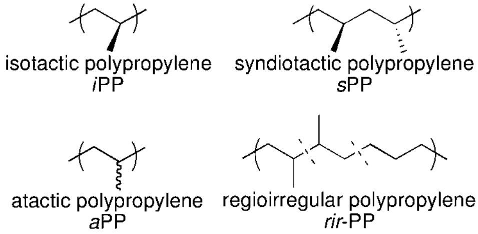
Scheme 4.2 ω,1 vs. ω,2-enchainment of 1-hexene.

Coates and coworkers have demonstrated control over polymer microstructure with the chiral, C_2-symmetric nickel diimine complex **35** (Figure 4.11) for living polymerization of α-olefins [70]. A hallmark of the original nickel diimine catalysts is the ability to undergo successive β-hydride eliminations/reinsertions, commonly referred to as "chain walking" [71]. This may lead to "chain straightening" with α-olefins, generating regioirregular polymers with less branching than expected. Careful tailoring of reaction conditions (low temperatures and high monomer concentration) with catalyst **35** generates high selectivity for ω,2-enchainment, generating predominantly methyl branches at regular intervals between methylene units (illustrated for 1-hexene in Scheme 4.2). The technique is applicable to a range of α-olefins, but selectivity for ω,2-enchainment was shown to decrease with increasing chain length (96 mol% ω,2-enchainment for 1-butene vs. 70% for 1-octene).

Bazan and coworkers recently described the synthesis and olefin polymerization behavior of a nickel α-keto-β-diimine complex [72]. Activation of **36** (Figure 4.11) with MAO in the presence of 1-hexene at 0 °C furnished *a*PH possessing $M_n = 157\,000\ \mathrm{g\ mol^{-1}}$ and $M_w/M_n = 1.2$. Microstructural analysis of the polymer by ^{13}C NMR spectroscopy revealed mainly butyl (81.9%) and methyl (12.0%) branches; signatures arising from 2,1-insertions were not detected.

4.3
Living Propylene Polymerization

While PH is an amorphous material regardless of the level of tacticity, PP can range from amorphous to semicrystalline because of the variability in the level of tacticity. The tacticity of the polymer is intimately related to its bulk properties, with atactic polypropylene (*a*PP; Figure 4.14) being an amorphous material with limited industrial uses (e.g., adhesives, sealants, and caulks) and syndiotactic polypropylene (*s*PP) and isotactic polypropylene (*i*PP) being semicrystalline materials with relatively high T_m values of ~150 and ~165 °C, respectively. The lower crystallinity and the fact that only a very few syndiospecific propylene polymerization catalysts have been discovered



Propylene Microstructure	Precatalysts for Living Polymerization
*i*PP	**13a, 19b, 26, 35, 58a-c, 59a-r, 60a,b, 61a-c, 63a,b, 64a-f**
*s*PP	**2, 37, 38, 42, 43, 45, 47, 49, 50, 51, 52a, 53a-e, 56**
*a*PP	**4a, 39, 40, 41, 44, 52b,c, 54, 55a,b, 58d,e, 62, 80a**
rir-PP	**30a,b, 32, 34b, 35, 64a-f**

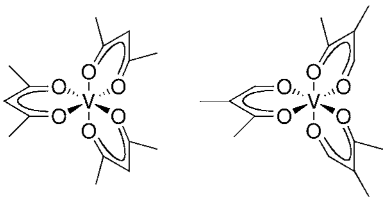
Figure 4.14 Microstructures of propylene homopolymers.

to date have limited the commercial impact of *s*PP. On the other hand, numerous catalysts, both heterogeneous and homogeneous, are capable of isospecific propylene polymerization. When combined with *i*PP's highly desirable mechanical properties (durability, chemical resistance, and stiffness), it is obvious why the vast majority of industrially produced PPs are of the isotactic variety [73].

4.3.1
Vanadium Acetylacetonoate Catalysts

In the 1960s, Natta and coworkers discovered that activation of VCl_4 with Et_2AlCl at −78 °C in the presence of propylene furnished syndio-enriched PP with linear growth of molecular weight over time for a period of 25 h [74]. In a subsequent report, the PPs produced by VCl_4/Et_2AlCl were shown to possess monomodal molecular weight distributions ($M_w/M_n = 1.4–1.9$) [75].

The first example of a truly living alkene polymerization catalyst was reported by Doi in 1979 [76, 77]. Upon activation of $V(acac)_3$ (**37**, Figure 4.15)



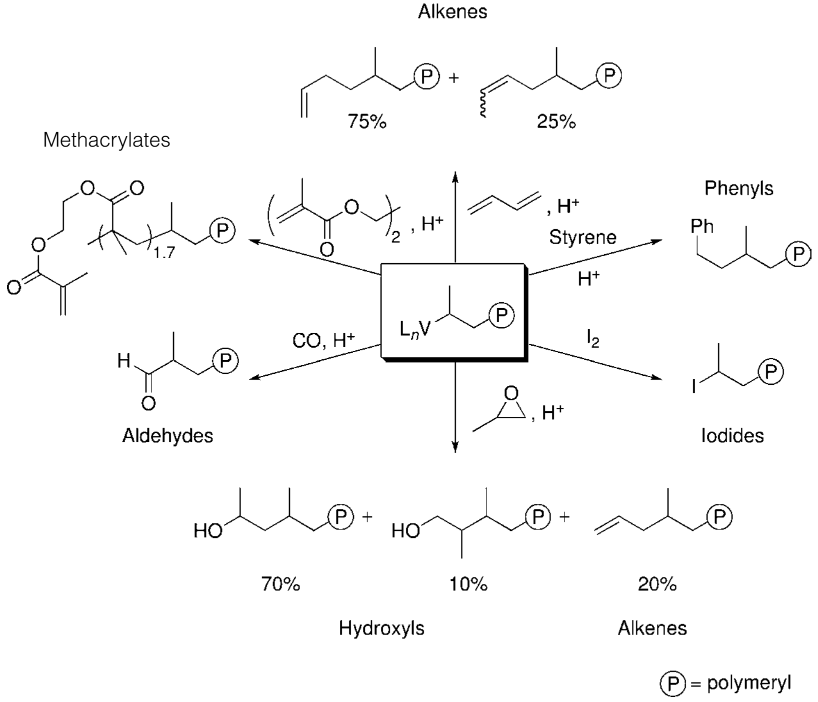
37 **38**

Figure 4.15 Vanadium catalysts for living olefin polymerization.

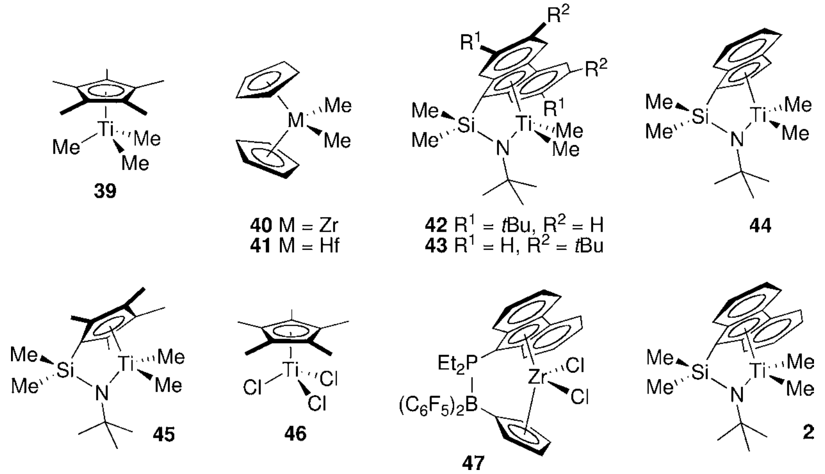
with Et_2AlCl in the presence of propylene at temperatures $\leq -65\,°C$, syndio-enriched PP ($[r] = 0.81$) was furnished exhibiting narrow molecular weight distributions ($M_w/M_n = 1.07{-}1.18$) and M_n as high as 100 000 g mol^{-1}. A linear increase in M_n with time over the course of 15 h was shown. However, only about 4% of vanadium centers were shown to be active, which can be partially alleviated by the addition of anisole leading to a threefold increase in the number of active vanadium centers [78].

By replacing the acetylacetonoate ligands of **37** with 2-methyl-1,3-butanedionato ligands (**38**, Figure 4.15), Doi and coworkers found that nearly all of the vanadium centers were active for polymerization with essentially the same degree of syndiotacticity as that formed by **37**/Et_2AlCl [79]. In addition, the living character of propylene polymerization by **38**/Et_2AlCl was maintained up to $-40\,°C$ (M_w/M_n as low as 1.4) [80, 81]. Copolymerization of propylene and ethylene by **38**/Et_2AlCl was also shown to be living [82].

One of the important applications of living olefin polymerization is in the synthesis of end-functionalized polymers, which is typically achieved by reaction of the living chain end with an electrophile. The vanadium-based living olefin polymerization catalysts discovered by Doi and coworkers proved to be particularly amenable to this application [83–87]. The structures of end-functionalized sPPs prepared in this manner are summarized in Scheme 4.3.



Scheme 4.3 Synthesis of end-functional polypropylenes with a vanadium-based catalyst.



39

40 M = Zr
41 M = Hf

42 R^1 = *t*Bu, R^2 = H
43 R^1 = H, R^2 = *t*Bu

44

45

46

47

2

Figure 4.16 Metallocene catalyst precursors for living propylene polymerization.

4.3.2
Metallocene-Based Catalysts

Bochmann and coworkers reported that **39** (Figure 4.16) activated with $B(C_6F_5)_3$ at −20 °C produces atactic, high molecular weight PP that exhibits elastomeric properties with $M_w = 1\,103\,000$ g mol^{-1} and $M_w/M_n = 1.4$ [88]. From analysis of the GPC trace for this sample, it was estimated that 48% of the polymer was composed of PP with a narrow molecular weight distribution ($M_w/M_n = 1.10$). The polymerization also showed a linear increase in molecular weight with time.

Fukui and coworkers have reported that $[Cp_2ZrMe_2]$ (**40**, Figure 4.16) activated with $B(C_6F_5)_3$ at −78 °C in the presence of $Al(n\text{Oct})_3$ produces PP with $M_w/M_n \leq 1.15$ ($M_n = 9400–27\,300$ g mol^{-1}) [18]. The polymerization shows a linear increase in M_n with time and it was later reported that quenching the polymerization with carbon monoxide (CO) resulted in aldehyde-functionalized polymer chains [89, 90]. The hafnium analog (**41**) was also shown to be living at −50 °C.

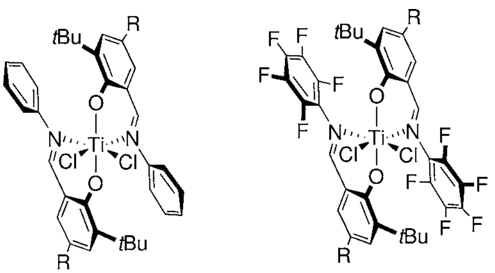
In addition to living 1-hexene polymerization, **2** (Figure 4.2) upon activation with $B(C_6F_5)_3$ in the presence of $Al(n\text{Oct})_3$ can also produce syndio-enriched PP ([*rr*] ∼ 0.49) at −50 °C in living fashion [19]. Subsequent studies showed that when activated with "dried" methylaluminoxane (dMAO) (free of trimethylaluminum), **2** could polymerize propylene at 0 °C producing PP with a higher degree of syndiotacticity ([*rr*] ∼ 0.63) and with a relatively narrow molecular weight distribution ($M_w/M_n = 1.22$, $M_n = 157\,000$ g mol^{-1}) [91]. Shiono and coworkers also demonstrated significant solvent effects on the tacticity of the resulting PP [92]. For example, polymerization of propylene in heptane at 0 °C with **2**/dMAO results in a polymer with higher tacticity than when the reaction is carried out in toluene ([*rr*] = 0.73 vs. 0.60) or chlorobenzene ([*rr*] = 0.42).

Shiono and coworkers examined structural variants of **2** (**42** and **43**, Figure 4.16) by introducing *tert*-butyl substituents into the fluorenyl ligand framework [93]. When activated with dried MMAO (dMMAO) at 0 °C, **42** produced *s*PP ([*rr*] ~ 0.83). While the molecular weight distribution was somewhat broad ($M_w/M_n = 1.68$, $M_n = 202\,000$ g mol^{-1}), a two-stage sequential polymerization of 0.63 g of propylene revealed a nearly doubling of molecular weight than was obtained from a single-stage polymerization. Catalyst **43**/dMMAO furnished a polymer with even higher tacticity ([*rr*] ~ 0.93) and lower molecular weight distribution ($M_w/M_n = 1.45$). Employing an indenyl-based ligand, **44**/dMAO at 0 °C affords iso-enriched PP ([*mm*] = 0.40) with quasiliving behavior [94]. Later, Dare and coworkers reported that a similar complex **45**/MAO furnished PP at 0 °C that was syndio-enriched ([*rr*] = 0.56) and exhibited a somewhat narrow PDI ($M_w/M_n = 1.37$, $M_n = 108\,000$ g mol^{-1}) [95]. Lastly, polymerizations employing catalyst mixtures were reported. Fukui and coworkers showed that iso-enriched PP ([*mm*] = 0.42) could be formed from a mixed catalyst system **40**/$B(C_6F_5)_3$/**46** at −50 °C [96]. The polymerization exhibits a linear increase in M_n with time over 26 h and M_n up to 17 600 g mol^{-1} ($M_w/M_n = 1.29$–1.41).

Starzewski and coworkers have reported a metallocene with the existence of donor and acceptor groups in the sandwich structure (**47**, Figure 4.16) that generates elastomeric PP in a syndioselective fashion ([*rr*] = 0.52) upon activation with MAO at −8 to −6 °C [97]. While the PDIs are somewhat broad ($M_w/M_n = 1.5$–1.6, M_n up to 531 000 g mol^{-1}), the M_n was shown to increase linearly with time over 1 h. The system was also shown to be living for ethylene and propylene copolymerization.

4.3.3
Catalysts Bearing Diamido Ligands

In 2002, Shiono and coworkers reported that upon activation with dMMAO at 0 °C, McConville's dimethyldiamidotitanium complex (**4a**, Figure 4.3) was capable of polymerizing propylene in a living manner [98]. The PPs obtained from **4a**/dMMAO were atactic and displayed narrow molecular weight distributions ($M_w/M_n = \sim 1.16$–1.3). The M_n was shown to increase linearly with polymerization time from 10 to 25 min (M_n up to about 30 000 g mol^{-1}). In subsequent reports, Shiono and coworkers discussed the effects of supported MMAOs on the propylene polymerization behavior of **4a** [99–102]. Three different supports for MMAO were investigated: SiO_2, Al_2O_3, and MgO. Regardless of the support, polymerization of propylene by **4a**/supported MMAO at 0 °C exhibited a linear increase of M_n with time.



48a R = H
48b R = tBu

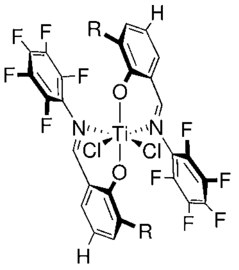
49 R = tBu
50 R = H

Figure 4.17 Early bis(phenoxyimine) titanium complexes.

4.3.4
Bis(phenoxyimine)titanium Catalysts

In 1999, Fujita and coworkers reported on a class of group IV complexes bearing chelating phenoxyimine ligands, including **48a** (Figure 4.17). When activated with MAO, these complexes showed extremely high activity for ethylene polymerization [103–105]. Interested in the development of catalysts that could produce stereoregular polymers, Coates and coworkers used a pooled combinatorial approach to screen Mitsui-type complexes for propylene polymerization behavior and found that **48b**/MAO furnished syndiotactic PP ($[r] = 0.94$) despite the C_2-symmetry of the catalyst precursor, which was the result of a chain-end control mechanism [106]. Later, several studies revealed an unusual 2,1-insertion mechanism [107–109]. In addition, calculations on the system have supported a ligand isomerization event that interconverts the Λ and Δ isomers of the active species between consecutive insertions, causing an alternation between *si* and *re* coordination of propylene which leads to syndiotactic polymer formation [110–112].

It was later found that the incorporation of fluorinated *N*-aryl moieties into the bis(phenoxyimine) ligand framework could provide catalyst precursors for the syndiotactic and living polymerization of propylene. When activated with MAO at 0 °C, **49** (Figure 4.17) produced highly syndiotactic PP ($[rrrr] = 0.96$) which exhibited a peak melting temperature of 148 °C [113]. The polymerization exhibited a linear increase in M_n with PP yield with narrow polydispersities ($M_w/M_n \leq 1.11$) for M_n up to $100\,000\ \text{g mol}^{-1}$. Fujita and coworkers independently reported that **50**/MAO was also living and syndioselective ($[rr] = 87\%$) for propylene polymerization at room temperature, producing polymer with $M_n = 28\,500–108\,000\ \text{g mol}^{-1}$ and $M_w/M_n = 1.07–1.14$ [114]. Employing a supported cocatalyst with **50** has also shown characteristics of living behavior. PP formed using **50**/$MgCl_2$/i-$Bu_nAl(OCH_2CH(Et)(CH_2)_3CH_3)_{3-n}$ had narrow PDIs ($M_w/M_n = 1.09–1.17$, $M_n = 53\,000–132\,000\ \text{g mol}^{-1}$) and the polymerization exhibited a linear increase in M_n with reaction time [115].

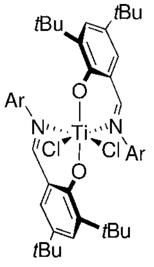


51 R = $SiMe_3$
52a R = $SiEt_3$
52b R = Me
52c R = *i*Pr

Figure 4.18 Bis(phenoxyimine) titanium complexes with various phenoxide substituents.

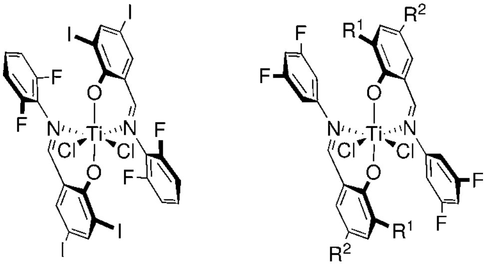
Changing the ortho substituents on the phenolate ring has yielded a number of new complexes. Of note, a complex bearing a *ortho*-phenolate trimethylsilyl group, **51** (Figure 4.18), has been shown to produce *s*PP with very high melting temperatures (T_m up to 156 °C) in a living fashion [116]. Changing the aforementioned ortho position to a larger triethylsilyl group (**52a**) gave similar results as **51** with lower activity [117]. However, employment of a methyl (**52b**) or isopropyl (**52c**) group in the ortho position resulted in a substantial loss of stereocontrol, producing amorphous PP that exhibited fairly narrow polydispersities ($M_w/M_n \sim 1.2$).

Studies on the effect of the fluorination pattern of the *N*-aryl ring have been conducted, and it has been revealed that complexes bearing the 2,4-di-*tert*-butyl phenoxide moiety require at least one *ortho*-fluorine on the *N*-aryl ring to exhibit living propylene polymerization behavior [118, 119]. As the amount of fluorination of the *N*-aryl moiety is decreased from the perfluoro complex **49** (Figure 4.17) to the monofluoro complex **53a** (Figure 4.19), activities and tacticities for propylene polymerization decrease, while the polydispersities remain consistently low ($M_w/M_n \leq 1.11$, M_n up to 28 900 g mol^{-1}) upon MAO activation. Installing a trifluoromethyl group at the para position of the *N*-aryl moiety (**53e**, Figure 4.19) led to an increase in activity of approximately 1.5 times that of **49**/MAO with similar tacticity ([*rrrr*] = 0.91) [120]. Interestingly, complexes related to **53a–c**, where the para substituent of the phenoxide moiety is H, produced amorphous PP upon MAO activation. These samples gave bimodal GPC traces, each composed of a narrow peak ($M_w/M_n \leq 1.10$) and a broad peak ($M_w/M_n = 4.19–14.9$) [121].



53a Ar = 2-FC_6H_4
53b Ar = 2,6-$F_2C_6H_3$
53c Ar = 2,4,6-$F_3C_6H_2$
53d Ar = 2,3,5,6-F_4C_6H
53e Ar = 2,3,5,6-F_4-4-CF_3-C_6

Figure 4.19 Bis(phenoxyimine) titanium complexes with varying *N*-aryl fluorine substitution patterns.



54

55a R^1 = Me, R^2 = Me
55b R^1 = *i*Pr, R^2 = H

Figure 4.20 Bis(phenoxyimine) titanium complexes.

Simultaneous changes to both the phenoxide and *N*-aryl moieties, relative to **49** (Figure 4.17) have also been made. For example, **54** (Figure 4.20) exhibits a 2,6-$F_2C_6H_3$ *N*-aryl moiety and iodine substituents on the phenolate ring. When activated with MAO at 25 °C, **54** was reported to produce amorphous PP which exhibited a narrow molecular weight distribution ($M_w/M_n = 1.17$, $M_n = 200\,000\ \mathrm{g\,mol^{-1}}$) [122, 123]. Complexes **55a** and **b** employ 3,5-difluorophenyl *N*-aryl groups and substituents smaller than *tert*-butyl in the ortho position of the phenoxide moiety. Both **55a** and **b**/MAO were shown to furnish amorphous PP ([*rrrr*] ≤ 0.48) with narrow molecular weight distributions ($M_w/M_n = 1.13$–1.16, M_n up to $240\,000\ \mathrm{g\,mol^{-1}}$) [124]. This finding was surprising in that both complexes lack *ortho*-fluorines on the *N*-aryl moiety.

One final variation to the bis(phenoxyimine) complexes involves the coordination of two different phenoxyimine ligands to one titanium center. Using GPC as a combinatorial screening method, a number of heteroligated phenoxyimine complexes bearing one nonliving (ortho-non-fluorinated ligand) and one living ligand (ortho-fluorinated ligand) were identified that displayed superior activities over their homoligated counterparts [119]. For example, PP produced with **48b**/MAO (Figure 4.17) exhibited a broad PDI ($M_w/M_n = 1.41$) and a turnover frequency (TOF) of 42 $\mathrm{h^{-1}}$ while **49**/MAO exhibited a narrow PDI ($M_w/M_n = 1.06$) and a TOF of 221 $\mathrm{h^{-1}}$. However, the heteroligated catalyst **56**/MAO (Figure 4.21) produced PP with $M_n = 70\,170\ \mathrm{g\,mol^{-1}}$ and

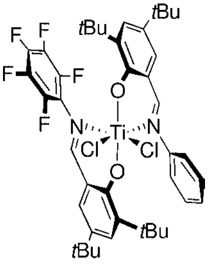


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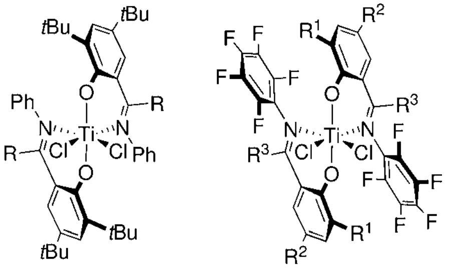
Figure 4.21 Heteroligated bis(phenoxyimine) titanium complex.



57a R = Me
57b R = Et
57c R = Ph

	R^1	R^2	R^3
58a	*i*Pr	*i*Pr	Ph
58b	Et	Me	Ph
58c	Me	Me	Ph
58d	H	Me	Ph
58e	Me	Me	H

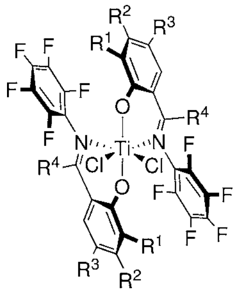
Figure 4.22 Bis(phenoxyketimine) titanium complexes.

$M_w/M_n = 1.16$ and exhibited a TOF of 760 h^{-1}. Syndiotactic polymer ([*rrrr*] = 0.91]) was formed with this heteroligated catalyst.

4.3.5
Bis(phenoxyketimine)titanium Catalysts

While bis(phenoxyimine) titanium complexes furnish *s*PP, it had been proposed that placing a substituent at the imine carbon of the phenoxyimine ligand could prevent the isomerization responsible for the production of *s*PP and lead to the formation of *i*PP [125]. Ketimine complexes **57a–c** (Figure 4.22) were sparingly active for propylene polymerization, despite the ability to polymerize ethylene in a living fashion upon activation [125, 126]. Complexes bearing smaller ortho substituents on the phenolate ring were reasoned to enable higher propylene activities by providing a sterically less-encumbered active site. With this in mind, complexes **58a–d** were synthesized and screened for propylene polymerization [125]. Upon activation with MAO at 0 °C, each complex produced PP with a narrow molecular weight distribution ($M_w/M_n = 1.12$–1.17, $M_n = 2700$–$35\,400$ g mol^{-1}) and **58c**/MAO was shown to exhibit a linear increase in M_n as a function of yield. The tacticities of the resulting polymers differed, with **58c**/MAO furnishing PP with the highest tacticity ([*mmmm*] = 0.53, $T_m = 69.5$ °C). The aldimine analog of **58c** (**58e**), in which $R^3 = H$, furnishes atactic PP with $M_n = 123\,100$ g mol^{-1} and $M_w/M_n = 1.13$.

In a subsequent report, Coates and coworkers systematically varied ortho-, meta-, and para-substituents on the phenoxide moiety in addition to the ketimine substituent in complexes **59a–r** (Figure 4.23) to obtain higher isoselectivity [127]. All the complexes produced PP with a narrow molecular weight distribution ($M_w/M_n = 1.07$–1.33, $M_n = 3000$–$364\,000$ g mol^{-1}) upon



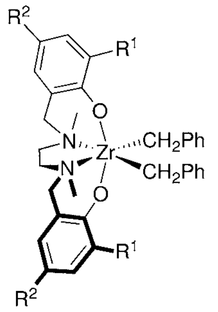
	R^1	R^2	R^3	R^4
59a	Cl	H	Me	Ph
59b	Br	H	Me	Ph
59c	Ph	H	Me	Ph
59d	Bn	H	Me	Ph
59e	$-(CH_2)_4-$		H	Ph
59f	Me	H	Cl	Ph
59g	Me	H	F	Ph
59h	Me	H	OMe	Ph
59i	Me	H	Me	Me
59j	Me	H	Me	*i*Pr
59k	Me	H	Me	Cy
59l	Me	H	Me	Cycloheptyl
59m	Me	H	Me	CF_3
59n	Me	H	Me	2-Naphthyl
59o	Me	H	Me	1-Naphthyl
59p	Me	H	Me	4-Methoxyphenyl
59q	Me	H	Me	Mesityl
59r	Me	H	Me	C_6F_5

Figure 4.23 Bis(phenoxyketimine) titanium complexes with varying phenoxide and ketimine substituents.

activation with MAO except those bearing ancillary methoxy groups in the ligand framework (**59h** and **59p**). The tacticities of the resulting polymers differed, with **59k**/MAO furnishing PP with the highest tacticity ($[mmmm] = 0.73$, $T_m = 116.8\,°C$) in addition to exhibiting a linear increase in M_n as a function of polymer yield.

4.3.6
Amine Bisphenolate Zirconium Catalysts

Busico and coworkers have investigated the propylene polymerization behavior of Kol's octahedral [ONNO] zirconium complexes **13a** and **b** (Figure 4.5) [128]. In contrast to the living 1-hexene polymerization observed for **13a**/$B(C_6F_5)_3$, the PPs produced by **13a** and **13b**/$[PhNMe_2H][B(C_6F_5)_4]/Al(i\text{Bu})_3$ showed evidence of termination via chain transfer to Al and β-H transfer to monomer. However, in a subsequent report, Busico and coworkers reported that through ligand modification, the controlled polymerization of propylene with this class of catalyst could be achieved [129]. Specifically, by installing a bulky 1-adamantyl (**60a**) or cumyl (**60b**) substituent at the ortho position of the phenol moiety (Figure 4.24), PPs with narrow molecular weight distributions were obtained ($M_w/M_n = 1.2–1.6$) under the same activation procedure. For **60a**/$[PhNMe_2H][B(C_6F_5)_4]/Al(i\text{Bu})_3$, a linear increase of M_n with time is



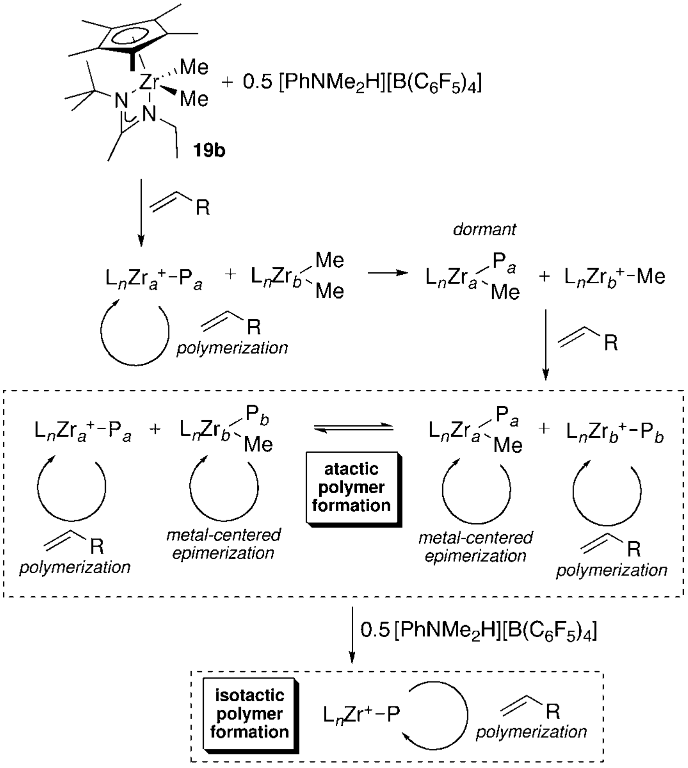
60a R^1 = 1-adamantyl, R^2 = Me
60b R^1 = cumyl, R^2 = Me

Figure 4.24 Zirconium complexes for isospecific propylene polymerization.

observed over the course of 3 h, while after 3 h resonances consistent with terminal vinylidene groups were apparent in the ^{13}C NMR spectrum. Chain transfer to aluminum was suppressed by the addition of 2,6-di-*tert*-butylphenol. The PP formed by **60a**/$[PhNMe_2H][B(C_6F_5)_4]/Al(i\text{Bu})_3$ was moderately isoenriched ([*mmmm*] = 0.985, $T_m = 151\,°C$).

4.3.7
Monocyclopentadienylzirconium Amidinate Catalysts

In addition to living 1-hexene polymerization, Sita and coworkers have shown that **19b** activated with $[PhNMe_2H][B(C_6F_5)_4]$ in a stoichiometric ratio furnished highly isotactic PP ([*mmmm*] = 0.71) in a living fashion ($M_w/M_n \leq 1.20$) [130]. Interestingly, activation with 0.5 equivalents of $[PhNMe_2H][B(C_6F_5)_4]$ resulted in the production of atactic PP, where the M_n was also shown to increase linearly with time ($M_w/M_n \sim 1.05$). A process of degenerative-transfer (DT) polymerization, which proceeds through a rapid and reversible methyl group transfer between the cationic (active) and neutral (dormant) zirconium centers, was considered as the mechanism for this living system (Scheme 4.4) [131]. In addition, the methyl-polymeryl dormant species can undergo epimerization, which is faster than propagation. Thus, through a combination of methyl group transfer and epimerization at dormant sites, each occurring faster than propagation, stereocontrol is greatly diminished leading to an atactic microstructure. However, upon addition of a second 0.5 equivalent of $[PhNMe_2H][B(C_6F_5)_4]$, all Zr species become active for polymerization thereby "turning off" DT and initiating isospecific polymerization, which can advantageously be used for the production of block copolymers (to be discussed in later sections). In a subsequent report, Sita and coworkers synthesized stereogradient PP by initial polymerization under DT polymerization conditions followed by slow introduction of $[PhNMe_2H][B(C_6F_5)_4]$ to 100% activation [132].



Scheme 4.4 Degenerative group transfer polymerization employing **19b**.

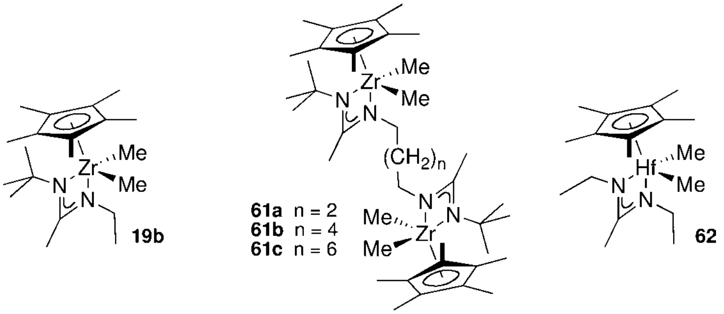


Figure 4.25 Cyclopentadienyl amidinate complexes.

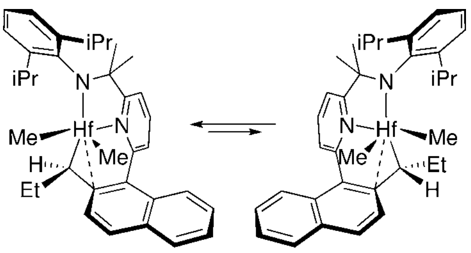
Sita and coworkers later prepared bimetallic analogs of **19b** to investigate further the effects of DT polymerization (**61a–c**, Figure 4.25) [133]. Compounds **61a–c** were all found to be living and isoselective for propylene polymerization upon activation with 2 equivalents of $[PhNMe_2H][B(C_6F_5)_4]$

at −10 °C (M_n up to 50 000 g mol^{-1}, $M_w/M_n = 1.1–1.2$), with the degree of stereoselectivity decreasing as the two metal centers are brought closer together. Activation under substoichiometric conditions led to living DT polymerization. Under these conditions, the frequency of [*mr*] stereoerrors in the PP decrease as the two metal centers are brought closer together resulting from an increased barrier to metal-centered epimerization of the dormant site. A linear increase in M_n with time was observed for **61a** under substoichiometric activation conditions to further illustrate the living behavior.

Sita and coworkers have also recently described a modified amidinate hafnium catalyst (**62**, Figure 4.25) that furnished atactic PP of high molecular weight ($M_n = 137\,000$ g mol^{-1}, $M_w/M_n = 1.12$) upon activation with one equivalent of $[PhNMe_2H][B(C_6F_5)_4]$ at −10 °C [134]. M_n of up to 830 000 g mol^{-1} could be obtained with this system; however, significant broadening of the PDI was observed ($M_w/M_n = 2.43$). Furthermore, this system demonstrated the first example of living coordinative chain-transfer polymerization (CCTP) [135] of propylene with diethyl zinc. It was further used for the living CCTP of ethylene, 1-hexene, 1-octene, and 1,5-hexadiene in addition to living CCTP copolymerization of ethylene with the aforementioned higher α-olefins [136].

4.3.8
Pyridylamidohafnium Catalysts

In addition to living 1-hexene polymerization, Coates and coworkers have shown that the C_s-symmetric pyridylamidohafnium complex (**26**, Figure 4.8) furnished isotactic PP ([*mmmm*] = 0.56) with a narrow molecular weight distribution ($M_n = 68\,600$ g mol^{-1}, $M_w/M_n = 1.05$) upon activation with $B(C_6F_5)_3$ at 20 °C [56]. The mechanism of stereocontrol proceeded by an enantiomorphic site control mechanism, which is quite unusual for a C_s-symmetric catalyst. Detailed mechanistic studies with **25** (Figure 4.8) by Froese *et al.* [54] have shown that the 1,2-insertion of an olefin into the Hf–C_{Aryl} bond generates an sp^3-hybridized carbon donor atom that supports the active metal center; it is likely that the isoselectivity observed with **26**/$B(C_6F_5)_3$ results from a similar activation mechanism. With this in mind, Coates and coworkers prepared a new pyridylamidohafnium complex (*rac*-**63a** and **b**, Figure 4.26) supported by an sp^3-carbon donor that was generated via insertion of a ligand-appended alkene into the neutral pyridylamidohafnium trimethyl precursor generating a mixture of diastereomers (61 : 39 ratio) [137]. Upon activation with $B(C_6F_5)_3$, *rac*-**63a** and **b** furnished isotactic PP ([*mmmm*] = 0.80) with a narrow molecular weight distribution ($M_w/M_n \leq 1.05$, M_n up to 124 400 g mol^{-1}) and TOF of 2800 h^{-1}. The M_n was shown to increase linearly with polymer yield over the course of 45 min.



rac-**63a,b**
61:39 mixture of diastereomers

Figure 4.26 Diastereomeric mixture of pyridylamidohafnium complexes.

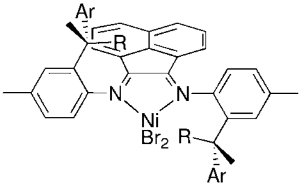
4.3.9
Late Transition Metal Catalysts

α-Diimine complexes of nickel were the first late transition metal catalysts reported for the living polymerization of propylene [60]. Catalyst **30a** (Figure 4.11), upon activation with MMAO at $-10\,^\circ$C, afforded PP with a narrow molecular weight distribution ($M_w/M_n = 1.13$; $M_n = 160\,000$ g mol^{-1}) and M_n was shown to increase linearly with conversion. The material obtained had 159 branches/1000 carbons, far fewer than the theoretical value of 333 for sequential 1,2-insertions, which was attributed to chain straightening. As branching decreased, T_g values decreased as well (as low as $-55\,^\circ$C), illustrating the dramatic effects of enchainment mechanism on physical properties.

Using Pd complexes of related diimine ligands, Gottfried and Brookhart observed a relatively linear increase in M_n with time up to approximately 40 000 g mol^{-1} at 0 °C using **34b** (Figure 4.13) [68]. However, living systems were not obtained when the palladium ester chelate catalyst **34a** was employed because of the slow initiation relative to propagation. Because the weakly bound nitrile group of **34b** is more easily displaced by propylene, this initiation problem could be circumvented. Consistent with previous results, PPs generated by this catalyst are chain straightened, containing approximately 253 branches per 1000 carbons.

Guan and coworkers reported a dramatic demonstration of chain straightening of propylene with the cyclophane Ni complex **32** (Figure 4.11) [66]. When activated with MAO, **32** showed good activity for propylene polymerization at temperatures up to 50 °C, with narrow molecular weight distributions ($M_w/M_n = 1.06$–1.16). In addition, M_n was shown to increase linearly with time at 50 °C. The PPs contain 104–113 branches/1000 carbons, indicative of extensive chain straightening. This implies that the cyclophane ligand geometry favors a 2,1-insertion mechanism.

Coates and coworkers have shown the chiral, C_2-symmetric nickel complex **35** (Figure 4.11) polymerizes propylene in a living fashion at temperatures up to 22 °C in the presence of MAO, with a narrow distribution of molecular weights



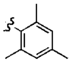
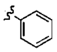
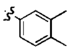
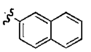
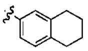
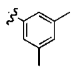
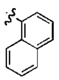
	35	64a	64b	64c	64d	64e	64f
R	H	Me	Me	Me	Me	Me	Me
Ar							

Figure 4.27 Chiral, C_2-symmetric nickel complexes.

($M_w/M_n \leq 1.11$) [138]. Both the regio- and stereocontrol of enchainment are temperature dependent, allowing access to a wide variety of polymer microstructures from a single monomer. At low temperatures (−78 °C), no chain straightening is observed, furnishing highly isotactic PP, but the percentage of 3,1-enchainment increases up to 56.2% at 22 °C producing an amorphous and regioirregular PP. Thus, this catalyst has the unique ability to maintain living behavior at a variety of temperatures, but with variable tacticity and levels of chain straightening. In a subsequent report, Coates and coworkers introduced new chiral, C_2-symmetric nickel diimine complexes featuring cumyl-derived ligands in an attempt to obtain higher regio- and isoselectivity at low reaction temperatures [139]. Each of the complexes (**64a–f**, Figure 4.27) exhibited higher regioselectivity than **35** at −60 °C in the presence of MAO. Nickel complex **64f** furnished isotactic PP at −78 °C with the highest melting temperature ($T_m = 149\,^\circ\text{C}$) of the complexes studied. Furthermore, a linear increase in M_n with polymer yield is observed at 0 °C.

Marques and Gomes achieved living polymerization of propylene with **30b** (Figure 4.11) [65]. At −11 °C, in the presence of MAO, the catalyst produced PP with narrow molecular weight distribution ($M_w/M_n = 1.17–1.19$) and a nearly linear increase in molecular weight over 2 h. Only minimal chain straightening was observed (316 branches/1000 carbons) and the polymer was somewhat syndio enriched ([*rr*] = 0.54).

In addition to living 1-hexene polymerization, Bazan and coworkers reported that **36**/MAO (Figure 4.11) was also living for propylene polymerization [72]. At 0 °C, the catalyst furnished PP of high molecular weight ($M_n = 138\,000\ \text{g mol}^{-1}$) and narrow polydispersity ($M_w/M_n = 1.1$). The polymers exhibited no signatures in their NMR spectra arising from 2,1-insertions.

4.4
Living Polymerization of Ethylene

Considering the simplicity of ethylene, the range of different polymer architectures derived from it is truly intriguing (Figure 4.28). The annual production of polyethylene (PE) worldwide is in excess of 80 billion pounds [140].

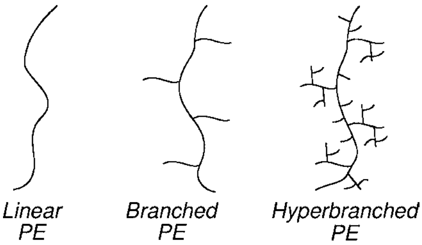


Figure 4.28 Polyethylene (PE) morphologies.

The properties of PEs vary greatly depending on the polymer's microstructure (i.e., branched or linear), from high-density plastics with relatively high melting points (linear PE: $T_m \sim 135\,^\circ C$), to low-density, branched material with T_m as low as 105 °C. The mechanism by which ethylene is polymerized will ultimately determine the microstructure and therefore the properties of the resultant PE. While most early transition metal olefin polymerization catalysts furnish linear PE, late metal catalysts based on nickel or palladium typically give rise to branched structures [71].

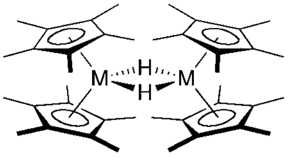
4.4.1
Non-Group 4 Early Metal Polymerization Catalysts

Marks and coworkers showed in 1985 that organolanthanide complexes were promising candidates for living ethylene polymerization [141]. The dimeric bis(Cp*) hydride complexes (**65a–c**, Figure 4.2) furnished high molecular weight PEs ($M_n = 96\,000–648\,000$ g mol^{-1}) and PDIs were for the most part lower than 2.0 (e.g., **65c** exhibited $M_w/M_n = 1.37–1.68$). The living nature of **65a–c** is further supported by observations that catalytic activity is maintained for up to two weeks, M_n increases with time, and the number of polymer chains per metal center is consistently less than 1.

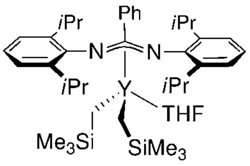
Hessen and coworkers reported on dialkyl(benzamidinate)yttrium complexes which displayed some characteristics of living behavior [142]. When treated with $[PhNMe_2H][B(C_6F_5)_4]$, **66** (Figure 4.29) furnished PE possessing narrow molecular weight distributions ($M_w/M_n = 1.1–1.2$) and high molecular weights ($M_w = 430\,000–1\,269\,000$ g mol^{-1}) with about 1.1 polymer chains per metal center being produced.

Nomura and coworkers reported that arylimido(aryloxo)vanadium dichloride complex **67** (Figure 4.29) activated with Et_2AlCl exhibited characteristics of living ethylene polymerization [143]. The PE furnished had a narrow molecular weight distribution ($M_w/M_n = 1.42$) and high molecular weight ($M_n = 2\,570\,000$ g mol^{-1}) at 0 °C. Additionally, the M_n was shown to increase in a linear fashion with increasing TON.

In 1993, Nakamura and coworkers reported on the synthesis and ethylene polymerization behavior of cyclopentadienyl(η^4-diene)tantalum complexes



65a M = La
65b M = Nd
65c M = Lu



66

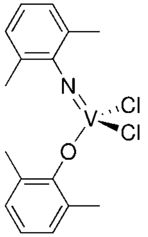


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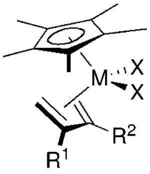
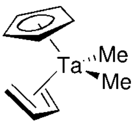
Figure 4.29 Lanthanide, group 3 metal, and vanadium-based catalysts for living ethylene polymerization.



	M	X	R1	R2
68a	Ta	Cl	H	H
68b	Ta	Cl	Me	H
68c	Ta	Cl	Me	Me
69a	Ta	Me	H	H
69b	Ta	Me	Me	Me
69c	Ta	Me	Me	H
71a	Nb	Cl	H	H
71b	Nb	Cl	Me	H
71c	Nb	Cl	Me	Me



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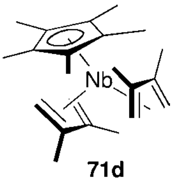
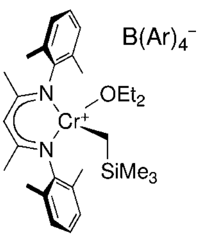


71d

Figure 4.30 Niobium and tantalum complexes for living ethylene polymerization.

[144]. Upon activation with MAO at temperatures of −20 °C or below, compounds **68a**, **69a**, and **70** (Figure 4.30) furnished PEs with narrow molecular weight distributions ($M_w/M_n \leq 1.4$, $M_n = 8600$–$42\,900\ \mathrm{g\ mol^{-1}}$). Additionally, below −20 °C, ethylene polymerization by **69a**/MAO displayed a linear increase of M_n with increasing reaction time. The activity for ethylene polymerization was shown to depend on the substitution pattern of the η^4-diene ligand, with the highest activity being obtained in the case where 2,3-dimethyl-1,3-butadiene is used (**69b**); the lowest when isoprene is employed (**69c**) [145]. The analogous niobium complexes (**71a–d**, Figure 4.30) were also shown to behave as living ethylene polymerization catalysts up to 20 °C when activated with MAO ($M_w/M_n = 1.05$–1.30, $M_n = 5100$–$105\,400\ \mathrm{g\ mol^{-1}}$) [146]. The dependence of activity on the η^4-diene ligand employed mirrored that observed for the analogous tantalum compounds.

Theopold and coworkers investigated chromium complexes bearing 2,4-pentane-*N*,*N*′-bis(aryl)ketiminato ((Ar)$_2$nacnac) ligands for ethylene polymerization [147]. When exposed to ethylene at room temperature, **72** (Figure 4.31) formed linear PE with narrow molecular weight distributions ($M_w/M_n = 1.17$–1.4). The M_n was shown to increase linearly with polymer yield. These results represented the first report of living ethylene polymerization with a chromium-based catalyst.



72

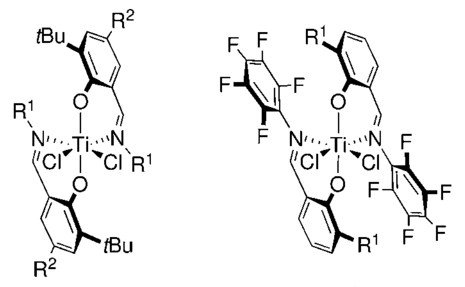
Figure 4.31 β-Diiminate chromium complex for living ethylene polymerization.

4.4.2
Bis(phenoxyimine)titanium Catalysts

Many of the same titanium bis(phenoxyimine) catalysts used for living propylene polymerization have also been reported for the living polymerization of ethylene. In 2001, Fujita and coworkers reported that at 25 °C **50**/MAO (Figure 4.17) furnished linear PE with a high molecular weight and narrow molecular weight distribution ($M_n = 412\,000$ g mol^{-1}, $M_w/M_n = 1.13$) [148]. Furthermore, polymerizations at 25 and 50 °C exhibited a linear increase in M_n with reaction time. Coates and coworkers showed that **49**/MAO could copolymerize ethylene and propylene in a living fashion by cleanly synthesizing a monodisperse PP-*b*-poly(E-*co*-P) sample ($M_w/M_n = 1.12$, $M_n = 145\,100$ g mol^{-1}) [113].

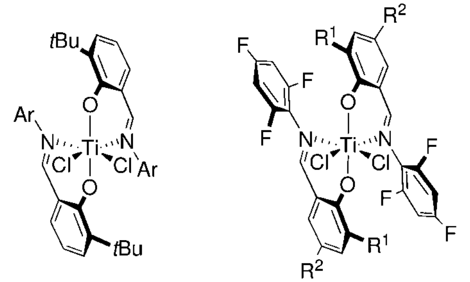
Some of the early titanium bis(phenoxyimine) catalysts have also been used for living ethylene polymerization. In 2003, Coates and coworkers reported that **48b**/MAO polymerized ethylene at 50 °C to produce PE with $M_w/M_n = 1.10$ and $M_n = 44\,500$ g mol^{-1} [126]. In 2004, Ivanchev *et al.* reported a near-linear increase in M_v with time for the polymerization of ethylene with **48a**/MAO at 30 °C [149]. Later, Fujita and coworkers reported on the same system and found that while molecular weight distributions were low at a reaction time of 1 min ($M_w/M_n = 1.12$, $M_n = 52\,000$ g mol^{-1}), the PDI broadened significantly at reaction times of just 5 min ($M_w/M_n = 1.61$, $M_n = 170\,000$ g mol^{-1}) [150]. Other related complexes were synthesized and screened for ethylene polymerization. Complexes **73a** and **b**/MAO (Figure 4.32) showed a near-linear increase in M_v with times up to about 20 min [151].

To investigate the effect of the substituent at the ortho position of the phenoxide moiety, complexes **74a** and **b** and **52b** and **c** (Figures 4.32 and 4.18) were screened for ethylene polymerization [152]. When activated with MAO at 25 °C, each complex produced PE with a narrow molecular weight distribution ($M_w/M_n = 1.05$–1.16, M_n up to 75 000 g mol^{-1}); however, reaction times were kept to 1 min. While all the catalysts were living, activities were about an order of magnitude less than with **50**/MAO. The role of *N*-aryl fluorination on ethylene polymerization behavior has



73a R^1 = Ph, R^2 = Me
73b R^1 = Cy, R^2 = Me

74a R^1 = Cy
74b R^1 = H



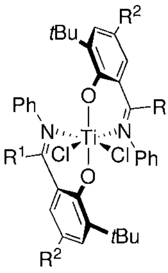
75a Ar = 2-FC_6H_4
75b Ar = 2,6-$F_2C_6H_3$
75c Ar = 2,4,6-$F_3C_6H_2$

76a R^1 = CMe_2Ph, R^2 = Me
76b R^1 = tBu, R^2 = H

Figure 4.32 Bis(phenoxyimine) titanium catalyst precursors for living ethylene polymerization.

also been explored. Each of the catalysts **75a–c**/MAO (Figure 4.32) has been shown to be well behaved for ethylene polymerization at 50 °C, and **75a**/MAO and **75b**/MAO produced polymer with narrow molecular weight distributions at reaction times between 1 and 5 min ($M_w/M_n \sim 1.05$, $M_n = 13\,000–64\,000$ g mol^{-1}) [153,154]. Lastly, Fujita and coworkers reported that $ZnEt_2$ could be used as a chain-transfer agent in the living ethylene polymerization employing **76a**/MAO (Figure 4.32) leading to zinc end-functionalized chains and a titanium species that reinitiates living ethylene polymerization upon the addition of monomer [155]. Despite being living for ethylene polymerization, **76b** was no longer living in the presence of $ZnEt_2$.

Fujita and coworkers later reported that addition of an equimolar amount of functionalized α-olefin, $H_2C{=}CH(CH_2)_n{-}Y$ ($Y = OAlMe_2$, $n = 4$ and $Y = OSiMe_3$, $n = 9$), to **50**/MAO, and the subsequent living ethylene polymerization furnished hydroxyl-terminated PEs upon acidic workup [156]. This strategy was also successful for the production of hydroxyl-terminated syndiotactic PP from **50**/MAO. It was also shown that addition of the aforementioned functionalized α-olefins as a chain-end capping agent furnished telechelic syndiotactic PPs bearing hydroxyl groups at both chain ends upon acidic workup.



	R^1	R^2
57a	Me	tBu
57b	Et	tBu
57c	Ph	tBu
77	Et	H

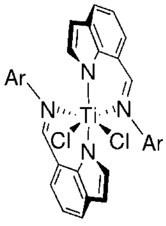
Figure 4.33 Bis(phenoxyketimine) titanium catalyst precursors for living ethylene polymerization.

4.4.3
Bis(phenoxyketimine)titanium Catalysts

Coates and coworkers reported that at 0 and 20 °C **57a–c**/MAO (Figure 4.33) all produced PE that exhibited a narrow molecular weight distribution ($M_w/M_n \leq 1.08$) and had number average molecular weights ($M_n =$ 15 000–47 000 g mol^{-1}) that coincided with M_n^{theo} [126]. A linear increase in M_n with polymer yield for the polymerization catalyzed by **57c**/MAO at 0 °C and for **57b**/MAO at 50 °C was demonstrated. A related complex (**77**, Figure 4.33), when activated with MAO at 50 °C, produced PE with $M_w/M_n = 1.08$ ($M_n = 9000$ g mol^{-1}) [150].

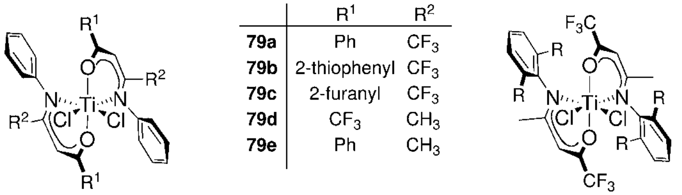
4.4.4
Titanium Indolide–Imine Catalysts

Fujita and coworkers synthesized structurally similar bis(indolide-imine) titanium complexes and evaluated their potential as ethylene polymerization catalysts [157–161]. When activated with MAO at room temperature, compounds **78a–c** (Figure 4.34) furnished PE with narrow molecular weight distributions ($M_w/M_n = 1.11–1.23$) with $M_n = 11\,000$ to $\sim 90\,000$ g mol^{-1}. A linear increase of M_n with increasing polymer yield was observed for **78a–c**/MAO at 25 °C. Exhaustive fluorination of the *N*-aryl moiety (**78d**) results in living behavior only at −10 °C ($M_w/M_n = 1.12–1.15$), while polymerization at 25 °C led to a broadened molecular weight distribution ($M_w/M_n = 1.93$) [158, 159].



78a Ar = Ph
78b Ar = 2,6-F_2-C_6H_3
78c Ar = 2,4,6-F_3-C_6H_2
78d Ar = C_6F_5

Figure 4.34 Bis(indolide-imine) titanium catalysts.



	R^1	R^2
79a	Ph	CF_3
79b	2-thiophenyl	CF_3
79c	2-furanyl	CF_3
79d	CF_3	CH_3
79e	Ph	CH_3

80a R = F
80b R = Me

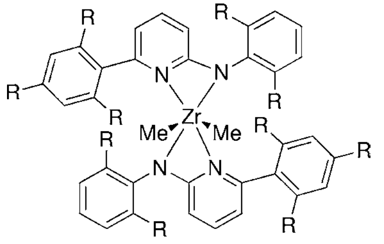
Figure 4.35 Bis(enaminoketonato) titanium complexes for living olefin polymerization.

4.4.5
Bis(enaminoketonato)titanium Catalysts

Li and coworkers reported on the synthesis and ethylene polymerization activity of bis(enaminoketonato)titanium complexes [162]. Upon activation with MMAO at 25 °C, **79a** and **b** (Figure 4.35) furnish linear PEs with narrow molecular weight distributions ($M_w/M_n = 1.25–1.45$) and $M_n = 51\,000–129\,000\ \text{g mol}^{-1}$. A linear increase in M_n with reaction time is observed with **79a**/MMAO at 25 °C. Mecking and coworkers reported that *ortho*-fluorination on the *N*-aryl moiety (**80a**, Figure 4.35) furnished living and thermally robust ethylene polymerization catalysts upon MAO activation [163]. A linear increase in M_n over time was observed at 25, 50, and up to 75 °C. Nonliving behavior observed for **80b**/MAO supports the fact that the living behavior of **80a**/MAO is not steric in nature, illustrating another example in which *ortho*-fluorination appears beneficial for living polymerization.

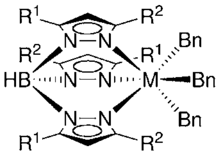
4.4.6
Aminopyridinatozirconium Catalysts

Kempe and coworkers have recently described a zirconium catalyst supported by bis(aminopyridinato) ligands (**81**, Figure 4.36), which was living for ethylene polymerization at elevated temperature [164]. Upon activation with



81 R = *i*Pr

Figure 4.36 Bis(aminopyridinato) zirconium complex for living ethylene polymerization.



	M	R^1	R^2
82	Zr	Me	Me
83	Hf	H	Ms

Figure 4.37 Tris(pyrazolyl) borate complexes.

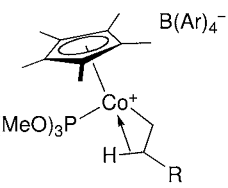
$[R_2NMeH][B(C_6F_5)_4]$ ($R = C_{16}H_{33}–C_{18}H_{37}$) in the presence of tetra-(2-phenyl-1-propyl)aluminoxane at 50 °C, **81** furnished linear PE of high molecular weight ($M_n = 1\,745\,000–2\,301\,000\ \text{g mol}^{-1}$, $M_w/M_n = 1.26–1.30$). No evidence for β-H elimination or chain transfer was evident, and continued chain growth was observed even after polymer precipitation.

4.4.7
Tris(pyrazolyl)borate Catalysts

In 2008, Jordan and coworkers described tris(pyrazolyl)borate complexes (**82** and **83** Figure 4.37) that displayed characteristics of living ethylene polymerization at low temperatures [165, 166]. Upon activation with $[Ph_3C][B(C_6F_5)_4]$ in the presence of 40 equivalents of ethylene at −78 °C, **82** furnished linear PE with $M_n = 2000\ \text{g mol}^{-1}$, which was in good agreement with M_n^{theo}. No olefinic resonances were observed in the NMR spectrum. Additionally, quenching with Br_2 furnished double-end-capped PE, bearing a benzyl group on one chain end and bromine on the other. Similar results were obtained with **83**/$[Ph_3C][B(C_6F_5)_4]$ in the presence of 38 equivalents of ethylene at −78 °C; however, the observed molecular weights ($M_n = 2800–3800\ \text{g mol}^{-1}$) were approximately three times higher than M_n^{theo}. The authors attribute this to incomplete activation. Double-end-capped PEs were also obtained upon quenching with Br_2.

4.4.8
Late Transition Metal Catalysts

In 1991, Brookhart and coworkers identified Cp* cobalt complex **84** (Figure 4.38) as a competent catalyst for polymerization of ethylene in a controlled fashion to obtain low molecular weights ($M_n = 13\,600\ \text{g mol}^{-1}$; $M_w/M_n = 1.17$) [167]. Soon thereafter, aryl or silyl groups were introduced in the catalyst framework that prevent chain migration and allow for the production of a variety of end-functionalized PEs under living conditions [168]. Reaction of **85a–e** with ethylene led to the formation of aryl-substituted PEs with very narrow molecular weight distributions (M_n up to $21\,200\ \text{g mol}^{-1}$;



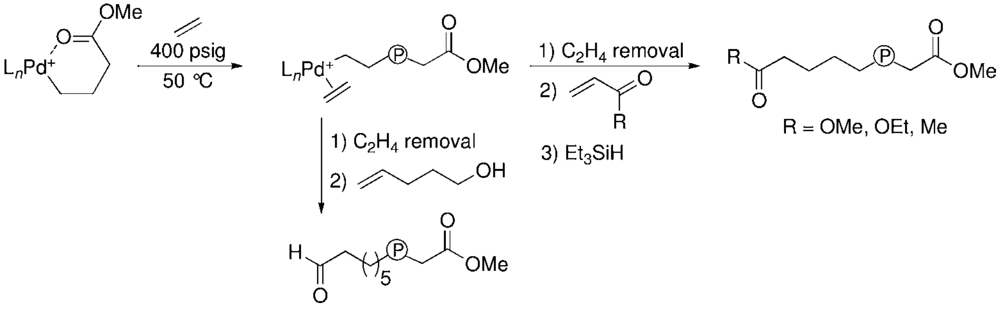
84 R = Me
85a R = C_6H_5
85b R = 4-Cl-C_6H_4
85c R = 4-OAc-C_6H_4
85d R = 4-CF_3-C_6H_4
85e R = C_6F_5
86a R = $(CH_2)_4SiEt_3$
86b R = $(CH_2)_4SiMe_2Cl$

Figure 4.38 Cobalt catalysts for ethylene polymerization.

$M_w/M_n = 1.11–1.16$). Triethylsilane-capped PEs were furnished with catalyst **86a** ($M_n = 16\,100$ g mol^{-1}; $M_w/M_n = 1.15$).

Brookhart and coworkers demonstrated that specific reaction conditions, particularly quenching reactions with Et_3SiH to prevent chain coupling, were crucial for achieving living polymerizations of ethylene with palladium catalysts **34a** and **b** (Figure 4.13) [169]. At 5 °C, highly branched (~100 branches/1000 carbons) amorphous PEs with very narrow molecular weight distributions ($M_w/M_n < 1.1$) were produced, and M_n was shown to increase linearly over at least 6 h. At 27 °C, M_n of 237 000 g mol^{-1} could be obtained in 2 h, but the molecular weight distributions broadened ($M_w/M_n = 1.19$). For **34a**, high pressures of ethylene (400 psig) were required to ensure rapid initiation by displacing the chelated carbonyl group, which is retained in the highly branched PE product. Compound **34b** exhibited similar activity at high pressures, while also yielding polymers with relatively narrow polydispersities ($M_w/M_n = 1.15$ at 5 °C) at 1 atm ethylene. A telechelic polymer could be produced with **34a** by addition of alkyl acrylates before the silane quench [68]. Acrylates undergo one insertion into the growing chain, forming stable chelates, but do not insert further, allowing for clean end functionalization to generate polymers with two distinct ester end groups. Additionally, aldehyde end groups could be generated by quenching with 4-penten-1-ol. The vinyl group inserts, followed by Pd migration down the chain, and finally β-hydride elimination to generate the difunctional polymers as shown in Scheme 4.5.

Modification of the palladium ester chelate (**34a**) by immobilization on a polyhedral oligomeric silsesquioxane (POSS) support (**87**, Figure 4.39) by



Scheme 4.5 Formation of telechelic polyethylene.

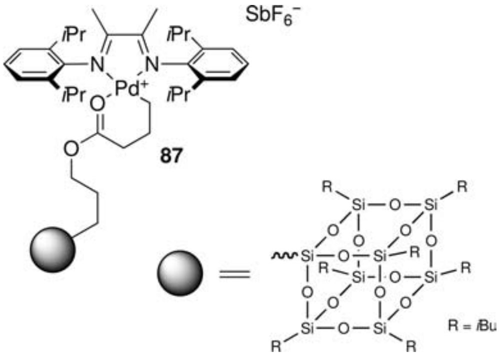
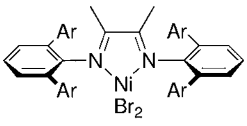


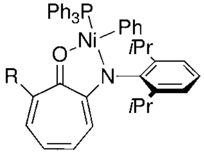
Figure 4.39 Polyhedral oligomeric silsesquioxane supported palladium complex.

Ye and coworkers furnished POSS end-functionalized PEs [170]. The M_n was shown to increase linearly with time. In a subsequent report, the authors immobilized the palladium ester chelate on silica nanoparticles as a versatile surface-initiated living ethylene polymerization technique for grafting from silica nanoparticles [171]. After cleavage of the PE brushes from the silica nanoparticles, the polymers were found to possess narrow PDIs ($M_w/M_n \sim 1.18$).

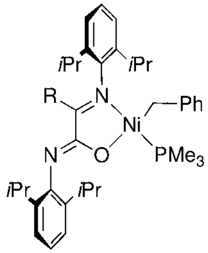
First-generation nickel α-diimine catalysts such as **30a** (Figure 4.11) do not polymerize ethylene in a living fashion because of relatively facile chain transfer. Rieger and coworkers have investigated modifications of this framework to prevent chain transfer by enhancing the steric bulk about the metal center [172]. Indeed, when **88** (Figure 4.40) was activated with MAO at ambient temperature, molecular weight distributions were decreased markedly (M_w/M_n as low as 1.3) for short reaction times, and ultrahigh molecular weight ($>4\,500\,000$ g mol^{-1}) highly linear PE was produced.



88 Ar = 4-*t*BuPh



89a R = H
89b R = phenyl
89c R = naphthyl



90a R = Me
90b R = Et
90c R = CH_2CHMe_2
90d R = $CHMe_2$
90e R = Ph
90f R = *p*-CF_3-Ph
90g R = *p*-OCH_3-Ph

Figure 4.40 Ni complexes for living alkene polymerization.

Guan and coworkers have extended the study of hindered diimine catalysts even further with cyclophane complex **32** (Figure 4.11) [173]. When activated with MMAO, **32** is highly active for production of branched PEs (66–97 branches/1000 carbons) with relatively narrow polydispersities (M_w/M_n as low as 1.23 at 50 °C). Most significantly, these catalysts exhibit impressive thermal stability, with good activities even up to 90 °C. However, the polydispersity increases and the activities decrease somewhat at higher temperatures. Interestingly, a related alkyl cyclophane Ni complex demonstrated almost no activity for ethylene polymerization [174].

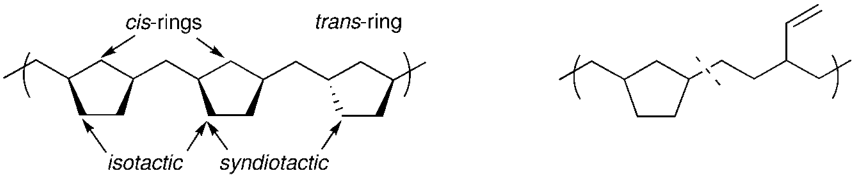
In addition to living 1-hexene and propylene polymerization, Bazan and coworkers have shown that **36**/MAO (Figure 4.11) is also living for ethylene polymerization [72]. At 10 °C, this catalyst produces branched PE (19 branches/1000 carbons) with $M_n = 260\,000$ g mol^{-1} and $M_w/M_n = 1.1$. At 32 °C, high molecular weight ($M_n = 1\,112\,000$ g mol^{-1}) branched PE (47 branches/1000 carbons) is obtained with a slightly broadened polydispersity ($M_w/M_n = 1.3$). Importantly, introduction of the carbonyl functionality in **36** leads to an increase in activity of approximately two orders of magnitude for ethylene polymerization over the analogous β-diimine catalyst with no carbonyl functionality. The increase in reactivity was attributed to the attachment of a Lewis acid (from the aluminum cocatalyst) to the exocyclic oxygen site on the propagating cationic species.

Brookhart and coworkers have investigated a series of anilinotropone-based nickel catalysts **89a–c** [175]. With activation by Ni(COD)$_2$ (COD=1,5-cyclooctadiene), high activities and long lifetimes were observed, particularly in the aryl-substituted cases **89b** and **c** (Figure 4.40). The M_n was shown to increase in nearly linear fashion with time. PDIs were relatively narrow (as low as 1.2 at room temperature), but increased at higher temperatures and with longer reaction times.

Finally, Bazan and coworkers have investigated nickel diimine variants **90a–g** (Figure 4.40) [176, 177]. With Ni(COD)$_2$ as activator, M_n increased linearly with time up to 30 min at 20 °C with **90a**, producing PE with low branching (12–19 methyl branches/1000 carbons). As the bulk of the ligand framework increases, an increase in activity is observed. The molecular weight distributions remained narrow for all the catalysts studied ($M_w/M_n = 1.1–1.4$).

4.5
Living Nonconjugated Diene Polymerization

Nonconjugated dienes are versatile monomers in that they can furnish polymers with a variety of microstructures depending on the mechanism by which they are polymerized. For example, 1,5-hexadiene can be cyclopolymerized to furnish a polymer with methylene-1,3-cyclopentane (MCP) units (Figure 4.41). Depending on the selectivity of the ring closing reaction, cis- or trans rings may be formed. Polymers containing mostly cis rings exhibit higher T_m values than those with mostly trans rings (e.g., for poly(methylene-1,3-cyclopentane)



Poly(methylene-1,3-cyclopentane)
PMCP

Poly(methylene-1,3-cyclopentane-*co*-3-vinyltetramethylene)
Poly(MCP-*co*-3-VTM)

Figure 4.41 Polymer structures derived from polymerization of 1,5-hexadiene.

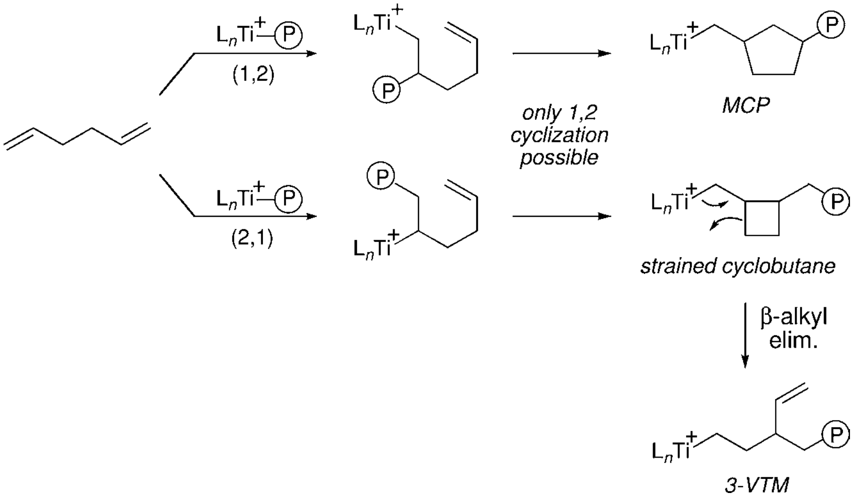
(PMCP) having >90% cis ring content, the T_m is 189 °C whereas those containing mostly trans rings are waxy materials with $T_m \leq 70\,^\circ\text{C}$) [178]. Polymerization of 1,5-hexadiene can also lead to vinyl-tetramethylene (VTM) units, which may serve as a synthetic handle by which polymer functionalization can be achieved [179].

4.5.1
Vanadium Acetylacetonoate Catalysts

In addition to living propylene polymerization, vanadium acetylacetonate complexes (Figure 4.15) have also been shown to be living for 1,5-hexadiene polymerization as well as for 1,5-hexadiene/propylene copolymerization [180]. At −78 °C, **37**/Et_2AlCl polymerized 1,5-hexadiene to produce a low molecular weight polymer ($M_n = 6600$ g mol^{-1}, $M_w/M_n = 1.4$) that contained a mixture of MCP and VTM units in a 54 : 46 ratio. The distribution of these two units varied in 1,5-hexadiene-propylene random copolymers as a function of 1,5-hexadiene incorporation.

4.5.2
Bis(phenoxyimine)titanium Catalysts

Coates and coworkers later reported that bis(phenoxyimine) titanium complex **49** (Figure 4.17) was also capable of living 1,5-hexadiene polymerization and 1,5-hexadiene/propylene copolymerization [181]. Homopolymerization of 1,5-hexadiene with **49**/MAO at 0 °C produced a high molecular weight polymer with a narrow PDI ($M_n = 268\,000$ g mol^{-1}, $M_w/M_n = 1.27$). The polymer showed the presence of two distinct units – the expected MCP units as well as 3-vinyl tetramethylene (3-VTM) units. As shown in Scheme 4.6, the MCP units are proposed to arise from 1,2-insertion of 1,5-hexadiene followed by a 1,2-cyclization. However, an initial 2,1-insertion of 1,5-hexadiene followed by a 1,2-cyclization forms a strained cyclobutane species. After a β-alkyl elimination, the 3-VTM unit is generated. Propylene/1,5-hexadiene copolymers with high



Scheme 4.6 Polymerization of 1,5-hexadiene with **49**/MAO.

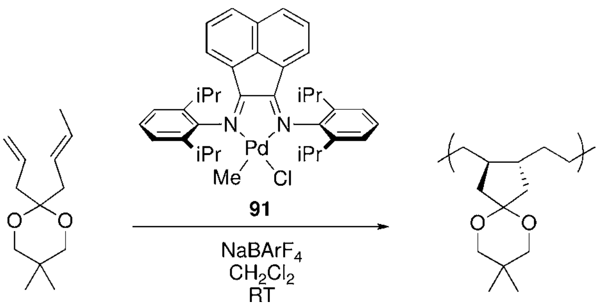
molecular weights have also been produced ($M_n = 119\,000–145\,000$ g mol^{-1}, $M_w/M_n = 1.09–1.16$).

4.5.3
Cyclopentadienyl Acetamidinate Zirconium Catalysts

In 2000, Sita and coworkers showed that **19a–c**/[PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (Figure 4.7) were active for the cyclopolymerization of 1,5-hexadiene at −10 °C [182]. The polymers produced possessed ≥98 % MCP units, and exhibited narrow polydispersities ($M_w/M_n = 1.03–1.09$). The selectivity of ring closure was ubiquitously trans; the stereoselectivity increasing with increasing steric bulk of the amidinate ligand (**21a**: %trans = 64; **21c**: %trans = 82).

4.5.4
Late Transition Metal Catalysts

In 2006, Osakada and coworkers reported the polymerization of a number of 1,6-dienes catalyzed by palladium complexes to afford polymers with *trans*-1,2-disubstituted five-membered rings [183]. In a subsequent report, living polymerization of 5-allyl-5-crotyl-2,2-dimethyl-1,3-dioxane with **91**/NaBArF$_4$ was shown (Scheme 4.7) [184]. A linear increase in M_n with monomer conversion was demonstrated, with molecular weight distributions remaining relatively narrow ($M_w/M_n = 1.20–1.24$).



Scheme 4.7 Polymerization of 5-allyl-5-crotyl-2,2-dimethyl-1,3-dioxane with **91**/NaBArF$_4$.

4.6
Living Homo- and Copolymerizations of Cyclic Olefins

Homopolymers of cyclic olefins (e.g., polycyclopentene, polynorbornene (PNB), Figure 4.42) are characterized by extremely high melting points and low solubility in most organic solvents. Taken together, these properties of cyclic olefin homopolymers make them difficult to process and are therefore commercially insignificant. However, upon incorporation into copolymers with α-olefins, materials with desirable properties can be obtained. The copolymers typically exhibit high chemical resistance, good optical properties, and facile processability [185].

4.6.1
Norbornene Homopolymerization

Risse has reported on the polymerization of norbornene (NB) in a controlled fashion with catalyst [Pd(MeCN)$_4$][BF$_4$]$_2$, obtaining saturated polymers [186]. Renewed chain growth was observed with sequential addition of monomer, but only for low conversion. At 0 °C, narrow molecular weight distributions were obtained for short reaction times ($t_{\mathrm{rxn}} = 20$ min; 54% conversion; $M_{\mathrm{n}} = 21\,400$ g mol^{-1}; $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.07$), but broadened as conversion increased ($M_{\mathrm{w}}/M_{\mathrm{n}} = 1.34$ at 100% conversion). Ester-functionalized NBs were also shown to polymerize in a living fashion [187].

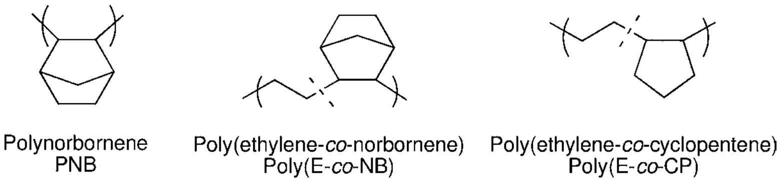


Figure 4.42 Homopolymers and copolymers of cyclic olefins.

Shiono and coworkers reported that activation of **43** (Figure 4.16) with dMMAO containing 0.4 mol% of triisobutylaluminum (TIBA) in the presence of NB catalyzed living polymerization at 20 °C [188]. The molecular weight distributions obtained were narrow ($M_w/M_n = 1.07–1.08$). A two-stage reaction was shown to increase the molecular weight of the second step by double that of the first step when each was carried to quantitative conversion.

4.6.2
Copolymers of Norbornene/Ethylene and Cyclopentene/Ethylene

4.6.2.1 Non-Group 4 Early Transition Metal Catalysts

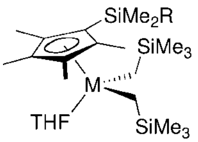
In addition to living ethylene polymerization, the ability of **67**/Et_2AlCl to catalyze the quasiliving copolymerization of ethylene and NB was also reported [143]. Poly(E-*co*-NB) with 5.1–39.9 mol% NB content was obtained from **67**/Et_2AlCl at 0 °C. The polymers exhibited narrow molecular weight distributions ($M_w/M_n = 1.29–1.73$) and high molecular weights ($M_n = 327\,000–2\,570\,000\ \mathrm{g\ mol^{-1}}$).

Tritto and coworkers have recently described the copolymerization of ethylene with NB catalyzed by rare earth metal half sandwich complexes **92a–d** (Figure 4.43) [189]. Upon activation with $[Ph_3C][B(C_6F_5)_4]$, **92a** and **b** showed excellent activities, whereas **92d** was inactive. Furthermore, **92b**/$[Ph_3C][B(C_6F_5)_4]$ furnished poly(E-*co*-NB) with 29–42 mol% NB content and a linear increase in M_n with time while maintaining a narrow PDI ($M_w/M_n = 1.22–1.35$).

4.6.2.2 Group 4 Metallocene-Based Catalysts

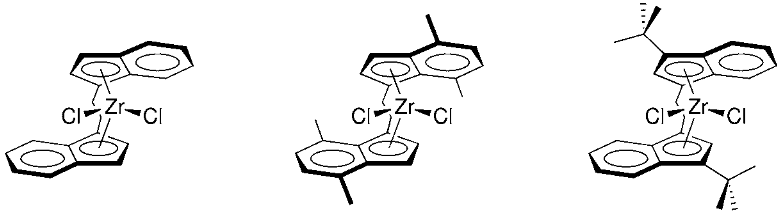
Catalyst **2**/MAO (Figure 4.2) can also be used for the living copolymerization of ethylene and NB. For example, at 0 °C **2**/MAO can furnish poly(E-*co*-NB) with 53 mol% NB and $M_n = 78\,000\ \mathrm{g\ mol^{-1}}$ with $M_w/M_n = 1.16$ [190]. In addition, a linear increase in M_n with reaction time was observed for this system. When activated with MAO at 40 °C, a similar compound **45** (Figure 4.16) also provided ethylene–NB copolymers with fairly narrow PDIs ($M_w/M_n = 1.21–1.27$) [191].

Shiono and coworkers also reported the living copolymerization of propylene and NB with **2**/dMAO (Figure 4.2) to produce copolymers with very high T_g values (249 °C) and narrow molecular weight distributions ($M_w/M_n = 1.16$) [192]. In a subsequent report, the copolymerization of higher α-olefins (1-hexene, 1-octene, and 1-decene) with NB by **2**/MAO was



92a M = Sc, R = Me
92b M = Sc, R = C_6F_5
92c M = Y, R = C_6F_5
92d M = Lu, R = C_6F_5

Figure 4.43 Rare earth metal half sandwich compounds.



93 *rac*-**94** **95**

Figure 4.44 Zirconocene precatalysts for living ethylene/norbornene copolymerization.

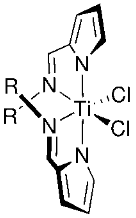
reported; however, molecular weight distributions were somewhat broadened ($M_w/M_n = 1.36–1.72$) [193].

Lastly, Tritto and coworkers have shown that *rac*-Et(Ind$_2$)ZrCl$_2$/MAO (**93**), 90% *rac*/10% *meso*-Et(4,7-Me$_2$Ind)$_2$ZrCl$_2$ (**94**), and *rac*-Et(3-*t*BuInd)$_2$ZrCl$_2$/MAO (**95**) exhibit quasiliving behavior for ethylene–NB copolymerization (Figure 4.44) [194, 195].

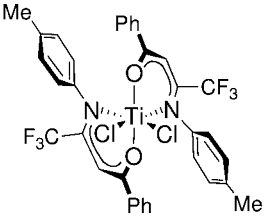
4.6.2.3 **Titanium Catalysts for Living Ethylene–Cyclic Olefin Copolymerization**

Bis(pyrrolide-imine)titanium complexes were initially reported by Fujita *et al.* in 2000 for ethylene polymerization; however living behavior was not observed [196]. Fujita and coworkers turned their attention to the copolymerization of ethylene and NB [197–199]. When activated with MAO at 25 °C, **96a–d** (Figure 4.45) furnished poly(E-*alt*-NB) with narrow molecular weight distributions and high molecular weights ($M_w/M_n = 1.10–1.24$, $M_n = 127\,000–600\,000\ \mathrm{g\ mol^{-1}}$). A linear increase of M_n with time over the course of 20 min was observed. The copolymers were found to contain 95.4% perfectly alternating units. The polymer chain-end structures were consistent with chain initiation by insertion of NB into the Ti–Me bond and a last inserted NB unit after termination by protonolysis. This suggests NB plays a stabilizing role for the active species against termination processes.

The copolymerization of ethylene and NB by **79a–d**/MMAO (Figure 4.35) was also shown to possess some characteristics of a living polymerization



96a R = Ph
96b R = Cy
96c R = Cyclooctyl
96d R = 4-*t*Bu-Cy



97

Figure 4.45 Bis(pyrrolide-imine) and bis(enaminoketonato) titanium catalysts.

[162]. The polymers obtained from polymerizations conducted at 25 °C exhibited narrow molecular weight distributions ($M_w/M_n = 1.07–1.54$) with $M_n = \sim 150\,000–580\,000$ g mol^{-1}. The NB content ranged from 35.3 to 55.4 mol%. A linear increase in M_n with reaction time was demonstrated for **79a**/MMAO at 25 °C over the course of 20 min. In a subsequent report Li and coworkers discussed the effects of further ligand modifications on the copolymerization behavior of bis(enaminoketonato)titanium catalysts [200]. At 25 °C, **97**/MMAO (Figure 4.45) produced poly(E-*co*-NB) with narrow polydispersities ($M_w/M_n = 1.18–1.31$, $M_n = \sim 200\,000–570\,000$ g mol^{-1}) and NB content ranging from 44.6 to 47.8 mol%. The polymerization displayed a linear increase of M_n with time with $t = 5–20$ min. The copolymerization of ethylene and cyclopentene (CP) by **79a**/MMAO and **79d**/MMAO was also shown to possess some characteristics of living behavior [201]. Poly(E-*co*-CP)s with narrow molecular weight distributions ($M_w/M_n = 1.23–1.82$) were produced at temperatures from −10 to 30 °C.

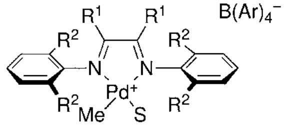
4.6.2.4 **Palladium α-Diimine Catalysts**

Kaminsky and Kiesewetter applied a combinatorial screening approach to identify catalysts for the copolymerization of NB with ethylene [202]. Catalysts **98a** and **b** (Figure 4.46) were identified and furnished poly(E-*co*-NB) with 9–62 mol% NB incorporation and relatively narrow molecular weight distributions (M_w/M_n as low as 1.4) indicating "quasiliving" behavior.

4.7
Random Copolymers

4.7.1
Random Copolymers Incorporating Polar Monomers

Copolymers of polar monomers with olefins are attractive because of enhanced physical properties such as biocompatibility and ease of processing [203]. Coates and coworkers synthesized polyolefin elastomers by addition of small amounts of ureidopyrimidone (UP) functionalized hexene to polymerizations of 1-hexene [204]. Nickel catalyst **30a**/Et_2AlCl (Figure 4.11) was used, exploiting



98a R^1 = H, R^2 = Me, S = CH_3CN
98b R^1 = Me, R^2 = *i*Pr, S = CH_3CN

Figure 4.46 Palladium catalysts for ethylene/norbornene copolymerization.

the dual ability of Et_2AlCl to activate the nickel center and to protect the Lewis basic nitrogen functional groups. Polymers incorporating ~2% UP-functionalized monomer were obtained with narrow molecular weight distributions ($M_w/M_n = 1.2–1.4$). The polymers obtained exhibited reversible, noncovalent cross-linking through hydrogen-bonding interactions, and thus have elastomeric properties at room temperature.

Bazan has achieved the first quasiliving copolymerization of ethylene with a polar monomer, 5-norbornen-2-yl acetate [176, 177]. Upon activation with $Ni(COD)_2$, **90a–g** (Figure 4.40) incorporated 1–17 mol% 5-norbornen-2-yl acetate into a PE backbone. Molecular weight distributions were relatively narrow ($M_w/M_n = 1.2–1.6$), and the M_n exhibited a nearly linear increase with conversion.

4.8
Block Copolymers

By far, the most important application of living olefin polymerization is the production of block copolymers, which is typically achieved via sequential monomer addition, furnishing a near-limitless number of materials. Physical blends or random copolymers often give rise to materials whose properties are intermediate between those of the respective homopolymers. Block copolymers, on the other hand, often furnish materials whose mechanical properties are superior to the sum of their parts. This unique behavior is due to microphase separation of the different segments of the block copolymer into discrete domains, which give rise to otherwise unattainable morphologies [205, 206]. One of the most highly sought goals in the field of olefin polymerization is the synthesis of block copolymers containing *i*PP domains that are envisioned to possess material properties of great industrial importance. For example, diblock copolymers containing *i*PP segments may serve as compatibilizers in blends containing *i*PP homopolymers [71]. One of the most actively pursued block copolymer structures are those with "hard" or semicrystalline end blocks (e.g., PE, *i*PP, and *s*PP) and amorphous midblocks (e.g., *a*PP and poly(E-*co*-P)); triblock copolymers of this type have been shown to behave as thermoplastic elastomers [127, 130, 139, 207–211].

4.8.1
Block Copolymers Containing Poly(α-olefin) Blocks

There are numerous catalysts that have been employed to prepare block copolymers containing poly(α-olefin) blocks; they are listed in Table 4.1. In section 4.2.2, living 1-hexene polymerization with **5**/$B(C_6F_5)_3$ (Figure 4.3) was discussed. Kim and coworkers further prepared a block copolymer of 1-hexene and 1-octene via sequential monomer addition [25]. The polymer

Table 4.1 Block copolymers based on higher α-olefins.

Entry	Block copolymer	Catalyst precursor(s) used
1	PH-*b*-PO	**5,14,15a,19b**
2	poly(VCH)-*b*-PH-*b*-poly(VCH)	**22c**
3	PE-*b*-poly(E-*co*-H)	**52b**
4	PE-*b*-POD	**34b**
5	PP-*b*-PH, PP-*b*-PH (chain straightened)	**30a,b**
6	PH-*b*-poly(P-*co*-H)-*b*-PH	**30b**
7	POD-*b*-poly(P-*co*-OD)-*b*-POD	**31**
8	PH/PE *multiblock* copolymer	**30a**

PH, poly(1-hexene); PO, poly(1-octene); VCH, vinylcyclohexane; PE, polyethylene; E, ethylene; H, 1-hexene; POD, poly(1-octadecene); PP, polypropylene; P, propylene.

produced at 0 °C possessed a narrow polydispersity ($M_w/M_n = 1.21$) and an $M_n = 108\,730$ g mol^{-1}.

Living homopolymerizations of 1-hexene catalyzed by amine bis(phenolate) titanium complexes were discussed in section 4.2.4. Kol and coworkers were also able to apply this class of catalyst to the synthesis of block copolymers of 1-hexene and 1-octene [39, 42]. Using **14**/$B(C_6F_5)_3$ (Figure 4.5), a block copolymer of 1-hexene and 1-octene was prepared via sequential monomer addition where each domain had an atactic microstructure. The polymer possessed a narrow molecular weight distribution ($M_w/M_n = 1.2$) and an $M_n = 11\,600$ g mol^{-1}. The extremely long-lived catalyst generated from **15a** (Figure 4.5) was also used to prepare a block copolymer of 1-hexene and 1-octene through sequential monomer addition to furnish PH-*b*-PO. The block copolymer had $M_n = 34\,000$ g mol^{-1} while maintaining a low $M_w/M_n = 1.16$.

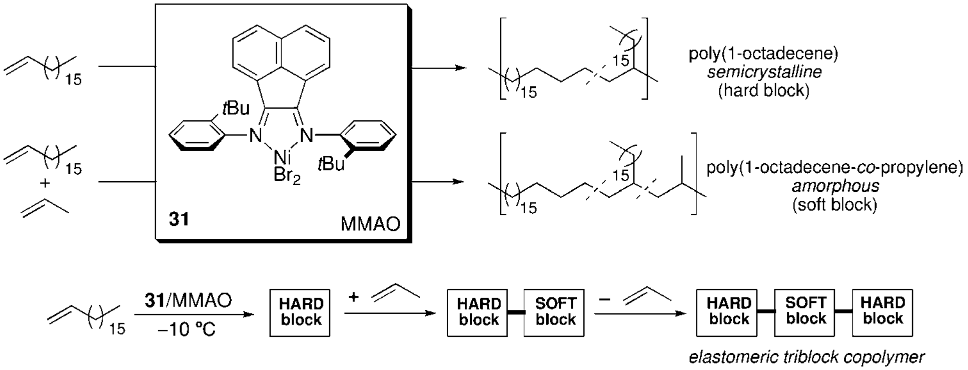
The 1-hexene and VCH homopolymerization behavior of **22c**/$[Ph_3C][B(C_6F_5)_4]$ (Figure 4.7) was discussed in section 4.2.5. Sita and coworkers were able to exploit the living nature of this catalyst to prepare a triblock copolymer of isotactic poly(VCH)-*b*-*a*PH-*b*-isotactic poly(VCH) via sequential monomer addition [50]. The triblock copolymer exhibited a narrow polydispersity ($M_w/M_n = 1.08$) and $M_n = 24\,400$ g mol^{-1} with a VCH content of 33 mol%.

Having shown that **50**, **52b**, and **74a** and **b**/MAO (Figures 4.17, 4.18, and 4.32) were living for ethylene polymerization as discussed in section 4.4.2, Fujita and coworkers investigated the ability of these catalysts to produce ethylene/α-olefin copolymers in a living fashion [152]. Copolymerizations with ethylene and either 1-hexene, 1-octene, or 1-decene were carried out with each catalyst at 25 °C. In all cases, polymers exhibiting narrow molecular weight distributions were obtained ($M_w/M_n \leq 1.22$). Increased α-olefin incorporation correlated with decreased ortho substituent bulk. A series of PE-*b*-poly(E-*co*-1-hexene) samples was produced using **52b**/MAO via sequential monomer addition.

Molecular weight distributions for the block copolymers were generally low ($M_w/M_n = 1.11–1.31$ for M_n up to 121 000 g mol^{-1}), and 1-hexene contents of up to 28.9 mol% were estimated.

As discussed in section 4.2.5, **19b**/[PhNMe$_2$H][B(C$_6$F$_5$)$_4$] polymerizes 1-hexene in a living manner to produce highly isotactic poly(1-hexene) with [*mmmm*] > 0.95. However, when a substoichiometric amount of the borate is used (e.g., [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] : [**19b**] = 0.5), the resulting polymer is considerably less isotactic with a [*mm*] content of approximately 45–50% resulting from DT polymerization (Scheme 4.4). This system has been employed to make a diblock poly(α-olefin) sample [131]. Initially, **19b** was activated with 0.5 equivalent of [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] and used to polymerize 1-hexene, resulting in the formation of an *a*PH block. After 2 h, 1-octene was added along with an additional 0.5 equivalent of the borate, leading to the growth of an isotactic PO block. GPC analysis revealed clean formation of the *a*PH-*b*-*i*-PO diblock copolymer with $M_n = 12\,400$ g mol^{-1} and $M_w/M_n = 1.04$.

Brookhart and coworkers demonstrated the living nature of nickel catalysts **30a** and **31** (Figure 4.11) with the synthesis of well-defined di- and triblock copolymers of α-olefins [62]. Activation of **30a** with MAO at −15 °C, followed by sequential addition of monomers afforded PP-*b*-PH with monomodal, narrow molecular weight distributions ($M_w/M_n = 1.11–1.13$), which exhibited less branching than predicted, owing to partial chain straightening. Further, triblocks were prepared by activation of **30a** or **31** with MMAO at −10 °C, followed by reaction with 1-octadecene to afford a semicrystalline, chain-straightened block as observed in homopolymerizations with that monomer. Sequential addition of propylene led to the formation of an amorphous block of poly(1-octadecene)-*co*-PP, which was followed by formation of a third block of poly(1-octadecene) as propylene was removed (Scheme 4.8). The resultant materials exhibited elastomeric properties as expected based on the "hard–soft–hard" triblock structure of the polymers.



Scheme 4.8 Synthesis of elastomeric triblock copolymers from 1-octadecene and propylene using **31**/MMAO.

Given that palladium diimine catalysts produce highly branched amorphous materials with ethylene, and produce semicrystalline polymers from long chain α-olefins via a ''chain straightening'' mechanism, copolymers containing these two segments are an attractive goal. Gottfried and Brookhart investigated this block copolymer synthesis in detail [68]. Block copolymers of ethylene and 1-octadecene were prepared with **34b** (Figure 4.13) by opposite orders of addition to furnish PE-*b*-poly(1-octadecene) and poly(1-octadecene)-*b*-PE. In all cases, materials with narrow molecular weight distributions were obtained ($M_w/M_n = 1.06{-}1.22$). The copolymer microstructures differed depending on the order of introduction of the blocks. The most obvious difference between the two structures is that, when ethylene is introduced first, the number of ethyl and propyl branches decreases substantially relative to the case where 1-octadecene is added first.

Marques and Gomes exploited the living nature of **30b** (Figure 4.11) for the production of di- and triblock copolymers [65]. When activated with MAO, **30b** polymerized propylene at $-15\,^{\circ}\mathrm{C}$, generating a syndio-rich PP block, followed by removal of excess monomer under vacuum. Addition of 1-hexene at the same temperature generated a diblock copolymer with $M_w/M_n = 1.18$ and $M_n = 46\,400\ \mathrm{g\ mol^{-1}}$. Triblocks were also produced with this catalyst. Polymerization of 1-hexene first, followed by introduction of propylene (with 1-hexene still present), followed by venting and then allowing the residual 1-hexene to react allowed the formation of a shorter ($M_n = 31\,100\ \mathrm{g\ mol^{-1}}$) ABA triblock copolymer, with the middle block composed of poly(propylene-*ran*-(1-hexene)).

4.8.2
Block Copolymers Containing Polypropylene Blocks

4.8.2.1 Isotactic Polypropylene-Containing Block Copolymers

The catalysts that have been used to prepare PP-based block copolymers are listed in Table 4.2. Until recently, methods of preparing *i*PP in a living manner have been elusive [125, 127, 130, 137–139]. Busico and coworkers reported in 2003 the preparation of a diblock copolymer of *i*PP and PE using Kol's diamino bis(phenolate)zirconium catalyst (**13a**, Figure 4.5) under ''quasiliving'' conditions [212]. Using **13a**/$[\mathrm{PhNMe_2H}][\mathrm{B(C_6F_5)_4}]$ with 2,6-di-*tert*-butylphenol modified Al(*i*Bu)$_3$ as scavenger, a diblock copolymer of ethylene and propylene was prepared by sequential monomer addition of ethylene (1.5 min) and propylene (20 min). The resultant copolymer possessed a narrow polydispersity (M_w/M_n as low as 1.2 when $M_n = 6500\ \mathrm{g\ mol^{-1}}$). Characterization of the copolymer by ^{13}C NMR spectroscopy and differential scanning colorimetry (DSC) was consistent with a block structure. These results represented the first synthesis of an *i*PP-*b*-PE copolymer via sequential monomer addition at polymerization durations greater than 1 min. In a subsequent report, **60a** (Figure 4.24) was employed under the same conditions

Table 4.2 Block copolymers based on propylene.

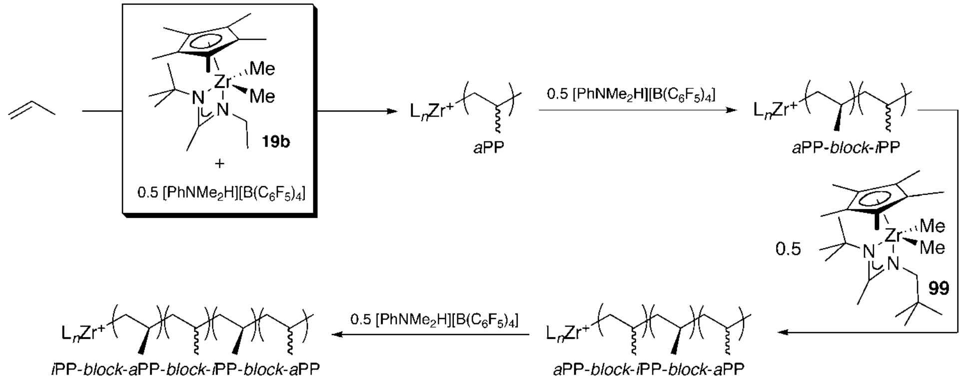
Entry	Block copolymer	Catalyst precursor(s) used
1	*i*PP-*b*-PE	**13a,60a**
2	*a*PP-*b*-*i*PP-*b*-*a*PP-*b*-*i*PP	**19b/99**
3	*i*PP-*b*-poly(E-*co*-P)	**58c,59k**
4	*i*PP-*b*-poly(E-*co*-P)-*b*-*i*PP-*b*-poly (E-*co*-P)-*b*-*i*PP-*b*-poly(E-*co*-P)-*b*-*i*PP	**59k**
5	*s*PP-*b*-poly(E-*co*-P)	**49,50**
6	*s*PP-*b*-poly(E-*co*-P)-*b*-*s*PP	**37,49**
7	*s*PP-*b*-*a*PP-*b*-*s*PP	**2**
8	PE-*b*-poly(E-*co*-P)-*b*-*s*PP	**50**
9	*a*PP-*b*-PE	**41,80a**
10	*a*PP-*b*-poly(E-*co*-P)	**40,41**
11	*i*PP-*b*-*rir*PP-*b*-*i*PP-*rir*PP-*b*-*i*PP	**35,64f**

*i*PP, isotactic polypropylene; PE, polyethylene; *a*PP, atactic polypropylene; E, ethylene; P, propylene; *s*PP, syndiotactic polypropylene; *rir*PP, regioirregular polypropylene.

to furnish *i*PP-*b*-PE with a higher molecular weight ($M_n = 22\,000$ g mol^{-1}, $M_w/M_n = 1.3$) and T_m of the *i*PP block (152 °C) [129].

The living DT system, which was employed by Sita and coworkers to make block copolymers from 1-hexene and 1-octene, was later applied to propylene polymerization [130]. Formation of a PP diblock copolymer with **19b**/[PhNMe$_2$H][B(C$_6$F$_5$)$_4$] was accomplished by first activation with 0.5 equivalents of [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] furnishing an atactic PP segment followed by complete activation with another 0.5 equivalents of [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] to furnish the *a*PP-*b*-*i*PP. It was found that related complex **99** could effectively reinvoke DT by *irreversibly* transferring a methyl group to the active polymerization species. In addition to synthesizing an *a*PP-*b*-*i*PP diblock copolymer, an *a*PP-*b*-*i*PP-*b*-*a*PP triblock and an *a*PP-*b*-*i*PP-*b*-*a*PP-*b*-*i*PP tetrablock sample were formed (Scheme 4.9). The polymers had very similar molecular weights ($M_n = 164\,200$–$172\,400$ g mol^{-1}, $M_w/M_n = 1.19$). Testing of the tensile properties of the block copolymers showed good elastomeric behavior. For example, the triblock copolymer displayed an elongation to break of 1530%, the highest of the three samples.

Further exemplifying the living nature of **58c**/MAO (Figure 4.22) for partially isospecific propylene polymerization, an *i*PP-*b*-poly(E-*co*-P) sample was produced with this catalyst [125]. After polymerization of propylene to form an *i*PP block of $M_n = 28\,100$ g mol^{-1} ($M_w/M_n = 1.10$), ethylene was added to the reaction, yielding a diblock copolymer with $M_n = 62\,000$ g mol^{-1} and $M_w/M_n = 1.10$. In a subsequent report, Coates and coworkers synthesized block copolymers containing *i*PP blocks of higher tacticity with **59k**/MAO (Figure 4.22) via sequential monomer addition [127]. Specifically, iPP-*b*-poly(E-*co*-P)-*b*-iPP,



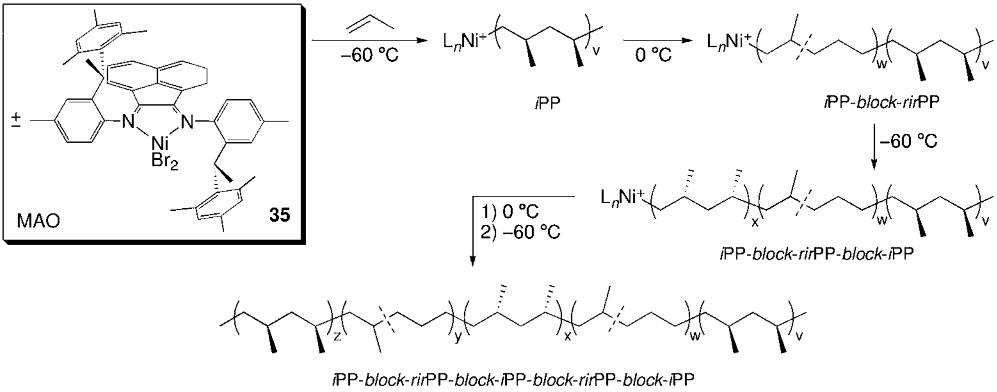
Scheme 4.9 Synthesis of elastomeric propylene-based stereoblock copolymers using **19b** and **99**.

iPP-*b*-poly(E-*co*-P)-*b*-iPP-*b*-poly(E-*co*-P)-*b*-iPP, and iPP-*b*-poly(E-*co*-P)-*b*-iPP-*b*-poly(E-*co*-P)-*b*-iPP-*b*-poly(E-*co*-P)-*b*-iPP copolymers were prepared. The polymers had narrow molecular weight distributions ($M_w/M_n = 1.13-1.30$) and high molecular weights ($M_n = 102\,000-235\,000$ g mol^{-1}). On testing, the tensile properties of the block copolymers showed good elastomeric behavior, with the triblock copolymer displaying an elongation to break of 1000%.

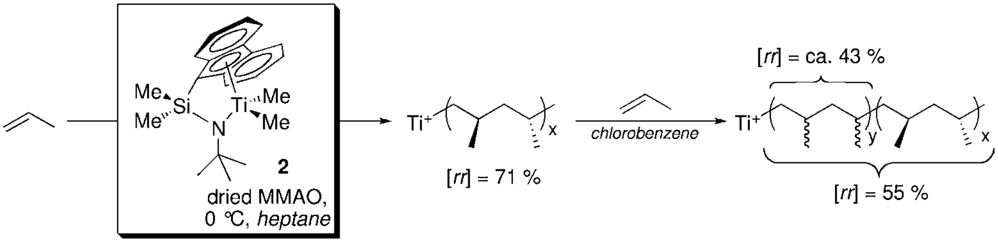
A strategy for the living formation of block copolymers with one monomer, simply by varying reaction temperature, was recently described by Coates and coworkers [138]. As previously described in section 4.3.9, catalyst **35** (Figure 4.11) polymerizes propylene with high isoselectivity and regioregularity at low temperatures. At higher temperatures, regioirregular, amorphous PP is generated. It was reported that **35**/MAO was used to synthesize regioblock PPs having good elastomeric properties [211]. Both a triblock and a pentablock copolymer were synthesized by simply varying the reaction temperature during the course of the polymerization (Scheme 4.10). For example, an *i*PP-*b*-*rir*PP-*b*-*i*PP ($M_n = 109\,000$ g mol^{-1}, $M_w/M_n = 1.14$) and an *i*PP-*b*-*rir*PP-*b*-*i*PP-*b*-*rir*PP-*b*-*i*PP ($M_n = 159\,000$ g mol^{-1}, $M_w/M_n = 1.39$) pentablock copolymer were prepared by toggling the reaction temperature between −60 and 0 °C. Transmission electron microscopy (TEM) revealed no microphase separation. However, the pentablock copolymer exhibited an exceptional strain-to-break of 2400% and good elastomeric recovery out to strains of 1000%. In a subsequent report, similar regioblock PPs were produced with **64f**/MAO (Figure 4.27), which exhibited improved elastomeric performance at elevated temperatures (e.g., 65 °C) over block copolymers synthesized with **35**/MAO [139].

4.8.2.2 **Syndiotactic Polypropylene-Containing Block Copolymers**

After the seminal report of living propylene polymerization catalyzed by **37**/Et_2AlCl (Figure 4.15) [76, 77] and discovering the activating effect of anisole



Scheme 4.10 Synthesis of elastomeric propylene-based regioblock copolymers using **35**/MAO.



Scheme 4.11 Synthesis of *s*PP-*b*-*a*PP using solvent polarity to control tacticity.

[78], Doi and coworkers applied this catalyst system to the synthesis of block copolymers of propylene and ethylene [213]. Specifically, a *s*PP-*b*-poly(E-*co*-P)-*b*-*s*PP triblock copolymer was synthesized via sequential monomer addition, which exhibited a narrow molecular weight distribution ($M_w/M_n = 1.24$) with $M_n = 94\,000$ g mol^{-1} and a propylene content of 70 mol%.

As previously described in section 4.3.2, the solvent polarity plays a critical role in determining the tacticity of PP generated from **2**/dMMAO (Figure 4.2) [92]. In a subsequent report, Shiono and coworkers cleverly applied this knowledge to prepare stereoblock copolymers of propylene-containing *s*PP and *a*PP segments (Scheme 4.11) by initial polymerization in heptane followed by addition of more propylene and chlorobenzene [214]. The resultant *s*PP-*b*-*a*PP had $M_n = 94\,700$ g mol^{-1} with a narrow PDI ($M_w/M_n = 1.27$). Shiono and coworkers have also recently described similar effects of the tacticity of PP generated from **2**/dMMAO under varying propylene pressures [215]. At low pressure (0.2 atm) atactic PP is furnished, but at higher pressure (1 atm) syndiotactic PP is generated. An *s*PP-*b*-*a*PP copolymer and an *s*PP-*b*-*a*PP-*b*-*s*PP copolymer were synthesized by varying propylene pressure over the course of the polymerization.

With the ability to produce both PE and *s*PP in a living manner as discussed in sections 4.3.4 and 4.4.2, bis(phenoxyimine) titanium complexes have been employed in the synthesis of ethylene- and propylene-containing block copolymers. For example, **49**/MAO (Figure 4.17) has been shown to produce *s*PP-*b*-poly(E-*co*-P) diblock copolymers of high molecular weight ($M_n = 145\,100$ g mol^{-1}, $M_w/M_n = 1.12$) through sequential monomer addition [113]. Several studies on the physical properties of sPP-*b*-poly(E-co-P) diblock copolymers made using **49**/MAO have been conducted, including those involving the morphology [216], thermodynamic behavior, and self-assembly [217] of the materials. The addition of a third block was later employed in the formation of a *s*PP-*b*-poly(E-*co*-P)-*b*-*s*PP triblock copolymer [211]. TEM revealed that the polymer exhibited a microphase-separated morphology with *s*PP cylinders in a poly(E-*co*-P) matrix. Tensile testing revealed a strain-to-break of about 550%.

Living ethylene/propylene copolymerization and block copolymer formation has also been demonstrated with related complex **50**/MAO [218]. Specifically, *s*PP-*b*-poly(E-*co*-P), PE-*b*-*s*PP, and PE-*b*-poly(E-*co*-P)-*b*-*s*PP have been prepared through sequential monomer addition [154, 219].

4.8.2.3 **Atactic Polypropylene-Containing Block Copolymers**

In 1991, Hlatky and Turner reported on the synthesis of diblock copolymers of ethylene and propylene using a hafnocene catalyst [220]. Activation of Cp_2HfMe_2 (**41**, Figure 4.16) with $[PhNMe_2H][B(C_6F_5)_4]$ in the presence of propylene furnishes atactic PP. At 0 °C, the rate of termination via β-H transfer was slow enough to allow for the synthesis of *a*PP-*b*-PE via sequential monomer addition. Both orders of monomer addition (ethylene followed by propylene and propylene followed by ethylene) were successful in furnishing a polymeric product, which contained mostly (50–60%) diblock material isolated by hexanes extraction.

In section 4.3.2, the low-temperature living polymerization of propylene by Cp_2ZrMe_2 (**40**)/$B(C_6F_5)_3$ and Cp_2HfMe_2 (**41**)/$B(C_6F_5)_3$ (Figure 4.16) as reported by Fukui and coworkers was discussed [18]. In a subsequent report, the synthesis of *a*PP-*b*-poly(E-*co*-P) diblock copolymers using **40**, **41**, and $Cp^*_2HfMe_2$ activated with $B(C_6F_3)_3$ and employing Al(*n*Oct)$_3$ as a scavenger was described through sequential monomer addition at low temperatures ($T_{rxn} = -78\,°C$ for **40** and Cp^*_2 HfMe$_2$; $T_{rxn} = -50\,°C$ for **41**) [90]. The resultant polymers exhibited narrow molecular weight distributions ($M_w/M_n = 1.07$–1.30) and $M_n = 71\,000$–$155\,000$ g mol^{-1} with propylene contents between 65 and 75 mol%.

Mecking and coworkers have used **80a**/MAO (Figure 4.35) for the synthesis of PE-*b*-*a*PP through sequential monomer addition [163]. Polymerization of ethylene in a living fashion followed by removal of excess monomer *in vacuo* and subsequent propylene polymerization furnished the diblock copolymer with $M_n = 190\,000$ g mol^{-1} and $M_w/M_n = 1.12$.

Table 4.3 Block copolymers based on ethylene.

Entry	Block copolymer	Catalyst precursor(s) used
1	PE-*b*-poly(E-*co*-P)	**50,54,78c**
2	PE-*b*-poly(E-*co*-P)-*b*-PE	**50**
3	PE-*b*-PS	**109**

PE, polyethylene; E, ethylene; P, propylene; PS, polystyrene.

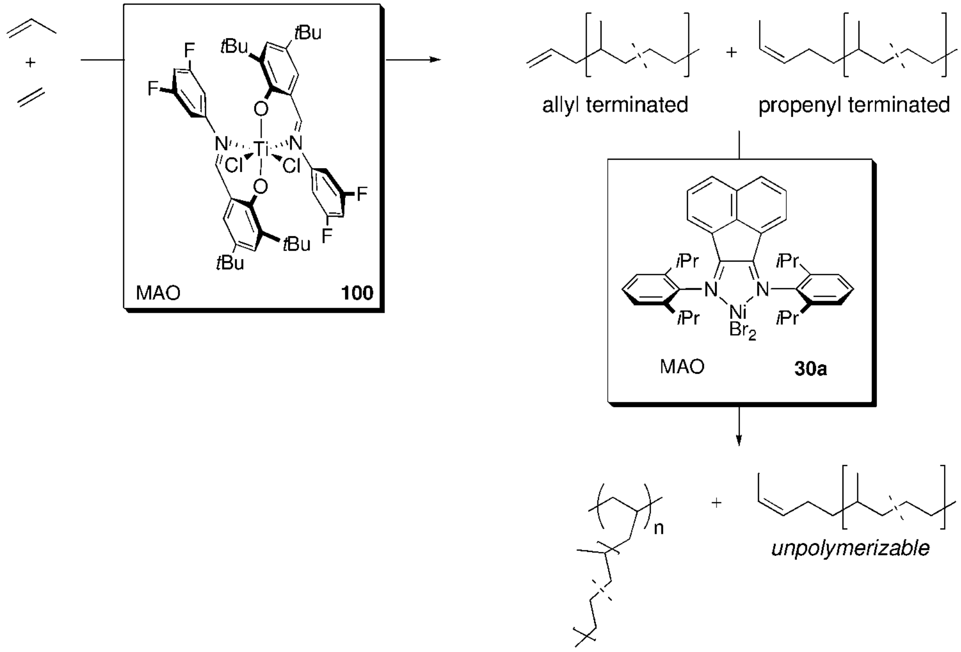
4.8.3

Polyethylene-Containing Block Copolymers

The catalysts that have been used to prepare PE-based block copolymers are listed in Table 4.3. While bis(phenoxyimine) titanium complexes can provide highly syndiotactic PP, copolymers that incorporate propylene as part of a poly(E-*co*-P) block have also been synthesized with these catalysts. Using **50**/MAO (Figure 4.17) a PE-*b*-poly(E-*co*-P) diblock and a PE-*b*-poly(E-*co*-P)-*b*-PE triblock copolymer have been synthesized through sequential monomer addition [154]. A PE-*b*-poly(E-*co*-P) diblock copolymer was also synthesized using **54**/MAO (Figure 4.20) [122, 221]. While the molecular weight of the polymer was quite high with $M_n = 2\,000\,000$ g mol^{-1}, the molecular weight distribution was fairly broad ($M_w/M_n = 1.60$).

The ethylene homopolymerization behavior of bis(indolide-imine)titanium complexes was discussed in section 4.4.4. Using **78c**/MAO (Figure 4.34), Fujita and coworkers were also able to prepare PE-*b*-poly(E-*co*-P) copolymers via sequential monomer addition with $M_w/M_n = 1.17$ and $M_n = 31\,400$ g mol^{-1} and overall propylene content of 8.0 mol% [159, 160]. TEM visualization of the block copolymer revealed microphase separation of the poly(E-*co*-P) and PE domains, which were evenly dispersed throughout the sample.

Coates and coworkers have combined two sequential polymerizations to generate a series of poly(E-*co*-P) comb polymers from the corresponding poly(E-*co*-P) macromonomers [222]. First, poly(E-*co*-P) macromonomers featuring one unsaturated chain end were synthesized using a nonliving titanium bis(phenoxyimine) catalyst, **100** (Scheme 4.12), generating allyl (polymerizable) and propenyl (unpolymerizable) end groups. The macromonomers were then homopolymerized using a living nickel diimine catalyst, **30a**/MAO (Figure 4.11, Scheme 4.12), to generate poly(E-*co*-P) comb polymers featuring approximately 7–14 arms/molecule after fractionation from the unpolymerizable residual macromonomer; these values correspond well to the theoretical values based on reaction stoichiometry. The molecular weight distributions remained relatively low ($M_w/M_n = 1.51$–1.90, $M_n = 74\,000$–$209\,000$ g mol^{-1}).



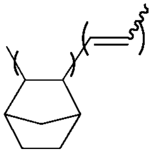
Scheme 4.12 Poly(E-*co*-P) comb synthesis.

4.8.4
Norbornene- and Cyclopentene-Containing Block Copolymers

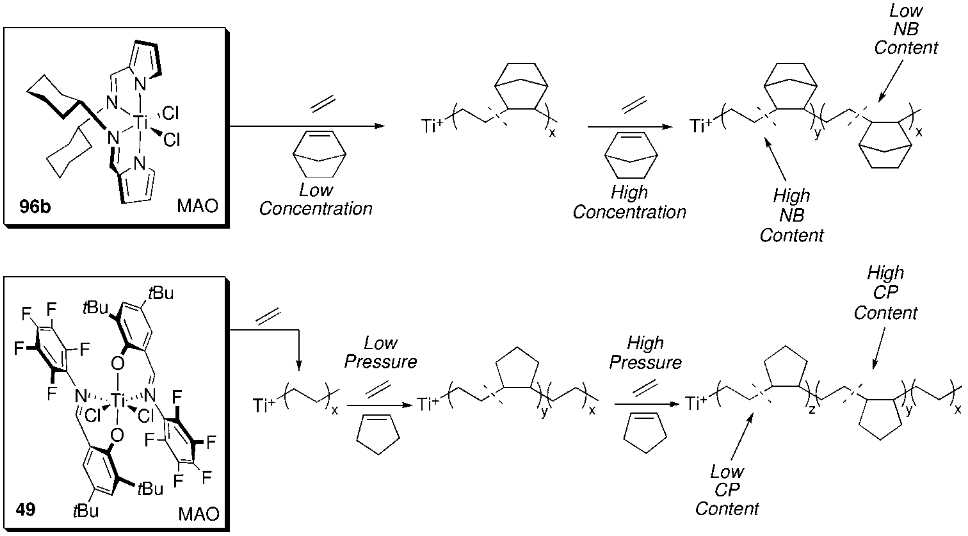
The catalysts that have been used to prepare block copolymers based on cyclic olefins are listed in Table 4.4. The alternating copolymerization of ethylene and NB using bis(pyrrolide-imine)titanium catalysts was discussed in section 4.6.2.3. Fujita and coworkers were able to utilize **96b**/MAO (Figure 4.45) to prepare block copolymers containing poly(E-*co*-NB) and PE segments as well as block copolymers containing poly(E-*co*-NB) segments with varying degrees of NB incorporation [199]. Block copolymers of the type poly(E-*co*-NB)$_x$-*b*-poly(E-*co*-NB)$_y$ with 7.6 mol% NB incorporation in the first block and 27.4 mol% NB overall were prepared by initiating the polymerization with ethylene containing the desired amount of NB. After the first block had been formed, additional NB was added while maintaining the ethylene feed (Scheme 4.13). PE-*b*-poly(E-*co*-NB) was prepared through sequential monomer addition. The diblock copolymer exhibited a narrow polydispersity ($M_w/M_n = 1.56$) and $M_n = 414\,000$ g mol^{-1} with a NB content of 31.5 mol%.

Bis(phenoxyimine) titanium complexes have been employed in the living copolymerization of ethylene and CP. By varying ethylene pressure, a series of poly(E-*co*-CP)s with different CP contents were prepared using **49**/MAO

Table 4.4 Block copolymers based on cycloolefins.

Entry	Block copolymer	Catalyst precursor(s) used
1	Poly(E-*co*-NB)$_x$-*b*-poly(E-*co*-NB)$_y$	96b
2	PE-*b*-poly(E-*co*-NB)	96b, 79a
3	PE-*b*-(E-*co*-CP)$_x$-*b*-(E-*co*-CP)$_y$	49
4	PE-*b*-poly(E-*co*-CP)	79a
5	*s*PP-*b*-poly(P-*co*-NB)	43
6	PNB-*b*-poly(P-*co*-NB)-*b*-PP	43
7	 PNB-*b*-poly(acetylene)	110

E, ethylene; NB, norbornene; PE, polyethylene; *s*PP, syndiotactic polypropylene; CP, cyclopentene; PNB, polynorbornene.



Scheme 4.13 Synthesis of ethylene/norbornene (NB) and ethylene/cyclopentene (CP) block copolymers.

(Figure 4.17, Scheme 4.13) [223]. When ethylene pressure was low (<1 psi), an almost perfectly alternating copolymer was formed ($M_n = 21\,000$ g mol^{-1}, $M_w/M_n = 1.34$, $T_g = 10.1\,°\mathrm{C}$). However, the use of higher ethylene pressures (3 psi) resulted in the formation of a random copolymer containing 36 mol%

CP ($M_n = 133\,000\ \mathrm{g\ mol^{-1}}$, $M_w/M_n = 1.24$, $T_g = -4.5\,°\mathrm{C}$). Microstructural analysis using ^{13}C NMR spectroscopy revealed that in both cases all CP units were isolated and enchained in a 1,2 fashion. Tri- and multiblock copolymers were synthesized in which the constituent blocks differed in their CP content.

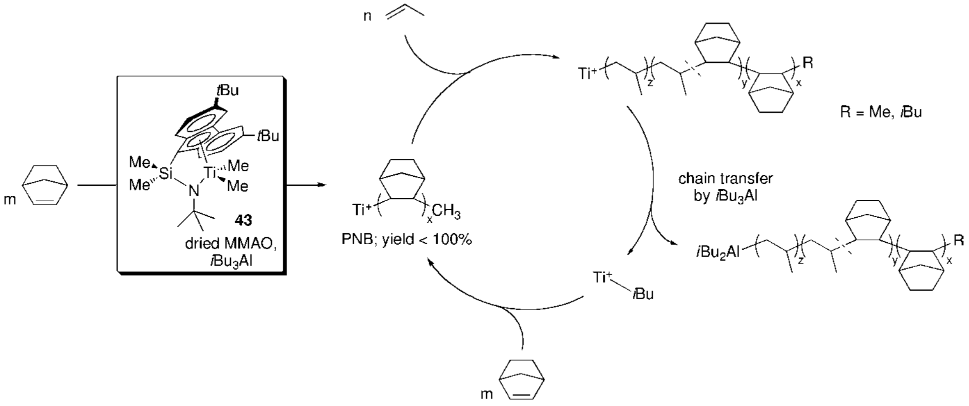
Copolymers from ethylene and NB have also been made using **49**/MAO [224]. With this catalyst, a high molecular weight, low PDI poly(E-*co*-NB) sample was prepared ($M_n = 238\,000\ \mathrm{g\ mol^{-1}}$, $M_w/M_n = 1.05$) containing 62 mol% ethylene and a T_g of 86.5 °C. In addition, **49**/MAO was also used to synthesize a high molecular weight poly(E-*co*-P)-*b*-poly(E-*co*-NB) sample ($M_n = 576\,000\ \mathrm{g\ mol^{-1}}$, $M_w/M_n = 1.13$).

Bis(enaminoketonato)titanium catalysts have been employed in the living copolymerization of ethylene and cyclic olefins. Li and coworkers have prepared a PE-*b*-poly(E-*co*-NB) block copolymer through sequential monomer addition with **79a**/MAO (Figure 4.35) [162]. The diblock copolymer had a narrow polydispersity ($M_w/M_n = 1.38$, $M_n = 143\,000\ \mathrm{g\ mol^{-1}}$) and a NB content of 11.1 mol%. In a subsequent report, PE-*b*-poly(E-*co*-CP) was prepared in a nearly identical manner [201].

As discussed in section 4.3.2, **43**/MAO (Figure 4.16) is living for the polymerization of propylene as well as for the copolymerization of ethylene and NB. In 2006, Shiono and coworkers were able to show that **43**/MAO could also copolymerize propylene and NB in a living fashion to form random and block copolymers [225]. For example, three *s*PP-*b*-poly(P-*co*-NB) diblock copolymers were synthesized through sequential monomer addition that had similar molecular weights ($M_n \sim 20\,000\ \mathrm{g\ mol^{-1}}$, $M_w/M_n = 1.21–1.32$). As was discussed in section 4.6.1, **43**/dMMAO containing 0.4 mol% TIBA is living for NB polymerization to furnish PNB. Shiono and coworkers were also able to show that **43**/dMMAO containing 1.8 mol% TIBA could furnish PNB-*b*-poly(P-*co*-NB)-*b*-PP triblock copolymers in a catalytic fashion [188]. The successive addition of NB and propylene before complete consumption of NB gives PNB-*b*-poly(P-*co*-NB)-*b*-PP terminated with a Ti–PP bond, which can be exchanged with TIBA. Repeated addition of NB and propylene gives a catalytic synthesis of the triblock copolymers in this system (Scheme 4.14).

4.8.5
Block Copolymers Containing Blocks Derived from 1,5-Hexadiene Polymerization

Several classes of catalysts have been used to prepare block copolymers derived from 1,5-hexadiene; these are listed in Table 4.5. The 1-hexene and 1,5-hexadiene homopolymerization behavior of **19b**/[PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (Figure 4.7) were discussed in sections 4.2.5 and 4.5.3. Sita and coworkers were able to prepare diblock and triblock copolymers of 1-hexene and 1,5-hexadiene [182]. Isotactic poly(1-hexene)-*b*-PMCP and isotactic poly(1-hexene)-*b*-PMCP-*b*-PH were obtained from **19b**/[PhNMe$_2$H][B(C$_6$F$_5$)$_4$] at −10 °C



Scheme 4.14 Catalytic synthesis of block copolymers from norbornene and propylene using **43**/dMMAO–TIBA.

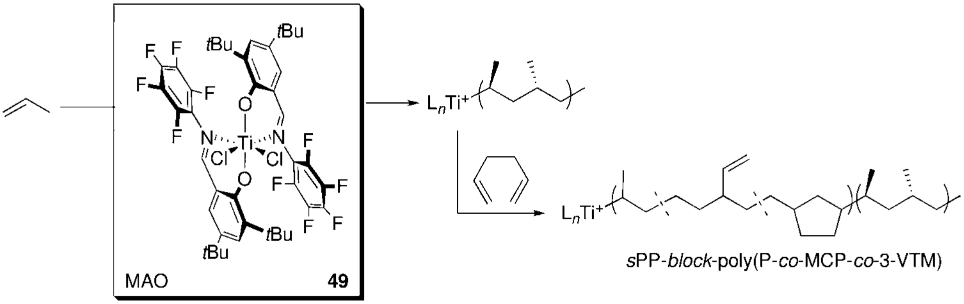
Table 4.5 Block copolymers based on 1,5-hexadiene.

Entry	Block copolymer	Catalyst precursor(s) used
1	*i*PH-*b*-PMCP-*b*-*i*PH	**19b**
2	*s*PP-*b*-poly(P-*co*-MCP-*co*-VTM)	**49**
3	Poly(E-*co*-P)-*b*-poly(MCP-*co*-VTM)	**49**
4	Poly(MCP-*b*-VTM)-*b*-poly(E-*co*-NB)	**49**

PH, poly(1-hexene); PMCP, poly(methylene-1,3-cyclopentane); *s*PP, syndiotactic polypropylene; VTM, vinyl-tetramethylene; E, ethylene; P, propylene; NB, norbornene.

through sequential monomer addition. The diblock copolymer possessed $M_w/M_n = 1.05$ and $M_n = 22\,800\ \text{g mol}^{-1}$ with $T_m = 91\,°\text{C}$. The triblock copolymer had $M_w/M_n = 1.10$, $M_n = 30\,900\ \text{g mol}^{-1}$, and $T_m = 79\,°\text{C}$. Atomic force microscopy (AFM) revealed that microphase separation of the crystalline PMCP and amorphous PH had occurred.

Using **49**/MAO (Figure 4.17), Coates and Hustad reported the living copolymerization of propylene and 1,5-hexadiene to produce random copolymers comprised of units of propylene, MCP, and 3-VTM [181]. A *s*PP-*b*-poly(P-*co*-MCP-*co*-3-VTM) diblock copolymer was also synthesized with **49**/MAO through sequential monomer addition (Scheme 4.15). The molecular weight distribution of the block copolymer was low ($M_w/M_n = 1.11$, $M_n = 93\,300\ \text{g mol}^{-1}$) and contained 4.3 mol% MCP units and 2.7 mol% 3-VTM units. A poly(E-*co*-P)-*b*-poly(MCP-*co*-3-VTM) was also synthesized ($M_n = 524\,700\ \text{g mol}^{-1}$, $M_w/M_n = 1.13$). Lastly, **49**/MAO has been used to produce a high molecular weight poly(MCP-*co*-3-VTM)-*b*-poly(E-*co*-NB) sample with $M_n = 451\,000\ \text{g mol}^{-1}$ and $M_w/M_n = 1.41$ [224].



Scheme 4.15 Synthesis of a block copolymer from propylene and 1,5-hexadiene using **49**/MAO.

Table 4.6 Block copolymers based on polar monomers.

Entry	Block copolymer	Catalyst precursor(s) used
1	*s*PP-*b*-poly(THF)	**37**
2	*s*PP-*b*-PMMA	**37**
3	PE-*b*-PMMA	**101,102**
4	PE-*b*-PCL	**101,102**
5	PE-*b*-PVL	**101**
6	PMMA-*b*-PE-*b*-PMMA	**106,107**
7	PCL-*b*-PE-*b*-PCL	**106,107**
8	PBA-*b*-PE	**109**

*s*PP, syndiotactic polypropylene; THF, tetrahydrofuran; PMMA, poly(methyl methacrylate); PCL, poly(ε-caprolactone); PVL, poly(δ-valerolactone); PBA, poly(*n*-butyl acrylate).

4.8.6
Block Copolymers Containing Blocks Derived from Polar Monomers

One of the most challenging goals in block copolymer synthesis is the incorporation of polar monomers because of the limited number of catalysts that can tolerate polar functionalities. Catalysts that have been employed in the synthesis of block copolymers incorporating polar monomers are listed in Table 4.6. In 1983, Doi reported the use of **37**/Et_2AlCl (Figure 4.15) for the synthesis of a series of PP-*b*-poly(THF) AB-type diblock copolymers by quenching a living propylene polymerization with iodine and using the iodide-terminated PP to initiate cationic polymerization of THF [83].

Catalyst **37**/Et_2AlCl has also been used to synthesize PP-*b*-PMMA (PMMA) = poly(methyl methacrylate) [226]. At −78 °C, **37**/Et_2AlCl was used to polymerize propylene to which MMA was then added. The MMA polymerization, which was proposed to proceed via a radical mechanism, was conducted at 25 °C to form the diblock copolymer.

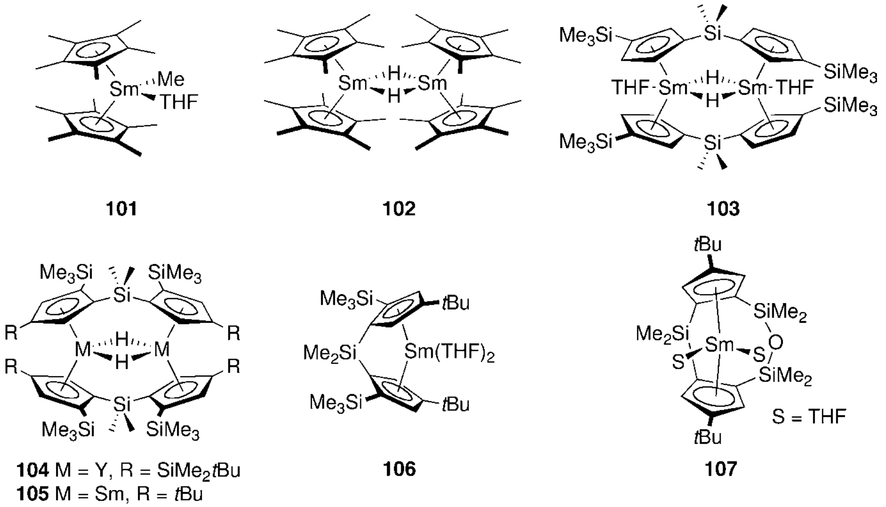
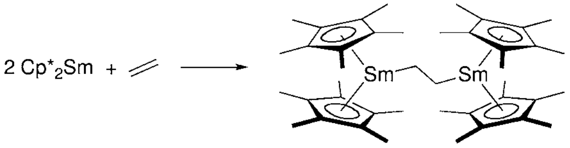


Figure 4.47 Rare earth metal catalysts for block copolymerization.

Yasuda and coworkers described the synthesis of block copolymers containing PE (insertion mechanism) with several polar monomers (noninsertion mechanism) such as MMA, methyl acrylate (MA), ethyl acrylate (EA), δ-valerolactone (VL), and ε-caprolactone (CL) via sequential addition using [$Cp^*_2SmMe(THF)$] and [$Cp^*_2SmH]_2$ (**101** and **102**, Figure 4.47) [227]. Ethylene was first polymerized ($M_w/M_n = 1.39–2.01$, $M_n = 6600–27\,000$ g mol^{-1}) followed by addition of the respective polar monomer to form a diblock copolymer. Reversal of monomer addition led to no block copolymer formation. Thus a PE-*b*-PMMA, PE-*b*-PMA, PE-*b*-PEA, PE-*b*-PVL, and PE-*b*-PCL were synthesized, which showed good material properties such as deep coloration with dyes. In a subsequent report, the structurally related **103** (Figure 4.47) was also shown to be a viable block copolymerization catalyst for ethylene, MMA, and CL [228]. Furthermore, in 2000 Yasuda and coworkers reported on the synthesis of diblock copolymers poly(1-pentene)-*b*-PH and PMMA-*b*-poly(ε-caprolactone) (PCL) using the structurally similar bridged Cp-bearing yttrium and samarium catalysts **104** and **105** (Figure 4.47) via sequential monomer addition [229].

It had been previously shown that Cp^*_2Sm is active for ethylene homopolymerization involving coordination of ethylene by two Sm^{II} centers followed by electron transfer to form a telechelic initiator (Scheme 4.16) [230]. Yasuda and coworkers cleverly applied this observation to the synthesis of triblock copolymers of ethylene and polar monomers [231]. Thus, triblock copolymers of PMMA-*b*-PE-*b*-PMMA, PCL-*b*-PE-*b*-PCL, and PDTC-*b*-PE-*b*-PDTC (PDTC) = poly(2,2-dimethyltrimethylene carbonate) were prepared through sequential monomer addition with **106** and **107** (Figure 4.47).

As discussed in section 4.2.9, **34c** (Figure 4.13) is quasiliving for 1-hexene polymerization [69]. It was also discovered that addition of CO

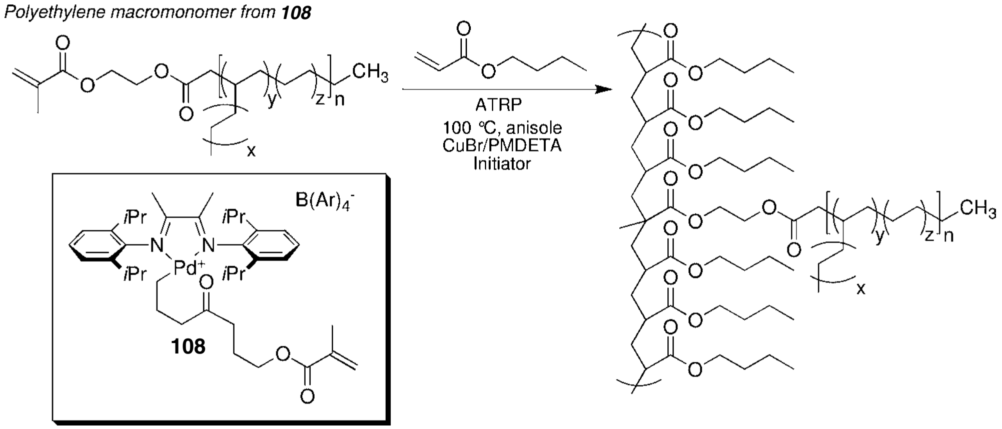


Scheme 4.16 Formation of telechelic initiator for ethylene polymerization from $Cp_2{}^*Sm$.

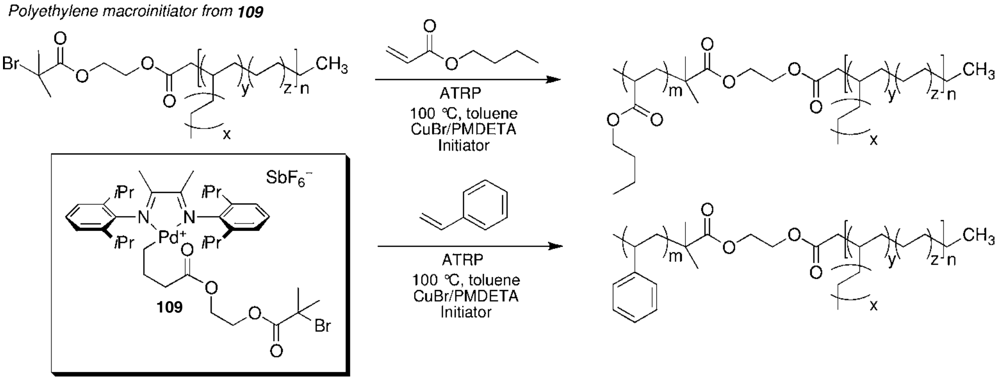
in the presence of 1-hexene afforded an alternating copolymer. Taking advantage of this, a PH-*b*-poly(1-hexene-*alt*-CO) diblock copolymer was made through sequential monomer addition. Similarly, a PE-*b*-poly(ethylene-*alt*-CO) diblock copolymer was also synthesized through sequential monomer addition.

Brookhart and Matyjaszewski combined living insertion polymerization with living ATRP (atom transfer radical polymerization) techniques to synthesize graft copolymers. Palladium diimine chelate complexes have been previously used for living polymerization of ethylene, affording end-functionalized branched PEs [232]. Catalyst **108** (Scheme 4.17) builds on this strategy by appending an acrylate ester, forming a PE macromonomer that was incorporated into a living ATRP of *n*-butyl acrylate to generate poly(*n*-butyl acrylate)-*g*-PE. Graft copolymers of moderate molecular weight (M_n = up to 115 000 g mol^{-1}) were obtained with approximately 4–5 grafts per chain and relatively narrow molecular weight distribution (M_w/M_n as low as 1.4).

Ye and coworkers combined living insertion polymerization with living ATRP techniques to generate block copolymers with a functionalized palladium diimine catalyst [233]. Catalyst **109** (Scheme 4.18) appended with bromo functionality forms a PE macroinitiator that was incorporated into a



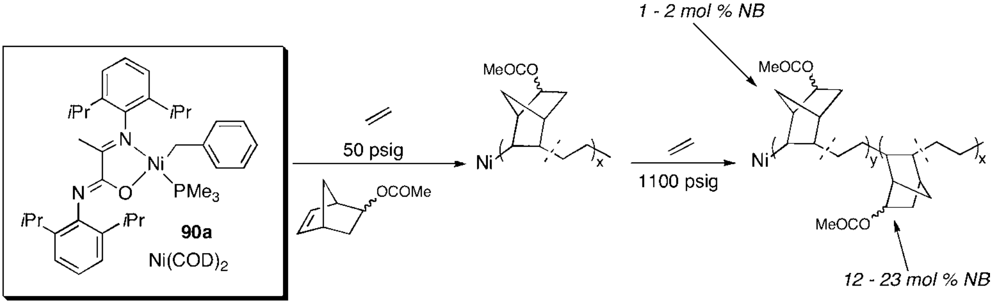
Scheme 4.17 Living insertion/ATRP graft copolymer synthesis.



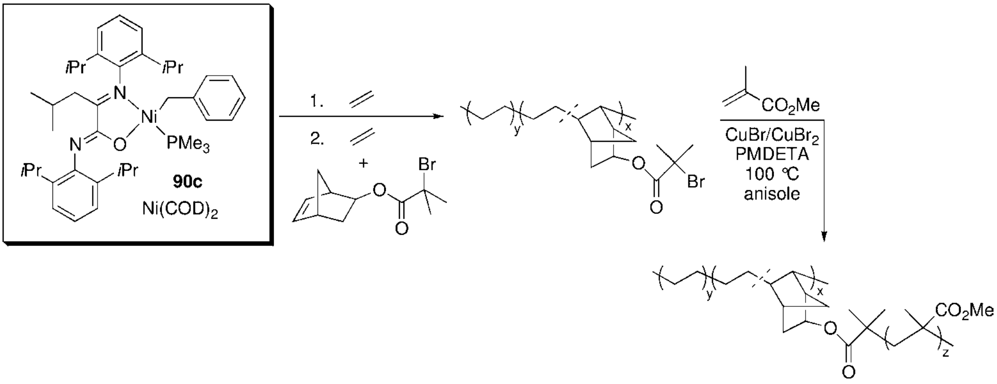
Scheme 4.18 Synthesis of PE-*b*-poly(*n*-butyl acrylate) and PE-*b*-polystyrene diblock copolymers.

living ATRP of *n*-butyl acrylate or styrene to generate poly(*n*-butyl acrylate)-*b*-PE and PS-*b*-PE diblock copolymers (Scheme 4.20).

Bazan and coworkers adopted a strategy based on a pressure-jump technique to synthesize block copolymers with different ratios of ethylene [234]. Catalyst **90a** (Figure 4.40) was previously shown to copolymerize ethylene with 5-norbornen-2-yl acetate with quasiliving behavior [176]. Polymerization of 5-norbornen-2-yl acetate and 50 psi ethylene generates an amorphous copolymer with approximately 25% polar monomer incorporation. After a given reaction time (8–45 min), the ethylene pressure was increased to 1100 psi, leading to formation of an essentially PE block (Scheme 4.19) with relatively narrow polydispersities ($M_w/M_n = 1.3–1.6$). GPC analysis is consistent with diblock formation, as are the DSC data. TEM analysis demonstrated that the materials are microphase-separated, consistent with blocks of distinct compositions. Tapered copolymers (TCPs) have also been prepared with this system, which allows depletion of 5-norbornen-2-yl acetate under a constant ethylene pressure



Scheme 4.19 Synthesis of block copolymers from ethylene and 5-norbornen-2-yl acetate using a neutral nickel catalyst.



Scheme 4.20 Synthesis of PE-*g*-PMMA copolymers using a neutral nickel catalyst and ATRP.

[235]. It was observed that as 5-norbornen-2-yl acetate concentration depletes, semicrystalline properties are obtained after specific reaction times, consistent with the fact that ethylene-rich segments are formed indicating pseudo-diblock copolymer formation. This strategy was used to make pseudo-tetrablock copolymers by addition of a second batch of 5-norbornen-2-yl acetate after a prescribed time [236]. Tensile testing revealed a strain-to-break of about 1000% at 65 °C with 80% elastic recovery.

In a subsequent report, Bazan and coworkers combined living insertion polymerization with living ATRP techniques to synthesize graft copolymers [237]. Polymerization of ethylene followed by copolymerization with 5-norbornen-2-yl-2′-bromo-2′-methyl propanoate using **90c** (Figure 4.40) activated with Ni(COD)$_2$ furnished a PE macroinitiator. Subsequent polymerization with MMA by living ATRP methods furnished PE-*g*-PMMA copolymers (Scheme 4.20).

Risse showed that [Pd(MeCN)$_4$][BF$_4$] polymerized a wide variety of ester-functionalized NBs, in some cases with narrow molecular weight distributions and with linear increase in M_n over time [187]. Sequential addition of a NB monomer with different substitution patterns afforded diblock copolymers of moderate molecular weight.

Novak significantly advanced the field of palladium-mediated living olefin polymerization with the design of σ,π-bicyclic Pd catalyst **110** (Figure 4.48), which is both highly air- and moisture-stable because of

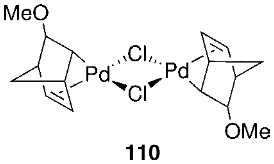


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Figure 4.48 Palladium catalyst used for the synthesis of norbornene/acetylene block copolymers.

the chelation by the appended olefin but exhibits good activity for living polymerization [238]. This unique and robust living behavior was demonstrated by the synthesis of well-defined block copolymers of NB and diethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate. A subsequent retro-Diels–Alder reaction on this polymer afforded a discrete PNB-*b*-poly(acetylene) copolymer.

4.9
Outlook and Summary

The last decade has seen significant new advances in the field of living olefin polymerization. Many efficient and selective catalysts are now available for the living polymerization of ethylene in addition to living and stereoselective polymerization of α-olefins. This allows the creation of unlimited new polymer architectures such as block copolymers and end-functionalized macromolecules. The ability to synthesize such polymers will allow the detailed study of the effect of polymer microstructure on the mechanical and physical properties of this new class of materials.

As we wrote in our previous reviews [2, 3], the main challenge facing this new field is that these expensive metal complexes form only one polymer chain during the polymerization reaction, resulting in economically nonviable materials for commodity applications. Significant research in developing catalytic systems that can produce multiple chains per metal center must be conducted. One strategy to accomplish this goal is to add excess amounts of an inexpensive metal complex, which will rapidly transmetallate the active living catalyst, producing many chains per metal center [134–136, 239–243]. This strategy can then be used to create multiple block copolymers per metal center by varying polymerization conditions [188, 244]. A second strategy is to add an external agent at specific intervals during the living polymerization to terminate a chain and begin a new one [155]. Third, metal complexes that transmetallate at rates slower than monomer enchainment but faster than chain formation have the potential to produce block copolymers when two different polymerization catalysts are used [209, 210, 245–247]. Finally, nonliving catalysts that can be induced to introduce blocks on a timescale faster than that of chain formation can be used to make block copolymers [208].

Future research will continue to uncover new living systems capable of making unique polyolefin structures, and these advances will greatly expand the range of polyolefin materials. New strategies for developing catalyst systems capable of furnishing multiple chains per metal center will allow commodity polyolefin production from living catalysts. Undoubtedly, the future for specialty materials is a bright one in light of continued new developments in the field of living olefin polymerization.

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5
Living Ring-Opening Polymerization of Heterocyclic Monomers

Stanislaw Penczek, Marek Cypryk, Andrzej Duda, Przemyslaw Kubisa, and Stanislaw Słomkowski

5.1
Introduction

The meaning of terms *controlled* and *living* polymerizations has been discussed a number of times. Comprehensive description of both terms has been given by Editors of this volume and more recently defined by the IUPAC Polymer Division.

Szwarc has never defined the ''living polymerization'', although stressed, that ''living polymers should retain at least some ability to grow'' [1]. IUPAC Subcommittee for Macromolecular Terminology (a part of the IUPAC Polymer Division) in a recently published document [2] proposed to embrace by living polymerization all processes ''from which termination and irreversible transfer are absent.'' In the explanatory note to this definition it is added, that reversible deactivation can take place in living polymerizations and the use of unclear/redundant terms like *quasiliving* or *immortal* polymerization is discouraged. In this chapter devoted to ring-opening polymerization (ROP) of heterocyclic monomers definitions given by Szwarc and by IUPAC Polymer Division will be retained.

Living anionic polymerization of vinyl and diene monomers discovered by Szwarc opened a new chapter in macromolecular science. The first papers from *Nature* [1] and *Journal of the American Chemical Society* [3] are still very often cited. Later appeared the monograph on living polymerization published in 1968, a masterpiece of lucid presentation of the most difficult fragments of kinetics and thermodynamics of polymerization [4].

The discovery of anionic polymerization led eventually to the development of controlled cationic [5] and radical [6] vinyl polymerizations, closely related to the living anionic polymerizations, in the way formulated by Szwarc [1, 3, 4]. Then, several coordination (Ziegler–Natta type) [7] and metathesis [8] polymerizations, as well as ROP, were found to operate in the living manner.

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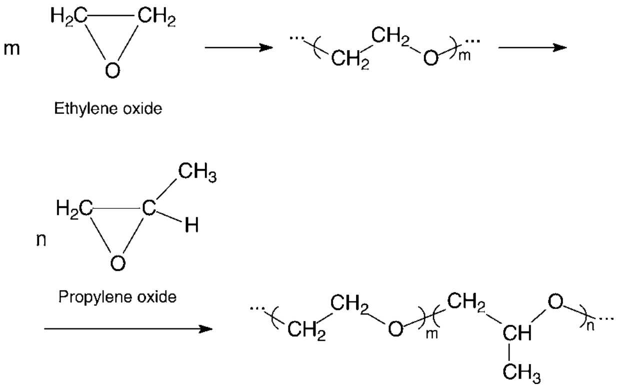
Szwarc used to call anionic vinyl polymerization “my baby”. In this respect the living ring-opening polymerization (LROP) is his grandchild.

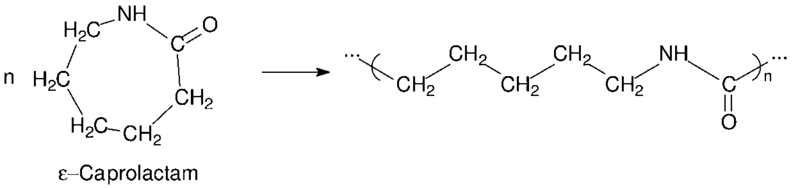
Technologies of polymers made by ROP are usually of much smaller scale and their total “tonnage” is much lower than that of vinyl or olefin polymers. Nevertheless, several technical polymers made by ROP could hardly be replaced by any other synthetic or natural material.

Poly(ethylene oxide) (PEO), one of the most hydrophilic polymers, finding hundreds of applications, particularly in the biomedical field, is a good example of these polymers based on ROP. Particularly well known are the oligomers of ethylene oxide (EO); the monomethyl ethers (MPEG) have found important application as modifiers (“PEGylation”) of biologically active polypeptides. This modification makes polypeptides more stable toward enzymatic hydrolysis. Medium molar mass copolymers of EO with propylene oxide (mostly diblock) contribute a large class of the hydrophilic – hydrophobic surfactants, probably in use in every household of developed countries (Scheme 5.1).

Among technical thermoplastics there are two, perhaps the largest scale, products. One of them is polyamide-6 (Nylon®-6), produced by ionic polymerization of ε-caprolactam. Anionic polymerization of ε-caprolactam directly in molds allows formation of large objects. Nylon-6 is also used for production of fibers (Scheme 5.2).



Scheme 5.1 Sequential polymerization of ethylene and propylene oxides leading to amphiphilic copolymers.



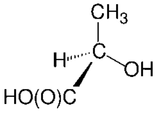
Scheme 5.2 ε-Caprolactam polymerization.

Not less important is polyacetal, another technical thermoplastic produced by cationic copolymerization of 1,3,5-trioxane with EO or 1,3-dioxolane (Scheme 5.3). This copolymerization provides chain-ends stabilized macromolecules eliminating backbiting depropagation.

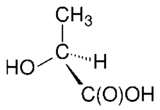
Polyacetal is particularly used for high-precision injection molding parts in various mass-production applications like in electronic devices, cars, various household articles, etc.

ε-Caprolactone (CL) and lactides are the only large scale industrially polymerized monomers in the aliphatic cyclic ester family. The corresponding polymers exhibit useful thermomechanical properties and are biodegradable (Scheme 5.4).

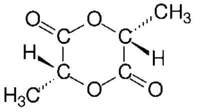
Owing to its chirality there are several lactides, cyclic esters of two molecules of lactic acid; structures of lactic acid are shown below:



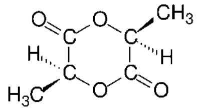
D(-)-Lactic acid



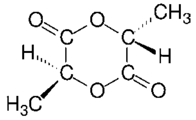
L(+)-Lactic acid



D,D-LA

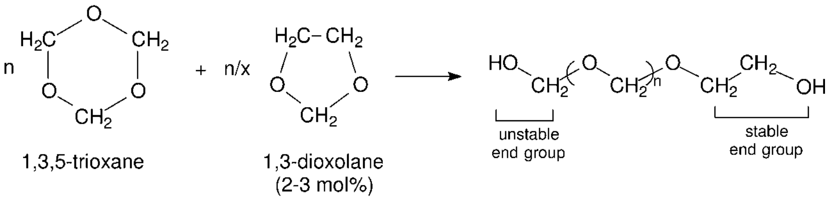


L,L-LA

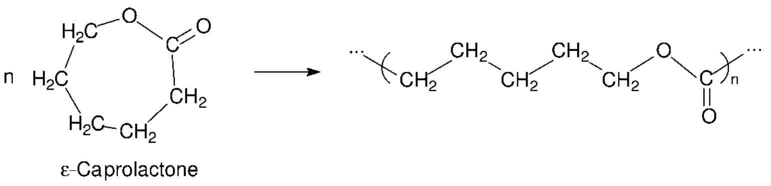


D,L-LA

Thus, lactides are either homochiral: D,D- and L,L- or heterochiral: (D,L-) and (L,D-).



Scheme 5.3 Stabilized poly(1,3,5-trioxane) formation.



Scheme 5.4 ε-Caprolactone polymerization.

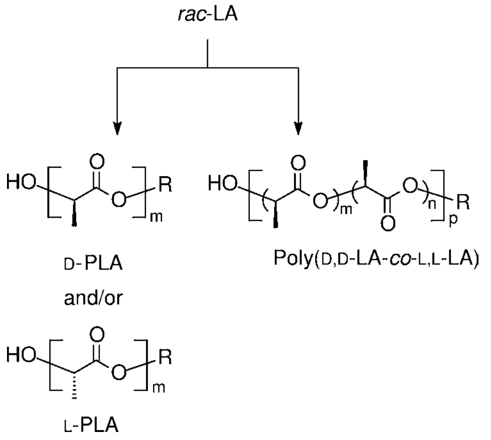
When the *rac*-LA is used for polymerization (Scheme 5.5) a large variety of products could result, depending on the initiator stereospecificity: from homochiral isotactic polylactides (D-PLA or L-PLA) or their equimolar mixture, via gradient poly(D,D-LA-*grad*-L,L-LA) to atactic poly(D,D-LA-*co*-L,L-LA) stereocopolymers. D-PLA/L-PLA equimolar mixture or the gradient stereocopolymer forms stereocomplexes, that reveal enhanced melting temperature compared to that of their homochiral counterparts (see [9] and references cited therein).

Today the major industrial polylactide, however, is poly(L,L-LA) (L-PLA) (e.g., 150 kt/year produced by Cargill in USA). Starting lactic acid for the monomer (L,L-lactide) is produced by fermentation of carbohydrates.

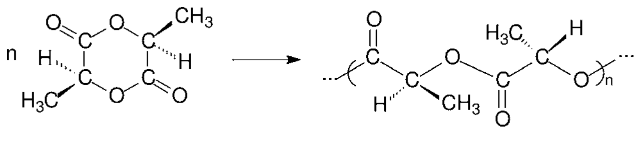
Industrial polymerization of L,L-LA is started by initiators leading to multicenter covalent propagation, excluding this way the possible racemization during the propagation process and leading to the optically active, almost exclusively isotactic polymer (approximately 5 mol% of the D-repeating units are introduced to increase flexibility) (Scheme 5.6) [10].

L-PLA is used either as biodegradable commodity plastic (mostly films for packaging, injection molding parts) or as medical devices. In this latter application amorphous polymers are prepared, produced by D,D-LA and L,L-LA copolymerization.

Polytetrahydrofuran is used either as a homopolymer (of medium molar mass) for press-sensitive adhesives or as an elastic (soft) block, in polyurethanes



Scheme 5.5 General scheme of racemic lactide polymerization.



Scheme 5.6 L,L-Lactide polymerization devoid of racemization.

as well as in the elastoplastic multiblocks, copolymer material, in which hard blocks are made of polyesters of terephthalic acid (Scheme 5.7).

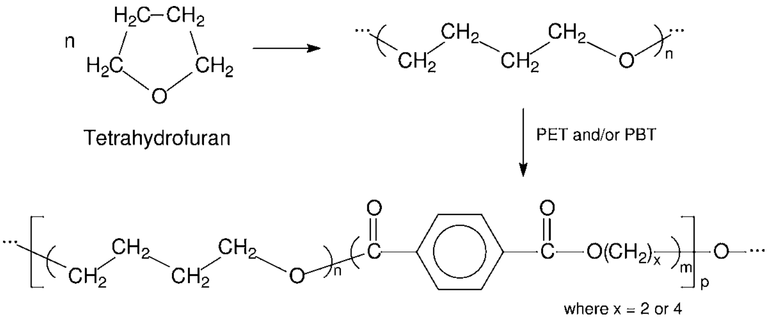
There are also some specialty polymers made or used to be made by ROP, like polyphosphazenes, poly(3,3-bis-chloromethyloxetane) (Penton®), or poly(α-epichlorohydrin). Some of these have disappeared already from the market.

ROP of cyclic oligodiorganosiloxanes is an alternative to the polycondensation method of manufacturing siloxane polymers [11, 12]. Commercially, the polymerization of unstrained octamethylcyclotetrasiloxane (D_4) is the most important. In the presence of catalysts such as strong acids or bases, D_4 undergoes equilibrium polymerization, which results in a mixture of high molecular weight (MW) polymer and low MW cyclic oligomers. The MW of the polymer is easily controlled in the wide range of MW by the amount of chain stopper added.

The synthesis of new, high performance materials requires the synthesis of well-defined, cyclic-free polymers. This can be accomplished by the kinetically controlled polymerization of the strained monomers, hexaalkylcyclotrisiloxanes. In the presence of the proper initiator and under the right reaction conditions, the polymerization of hexamethylcyclotrisiloxane (D_3) can proceed as a classical living polymerization. The most frequently used initiator, lithium silanolate, in the presence of a cation-interacting solvent such as tetrahydrofuran (THF) or nucleophilic additives such as hexamethylphosphoric triamide (HMPT) or dimethyl sulfoxide (DMSO), as well as chelating agents such as cryptands provides fast and quantitative initiation and a propagation that is free of depolymerization or chain-scrambling processes. The nucleophilic additives interact strongly with the lithium cation and convert the intimate ion pair into a more reactive, separated one.

The cationic polymerization of cyclic siloxanes is usually applied to the synthesis of polysiloxanes having base-sensitive substituents such as Si–H.

ROP has been reviewed in the past in a few monographs and book chapters [13–19]. The present review differs in content and in style from the previous



Scheme 5.7 Elastoplastic multiblock copolymer formation involving polytetrahydrofuran blocks.

reviews on ROP. It is not as comprehensive as, for instance, the two volumes of review on cationic ROP [15] and the several chapters in *Comprehensive Polymer Science* [16], or monographs, in which basic principles of living ROP were reviewed [14, 18a-c]. This difference stems not only from the availability of the previous reviews, but also from an easy access to the required information in the Internet. Moreover, the present review is devoted almost exclusively to the controlled ring-opening polymerization (CROP) and LROP. In some chapters deviations from the features of living process are also discussed.

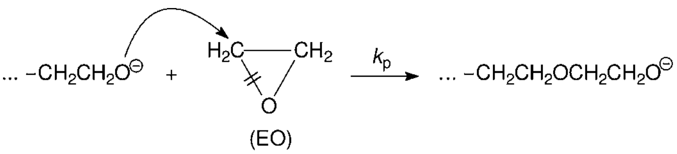
5.2
Anionic and Coordination Living Ring-Opening Polymerization (LROP)

Anionic polymerization of EO is the best known example of LROP and has been extensively studied by a number of authors. In the mid-1940s, Flory observed that propagation in anionic polymerization of EO might proceed without side reactions, such as irreversible transfer and termination [20, 21]. Elementary act of the chain growth in this polymerization, as well as in other anionic LROPs, proceeds in agreement with the S_N2 mechanism, that is nucleophilic bimolecular substitution at the carbon atom (Scheme 5.8).

Analysis of this process presented by Flory pointed to the molar mass control given by molar ratio of the consumed monomer to initiator and Poissonian molar mass distribution (MMD) of the resulting PEO [20]. Despite an apparent simplicity of the anionic polymerization of EO, controlled synthesis of PEO, with regard to its molar mass (M_n) and end–groups structure requires special precautions (see, e.g., Refs [22, 23]).

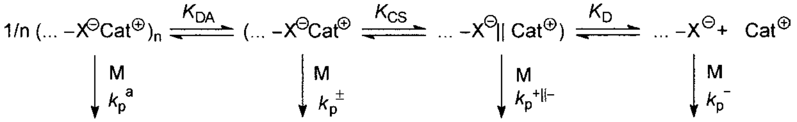
Ionic (e.g., alkoxide) active species can participate in the polymerization in a number of different physical forms: ions, ion pairs, and ionic aggregates, being in slower or faster interexchange (Scheme 5.9 and Table 5.1). Each of these structures can participate in propagation with its own propagation rate constant, as it has been described for the vinyl anionic polymerization [4].

In Table 5.1 taken from Ref. [18a], dissociation constants and interionic distances are collected. The actual structures of active centers have been determined by ion trapping technique, in which the original species have been converted into the derivatives containing the phosphorus atoms [24]. Then, by



Counterion omitted
k_p – rate constant of propagation

Scheme 5.8 Propagation in anionic polymerization of ethylene oxide (EO).



Cat ⊕ – counterion
M – monomer molecule
K_{DA}, K_{CS}, and K_D – equilibrium constants of deaggregation, between contact and separated ion pairs, and of dissociation, respectively
k_p^a, $k_p^{\pm}$, $k_p^{+||-}$ and k_p^- – the corresponding rate constants of propagation

Scheme 5.9 General scheme of interconversion of active species in anionic polymerizations (the same scheme, with opposite charges, applies also for cationic polymerization).

Table 5.1 Dissociation constants (K_D) and interionic distance parameters (*a*) of ion pairs as determined for the anionic polymerization of heterocyclic monomers [18a].

Monomer	Solvent	*T* (K)	Ion pair	K_D (mol l^{-1})	*a* (Å)
EO	THF	293	...–$CH_2CH_2O^-K^+$	1.8×10^{-10}	2.6
	THF	293	...–$CH_2CH_2O^-Cs^+$	2.7×10^{-10}	3.04
	THF	293	...–$CH_2CH_2O^-K^+\cdot$ [2,2,2]	3.0×10^{-7}	4.60
PL	CH_2Cl_2				
	$[M]_0 = 3$ mol l^{-1}	298	...–$CH_2CH_2COO^-K^+\cdot$ DBC	5.0×10^{-5}	2.70
	$[M]_0 = 1$ mol l^{-1}	298	...–$CH_2CH_2COO^-K^+\cdot$ DBC	5.6×10^{-6}	3.40
	DMF				
	$[M]_0 = 0.5$ mol l^{-1}	298	...–$CH_2CH_2COO^-K^+\cdot$ DBC	4.2×10^{-4}	0.5
	$[M]_0 = 1$ mol l^{-1}	298	...–$CH_2CH_2COO^-K^+\cdot$ DBC	2.5×10^{-4}	
CL	THF	293	...–C(O)$(CH_2)_5O^-K^+$	4×0^{-10}	2.80
	THF	293	...–C(O)$(CH_2)_5O^-K^+\cdot$ DBC	7.7×10^{-5}	

EO, ethylene oxide; PL, β-propiolactone; CL, ε-caprolactone; THF, tetrahydrofuran; *T*, temperature; [2,2,2] and DBC, a corresponding cryptand and a dibenzo-18-crown-6 ether, respectively.

^{31}P NMR the observed chemical shifts were compared with chemical shifts of the expected models.

Typically, end capping with diphenylchlorophosphorane (ClP(=O)$(OC_6H_5)_2$) has been applied in the polymerization of oxiranes, thiiranes, lactones, cyclic carbonates, and cyclic siloxanes allowing not only the structure, but also the concentration of active centers to be determined. In the polymerization of substituted oxiranes it was possible to discriminate between the primary and secondary alkoxide anions comparing the end-capped polymerization product with the corresponding models: $C_6H_5CH_2CH_2OP(=O)(OC_6H_5)_2$ and $CH_3CH(C_6H_5)OP(=O)(OC_6H_5)_2$ absorbing at −12.7 and −13.1 ppm δ, respectively. In the P end-capped anionic ROP of styrene oxide signal at

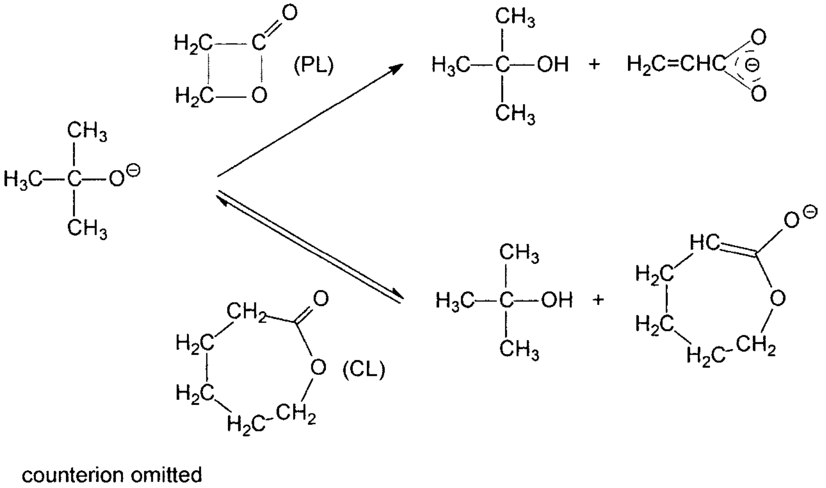
−13.0 ppm δ was observed, pointing to secondary alkoxide anions as the active centers. In the same way it was established, that in polymerization of CL active centers there are alkoxide anions and in polymerization of β-propiolactone (PL) carboxylate anions.

The dissociation constants K_D for alkoxide anions are very low, unless large cations are used, or those complexed with cryptands or crown ethers are used as counterions. Sulfide and carboxylate anions dissociate much easier because of the much more diffused negative charge, and particularly when paired with larger cations in highly polar solvents, with high solvating ability.

5.2.1
Initiation in the Anionic LROP

Initiating systems are known for major cyclic ethers, sulfides, lactones, siloxanes, and cyclic esters of phosphoric acid to start polymerization without any side reactions. These are carboxylic salts for β-lactones [25, 26], alkoxide anions for higher lactones [27], thiolate anions for cyclic sulfides [28, 29] and polysulfides [29, 30], and silanolates for cyclic siloxanes [31]. Therefore, any discussion on the side reactions in initiation pertaining to some other initiating systems from the past does not have to be covered or even remembered. Indeed, hundreds of various compounds have unsuccessfully been used, although the resulting reports have successfully been published.

Anions with high basicity and, because of steric hindrance, low nucleophilicity (e.g., *tert*-butoxide) initiate polymerization mostly with proton transfer in an irreversible [e.g., with PL] or reversible [e.g., with CL] manner (Scheme 5.10) [32].



Scheme 5.10 Initiation of lactone polymerization with anions of high basicity.

Initiation of this class of monomers by some other initiators including several alkoxides also leads finally to the carboxylate anions. The idea of the . . .–C–C–. . . bond breaking in initiation of the four membered lactones has recently been shown to be not true [33]. Actually, Szwarc himself had much earlier expressed some doubts about this unusual hypothesis (p. 69 in Ref. [34]).

Carboxylates are much less nucleophilic than alkoxides and therefore, less efficient as initiators. Acetates are known to initiate the anionic ROP of strained, four membered β-lactones but do not initiate polymerization of the less strained lactones with higher-membered rings. Acetate and benzoate with potassium counterion complexed with crown ether initiate polymerization of EO, propylene oxide, styrene oxide, and cyclosiloxanes [35].

An unusual phenomenon that is not observed in vinyl anionic polymerization, was revealed in reaction of some heterocyclic monomers with ions and cryptated ion pairs. The rate constants of the addition of propylene sulfide (PS) to carbazyl alkali metal salts, studied extensively by Paris group (Sigwalt, Boileau, and Hemery), were found to be strongly dependent on the nature of counterion [36]. With increasing size of counterion the initiation rate constants for the PS polymerization also increase, and eventually, for the cryptated counterion the initiation rate constant on ion pairs becomes higher than that for the free ions (e.g., at certain conditions, $k_{\mathrm{i}}{}^{-} = 4.7 \times 10^{-3}\ \mathrm{l\ mol}^{-l}\ \mathrm{s}^{-1}$, $k_{\mathrm{i}}{}^{\pm} = 1.4 \times 10^{-2}\ \mathrm{l\ mol}^{-l}\ \mathrm{s}^{-1}$; the activation parameters are not available).

The differences in activation energies for ions and ion pairs are related to the Coulombic attraction in ion pairs not existing as ions. However, if activation of a monomer by its complexation with cation is giving a larger gain of energy than the difference in energies of activation due to Coulombic attraction, in reaction with ions and cryptated ion pairs (where the Coulombic attraction is highly weakened), the cryptated ions may become more reactive. This explanation was given by Boileau *et al.* Another explanation could be related to the differences in solvation of ions and ion pairs, like in the process described in the next section for PL and CL, where inversion of reactivities of ions and ion pairs was observed at the isokinetic point.

The ROP has also been initiated by strong organic bases like amines or phosphines (mostly tertiary ones). It was shown that zwitterions are formed [37] and kinetics of their formation was studied [38]. More recent studies on cyclic ester polymerization, however, point to a rather limited possibility of the polymerization control with these organocatalytic systems [39]. For reasons that are not yet clear, formation of the high molar mass ($>10^5$) has not been achieved.

5.2.2
Propagation in the Anionic LROP

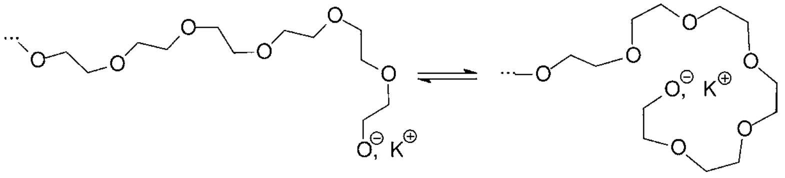
5.2.2.1 Polymerization of O- and S-Heterocyclic Monomers

Propagation of cyclic ethers and cyclic sulfides was in some detail summarized in the earlier published review [18a]. Ethylene and propylene oxides behave in a "normal" way. Ions are much more reactive than ion pairs although the difference is becoming less significant when crowned or cryptated ion pairs are compared with free ions.

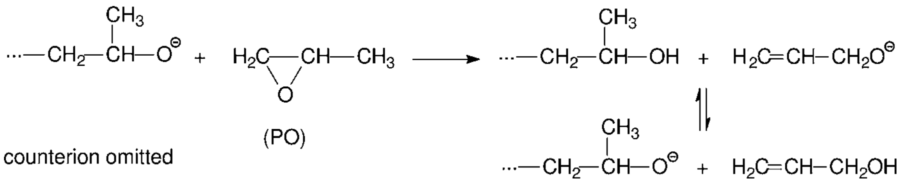
Polymerization of EO in THF solvent, initiated in various ways, gives living polymers in the controlled polymerization process. Strong aggregation (association) of active centers was clearly observed as polymerization, which is first order in active species at low concentration (below 10^{-4} mol l^{-1} for K^+ and Cs^+ as counterions), becomes of a fractional order at higher concentrations [40, 41]. Some of these results were later analyzed again and the degrees of aggregation as well as the corresponding rate constants of propagation (as elementary reaction) were determined [42]. Polymerization, with K^+ as counterion in THF solvent, proceeds with auto acceleration. This is because the polyether chains can solvate the K^+ counterion increasing this way the propagation rate constant of ion pairs by shifting the corresponding equilibrium from contact to separated species and/or increasing the degree of dissociation of ion pairs into ions with monomer conversion (Scheme 5.11).

Anionic polymerization of 1,2-propylene oxide (PO) is an industrial process for the preparation of block copolymers with EO as oligomers, mostly used as nonionic amphiphilic surfactants, as already discussed. High molar mass polymers cannot be prepared this way, because of an extensive chain transfer to PO, typical for the substituted oxiranes (see, e.g., Ref. [43] and the papers cited therein) (Scheme 5.12).

The transfer side reaction can be depressed to some extent by counterion complexation with crown ethers or applications of cations with larger ionic radii, such as Rb^+ or Cs^+ [44]. Nevertheless, even in such systems M_n of poly(1,2-propylene oxide) (PPO) did not exceed 1.5×10^4. Introduction of the



Scheme 5.11 Complexation of the alkoxide active center with the growing PEO chain.



Scheme 5.12 Chain transfer to monomer in the anionic polymerization of 1,2-propylene oxide (PO).

double metal cyanide complexes, based on $Zn_3[Co(CN)_6]_2$, allows preparation of PPO with low degree of unsaturation and better controlled M_n. The corresponding polymerization mechanism remains still obscure [45].

More recently, Billuard *et al.* [46] have shown that polymerization of PO initiated with alkaline metal alkoxides in hydrocarbon solvents can substantially be accelerated in the presence of more than threefold molar excess of trialkylaluminum (AlR_3), with regard to the alkoxide initiator. The chain transfer is also strongly reduced, allowing controlled preparation of PPO up to $M_n \geq 2 \times 10^4$. The role of the added AlR_3 was explained assuming activation of both PO monomer and alkoxide growing species. In this way, the selectivity of the propagation versus transfer was increased. Then, studies of ammonium salts (NBu_4Cl and $NOct_4Br$), and phosphonium salts (PBu_4Cl) in combination with triisobutylaluminum revealed that controlled molar masses as high as $M_n = 1.5 \times 10^5$ in short reaction times can be obtained with these initiating systems [47]. Similar kind of complexation by bulky Al Lewis acid, resulting in an excellent regiocontrol of PO polymerization has been reported by Braune and Okuda [48].

These results bear resemblance to the activation by bulky aluminum aryloxides of PO polymerization, initiated with aluminum porphyrins, discovered and described in detail by Sugimoto *et al.* [49]. Some polymerizations were reported to be accelerated up to 10^3 times, when compared with nonactivated systems. However, it looks that this direction of studies was not further developed, although these initiators, stimulated photochemically, initiated also polymerization of methacrylates. Perhaps one of the reasons is related to the practical difficulty of removing these highly colored ligands from the final products, making the porphyrin-based process not attractive industrially.

The quantitative studies of elementary reactions in the polymerization of cyclic esters, were started by converting or "upgrading" polymerization of PL from the nonliving to the living conditions. This happened thirty years ago when two papers appeared in the same issue of *Macromolecules* revealing that application of crown ethers [50] or cryptates [51] leads to the large increase of the observed rate of polymerization and depression of transfer reactions. This increase of the rate of polymerization when initiated with crowned potassium acetate was over 10^2 times. In agreement with the existing knowledge on the influence of crown ethers and cryptates on the behavior of ionic reactions, it was assumed that these additives broke down aggregates of ion pairs, converting the otherwise unreactive aggregates into the unimeric ion pairs with complexed cations. The next consequence was the increase of concentration of the free ions, as a result of the much higher dissociation constant of the crowned ion pairs.

Polymerization was internally first order in monomer and the apparent rate constant increased with the independently determined degree of ionization (α). Besides, molar masses were linear functions of conversion up to $M_n = 2 \times 10^4$. From the corresponding plots of the apparent rate constant of propagation (k_p^{app}) against α (similar to the "Szwarc's plot") both $k_p{}^-$ and $k_p{}^\pm$ have been

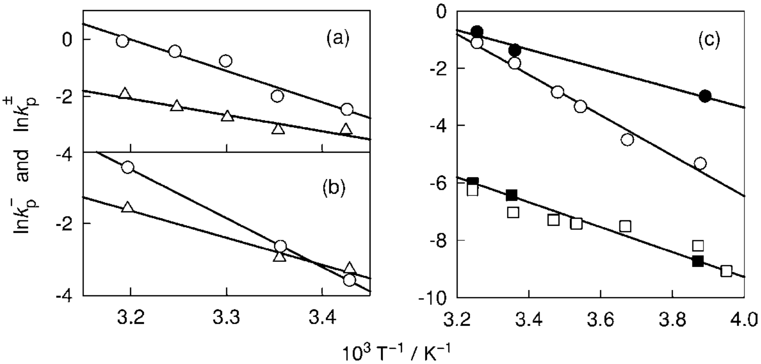


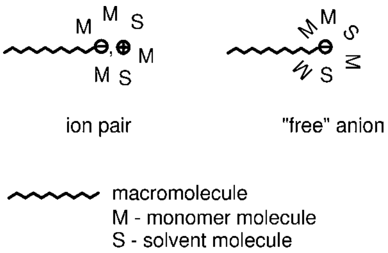
Figure 5.1 Semilogarithmic dependences of the rate constants of propagation on ions (k_p^-) and ion pairs ($k_p^{\pm}$) versus reciprocal of the absolute temperature in the polymerization of PL. (a) k_p^- (○), $k_p^{\pm}$ (△), $[PL]_0 = 5 \times 10^{-1}$ mol l^{-1} in DMF; (b) k_p^- (○), $k_p^{\pm}$ (△), $[PL]_0 = 1$ mol l^{-1} in DMF; (c) k_p^- (●) $[PL]_0 = 1$ mol l^{-1}, k_p^- (○) $[PL]_0 = 3$ mol l^{-1}, $k_p^{\pm}$ (■) $[PL]_0 = 1$ mol l^{-1}, and $k_p^{\pm}$ (□) $[PL]_0 = 3$ mol l^{-1} in CH_2Cl_2 [52, 53].

determined [52]. Later on, Slomkowski was able to go first up to $M_n = 1.5 \times 10^5$ in a controlled way [53] and eventually prepared polymers with $M_n \sim 5 \times 10^5$, which seems to be the limit, at least at room temperature, set by the chain transfer on monomer. The k_p/k_{tr} for PL was later estimated by Duda as equal to 10^4, at least one hundred times larger than that for the methyl-substituted PL (i.e., β-butyrolactone) [26]. On this basis, it was possible to move further on and study the actual propagation process.

Results of these measurements have led to the observation of an unexpected phenomenon. The ion pairs behave in a "normal" way; at 1.0 and 3.0 mol l^{-1} of $[PL]_0$ and their reactivity remains the same (Figure 5.1c), meaning, that the crowned ion pairs are not specifically solvated by components of the system. This is because ion pairs are electrically neutral. On the contrary, the reactivities (expressed by the rate constants values) of ions depend on $[PL]_0$, that is on the solvating power of the milieu (it has been assumed, that monomer can solvate ions).

Comparison of k_p^- and $k_p^{\pm}$ at various temperatures is given in Figure 5.1. At low temperature the reactivity of ions approaches the reactivity of the ion pairs in both CH_2Cl_2 and *N*,*N*-dimethylformamide (DMF) solvents. In DMF it was possible to reach a temperature, at which inversion of reactivities of both species takes place (isokinetic point). Apparently at this low temperature the solvation of ions is so strong, that additional energy is required to remove solvating molecules from its immediate surroundings. Thus, ions are becoming relatively less reactive. Similar phenomena were also observed in the polymerization of CL [54].

Thus, we assume that around the macroion pair (−, +) solvent (S) and monomer (M) molecules are packed disorderly in the available space and are



Scheme 5.13 Ion pair and "free" ion solvation phenomena.

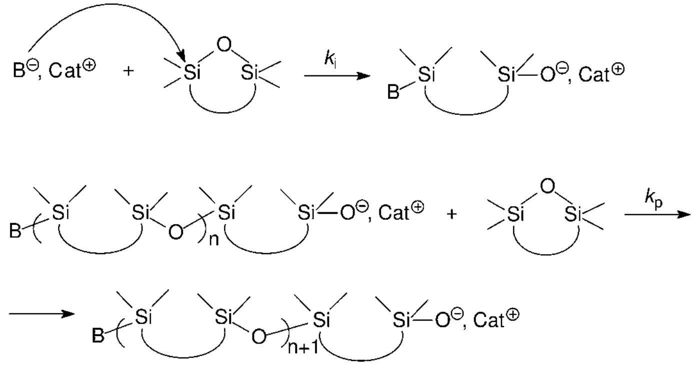
not oriented in any specific way. On the contrary, macroanion is specifically solvated, and thermodynamic potential of the monomer molecules solvating the active species differs from that of monomer in solution (Scheme 5.13).

The lower the temperature the more perfect becomes the solvation shell around ions and removal of solvent and/or monomer molecules, a necessary step preceding propagation, becomes more and more difficult. Thus, the activity of ions decreases faster than the reactivity of ion pairs with lowering of temperature, where the solvation is not important. Then, at a certain temperature, reactivities become equal to one another, which is followed by their inversion after further temperature decrease. Szwarc and van Beylen discussed this system in their book [55], and expressed some doubts on the above presented picture. Particularly they say (Ref. [55], p. 112) "Since the solvated ions contribute to the electric conductance but not to the propagation and the fraction of the free ions was determined by conductance, the propagation rate constant, k_p, is too low." This statement points to another explanation than that given in the original papers [53, 54]. It has been assumed there, that all of the "free" ions are solvated, and that there are no two distinct populations, namely solvated (low reactivity, if any) and nonsolvated with higher reactivity. In the next part of the cited monograph it is however added Ref. [55] "If, however, its (monomer) orientation in the solvation shell is improper for its insertion and its presence hinders the addition of another monomer, the reactivity of the solvated ion might indeed be very low." This second approach of the authors looks to be much closer to the original explanation given in Refs [53, 54].

5.2.2.2 **Polymerization of Si-, N-, and P-Heterocyclic Monomers**

Cyclic Siloxanes Another group of monomers that effectively undergoes anionic CROP and/or LROP are cyclic siloxanes. The basic features of their polymerization have comprehensively been reviewed several times [56–62]. Anionic polymerization of cyclic siloxanes is initiated by strong inorganic, organic, or organometallic bases. The initiation leads to the formation of a silanolate anion which is an active center of propagation (Scheme 5.14).

In a majority of systems, free silanolate ion does not appear in a kinetically significant concentration and the ion pairs are the actual active centers of



$Cat^{\oplus}$ - alkali metal cation, $R_4N^{\oplus}$ or $R_4P^{\oplus}$; $B^{\ominus}$ - $HO^{\ominus}$, $R^{\ominus}$, $R_3SiO^{\ominus}$

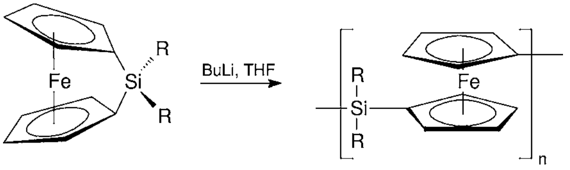
Scheme 5.14 Anionic ring-opening polymerization of cyclic siloxanes.

propagation. Usually, the unimeric silanolate anions exist in equilibrium with higher aggregates. As the aggregated species are much less reactive in propagation than the nonaggregated ion pairs, this phenomenon strongly influences the apparent polymerization rate constants and leads to the fractional order (externally) in the silanolate species (cf. a similar phenomenon observed in the coordination polymerization of cyclic esters discussed in more detail in Section 5.2.3). The average degree of aggregation varies with concentration but is hardly affected by temperature; thus, it is mostly controlled by entropy factors.

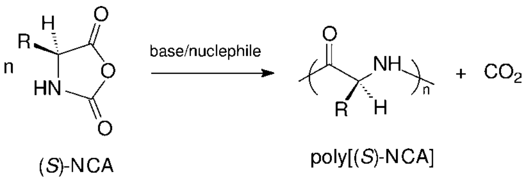
The rate of polymerization of cyclosiloxanes in bulk strongly increases in the series of silanolates SiOLi < SiONa < SiOK < SiORb < SiOCs ≈ $SiONMe_4$ ≈ $SiOPBu_4$ because of the decrease of the anion–cation interaction strength with increase of the cation size, which shifts the equilibrium toward more reactive unimeric ion pairs. Thus, for example, the polymerization of hexamethylcyclotrisiloxane (D_3) initiated with trimethylammonium silanolate is first order in silanolate species. Phosphazene superbase derivatives are very effective initiators of the anionic ROP of cyclosiloxanes [60–66]. As the positive charge in phosphazenium cation is effectively delocalized by the resonance effect, the existence of the free silanolate anion in such systems is highly favorable.

Uncharged nucleophiles, such as HMPT, DMSO, and DMF, as well as crown ethers and cryptands, capable of interacting with metal cations, substantially reduce the strength of the anion–cation interaction and dramatically increase the polymerization rate [56–61]. In nonpolar media, the multidendate interaction of metal cation with siloxane chain plays an important role [58, 59] like that described in Section 5.2.2.1, solvation of potassium cation by the PEO chain.

Although neither termination nor irreversible transfer occurs in the anionic ROP of cyclic siloxanes, only the process involving cyclotrisiloxanes in the presence of nucleophilic promoters may be considered as conforming to living and controlled system. Because of the high reactivity of these monomers,



Scheme 5.15 Polymerization of ferrocenylsilanes.



Scheme 5.16 Anionic ring-opening polymerization of *N*-carboxyanhydrides (NCAs).

initiation is fast and the side reactions are negligible up to almost complete monomer conversion. The yield of polymer may be almost quantitative, M_ns increase linearly with conversion and are controlled by the starting monomer to initiator molar ratio. M_ns of the resulting polysiloxanes may exceed 10^6 and are limited by the level of impurities in the system. Typically, the Poissonian MMD is observed in these systems ($M_w/M_n < 1.1$).

A novel process of polymerization of cyclic siloxanes has been developed by De Gunzbourg *et al.* [67a]. Anionic miniemulsion process was also used for polymerization cyclotrisiloxanes with substituents other than methyl. The process is experimentally rather simple, although the description is very complex. A kinetic study of polymerization of 1,3,5-tris(trifluoropropyl)trimethylcyclotrisiloxane (F_3) showed that polymerization occurs in two stages. During the first stage, which corresponds to the anionic nonequilibrium ROP of F_3, the backbiting and condensation reactions are insignificant and well-defined α,ω-dihydroxy-terminated polymer is produced in very high yields and with molar masses ranging from 2500 to 3500. In the second stage condensation and backbiting reactions become dominating. M_n of polymer increases up to $3-6 \times 10^4$ and dispersity ($D_n = M_w/M_n$)) approaches 2.0 [67b].

The incorporation of transition metals and main group elements into the main chain provides new interesting self-assembled materials. The example of such polymers are poly(ferrocenylsilane)s (PFSs) and its block copolymers. Living carbanionic ROP permitted the synthesis of PFS with predictable MWs and narrow MW distributions (Scheme 5.15) [68a,b].

Lactams and *N*-Carboxyanhydrides There are two major classes of cyclic monomers providing polyamide: lactams, employed for large scale engineering thermoplastic and fiber forming material production, and *N*-carboxyanhydrides (NCAs) of α-amino acids mostly used for preparation of polymers resembling proteins.

Anionic polymerization of lactams has recently been reviewed by Hashimoto [69]. Other, comprehensive reviews were published several years ago by the most active researchers in this field, namely Sekiguchi [70] and Sebenda [71, 72]. In these reviews major features of the anionic polymerizations are described, encompassing also the active chain end (ACE) (including hydrolytic polymerization), as well as activated monomer (AM) polymerizations. The expression ''AM'' mechanism was coined by Szwarc [73] to explain the mechanism of NCA's polymerization and has also been adopted for the anionic polymerization of lactams [71].

Conditions of polymerization have been found for living polymerization of these monomers. Both basic and nucleophilic initiators were able to give high molar mass polymers without detectable racemization at the centers of chirality (Scheme 5.16) [74–78].

Initially, it was not possible to achieve controlled polymerization of NCA. Chain termination and transfer of various origins prohibited molar mass control and led to broad MMDs. Therefore, in synthesis of block copolymers, the expected products were contaminated by the undesired homopolymer fractions. This was caused by various factors, such as insufficient purity of components of the reacting mixture or simultaneous presence of different polymerization modes (e.g., amine vs. AM competition).

Propagation in ''amine mechanism'' is based on the nucleophilic attack of the primary amine on the carbonyl carbon atom followed by the acyl–oxygen bond scission and the proton transfer; finally CO_2 is liberated. Proton abstraction from a NCA monomer leads to the AM pathway and can be considered as a chain transfer to monomer (Scheme 5.17).

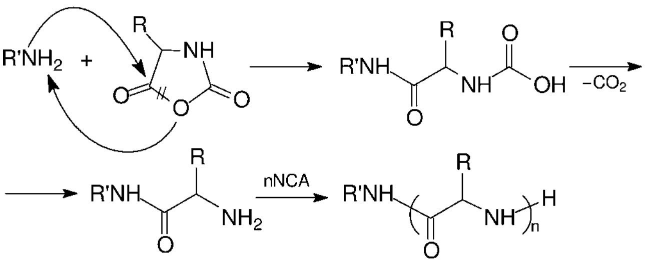
Schlaad *et al.* [79–81] have shown recently that the proton abstraction side reaction can be considerably depressed by initiating the NCA polymerization with primary amine hydrochloride ($R'NH_3^+Cl^-$) instead of amine. Most probably $R'NH_3^+Cl^-$ plays a double role: as a dormant form of $R'NH_2$ and as a source of protons deactivating the already formed AM (NCA^-).

Independently, Hadjichristidis *et al.* [82, 83] applied high vacuum technique for ROP of NCA, initiator and solvent purification, and for carrying out polymerizations. They claimed that the purity of the reacting mixture was sufficient to realize control in NCA polymerization, at least for the primary amine initiated process.

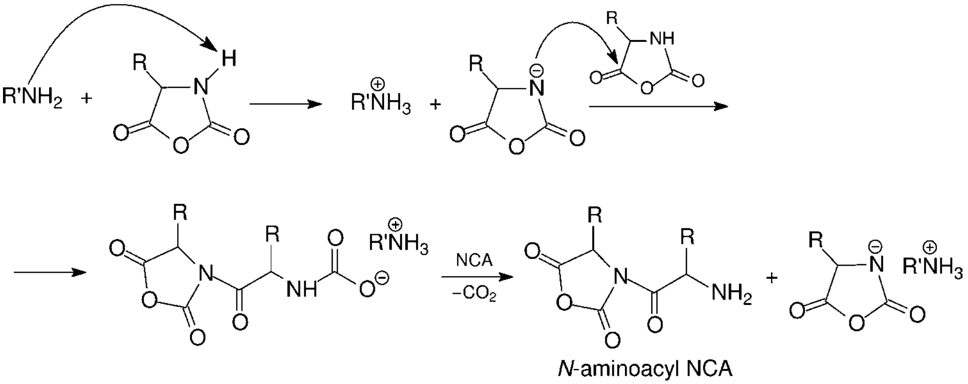
This observation shows once again that some systems could be converted into controlled/living ones by simply changing minute elements of the process.

Cyclic Esters of the Acids of Phosphorus (Phosphoric, Phosphonic) Anionic polymerization of five- and six-membered cyclic ethers of phosphoric and phosphonic acids may also lead to controlled/living processes when proper conditions are found [84, 85]. Kinetic studies were carried out for 2-methoxy-2-oxo-1,3,2-dioxaphospholane [86], 2-methoxy-2-oxo-1,3,2-dioxaphosphorinane

(a) amine mechanism



(b) activated monomer mechanism

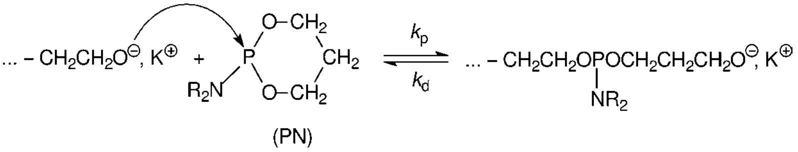


Scheme 5.17 Competition of "amine" and "activated monomer" mechanisms in polymerization of *N*-carboxyanhydrides (NCAs).

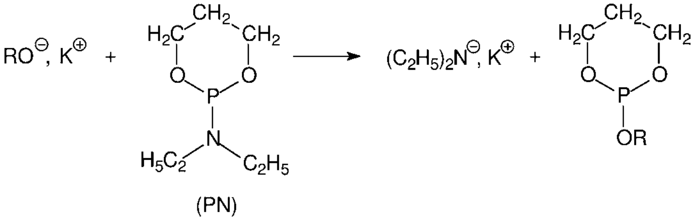
[87], and 2-*N*,*N*-dimethylamino-2-oxo-1,3,2-dioxaphospholane [88] polymerizations.

Model studies have revealed, that polymerization initiated with alkoxide anions proceeds with anions of the same structure as the growing species (Scheme 5.18) [88].

Initiation with ${}^tC_4H_9O^-$, K^+ has shown that ${}^tC_4H_9O$ moiety is directly attached to the phosphorus atom (as revealed by ${}^1H$ and ${}^{31}P$ NMR studies) and



Scheme 5.18 Propagation in anionic polymerization of 2-*N*,*N*-dialkylamino-1,2,3-dioxaphosphorinane (PN).



Scheme 5.19 Termination of the polymer chain growth in anionic polymerization of the PN monomer.

not to the carbon atom, indicating that in the chain growth the nucleophilic attack on the P atom leads to the ...–P–O–... bond scission with reforming of the alkoxide anion in every next propagation step.

Kinetic plots of propagation are linear in the semilogarithmic coordinates, allowing determination of the pertinent rate constant of propagation (e.g., $k_p = 3.4 \times 10^{-4}$ l mol^{-1} s^{-1}, in THF solvent, at 25 °C for the PN monomer). Thus, this is a relatively slow process, easy to handle. Nevertheless, in spite of the original linearity of the kinetic plots, some curvature is observed at higher monomer conversion, indicating that sufficient control is only possible below a certain conversion. These conversions, however, would differ depending on the polymerization conditions; lowering the polymerization temperature seems to allow a better control.

Moreover, when monomer was mixed with initiator at comparable concentrations, a new resonance peak appeared in the ^{31}P NMR spectrum. Its position is identical with that of 2-*tert*-butoxy-1,3,2-dioxaphosphorinane. Thus, the process visualized in Scheme 5.19 takes place.

Similar reaction may take place between a growing alkoxide anion and both monomer and polymer units, leading to termination and hence, curvature of the kinetic semilogarithmic plots. Indeed, in an independent experiment it has been shown that potassium ethylamide, $(C_2H_5)_2N^-K^+$, does not initiate polymerization.

The kinetic scheme, involving termination, as described above, is shown in Scheme 5.20.

This scheme gives finally Eq. (5.1) enabling determination of k_p and k_t.

$$\ln \frac{-\mathrm{d}[M]}{([M]-[M]_{eq})\mathrm{d}t} = \ln k_p[I]_0 - k_t M]_0 \cdot t \tag{5.1}$$

where $[M]$, $[M]_0$, and $[M]_{eq} = k_d/k_p$ denote instantaneous, starting, and equilibrium concentration of monomer, respectively; $[I]_0$ – the starting concentration of initiator.

Termination is of a minor importance, as k_t has been found to be equal to $\approx 1.0 \times 10^{-6}$ l mol^{-1} s^{-1} in THF at 25 °C and the ratio $k_p/k_t \approx 300$. This ratio corresponds to the polymerization degrees (P_ns), which eventually can be reached. Therefore, at these conditions there is a departure from livingness,

$$\text{Propagation:}\quad P_i^* + M(P) \xrightarrow{k_t} P_i + M'(P')$$

$$\text{Termination:}\quad P_i^* + M \underset{k_d}{\overset{k_p}{\rightleftharpoons}} P_{i+1}^*$$

P_i^* and P_{i+1}^* - living macromolecules
P_i - terminated macromolecule
M and M' - amino and modified (alkoxy) monomer molecules, respectively
P and P' - amino and modified (alkoxy) repeating units, respectively
k_p, k_d, and k_t - the corresponding rate constants

Scheme 5.20 Kinetic scheme of anionic polymerization of the PN monomer [88].

because of the irreversible chain transfer to monomer and polymer. At lower temperatures this transfer becomes negligible, as indicated above.

5.2.3
Coordination Polymerization

Anionic active species, for example simple alkoxides, are more reactive than the "similar" covalent active species, like multivalent metal alkoxides [e.g., aluminum tris-alkoxides ($Al(OR)_3$)], operating in the coordination polymerization. This difference was quantitatively analyzed taking the corresponding rate constants of propagation (k_p) as a measure of reactivities. Some cyclic monomers could not be initiated with covalent initiators (e.g., oxiranes or cyclic siloxanes could not be initiated by aluminum mono- and tris-alkoxides). However, when initiation and then the propagation are possible, the side reactions are depressed (i.e., selectivity is increased) [89].

The quantitative data for k_p in coordination polymerization are available almost exclusively for cyclic esters and therefore, only polymerizations of these monomers are discussed in the present section. More detailed analysis of the reactivity–selectivity relationships has been presented in the already published review papers [90–93].

Among the first works when coordination initiators have been used, the works of Teyssie *et al.* on aluminum tris-isopropoxide [$Al(O^iPr)_3$] [94, 95] and the bimetallic μ-oxo-alkoxides have to be mentioned [96, 97]. PL, δ-valerolactone, and CL have been polymerized and the rates of polymerization were related to the ring size, giving similar order as known from anionic polymerization. The actual step of propagation on the $>$ Al–O–... bond has been described in terms close to our present understanding of this reaction. The living character of polymerization has also been demonstrated. Some time later, Kricheldorf *et al.* [98] described similar behavior for other multivalent metal [Sn(IV), Ti, Zr] alkoxides.

Some initiators applied in the coordination polymerization, being eventually transformed into the covalent active species, are known to exist mostly in the aggregated forms. For instance, $Al(O^iPr)_3$ is known to form trimeric (A_3) and tetrameric (A_4) aggregates. ^1H NMR and kinetic measurements have shown that in polymerization of CL [99, 100] initiated with a mixture of A_3 and A_4 aggregates at ambient temperatures exclusively the trimeric aggregate is initiating polymerization. The propagation is over before the tetrameric $Al(O^iPr)_3$ reacts to the observable degree. When polymerization comes to the living polymer–monomer equilibrium the mostly unreacted A_4 is introduced slowly into the polymer chains via the alkoxide-ester group transesterification reactions. Eventually, because of the segmental exchange between living macromolecules there is only one population of macromolecules having the most probable distribution of the molar masses.

When the A_3/A_4 mixture is used to initiate polymerization at the sufficiently high temperature, that is at conditions when the rate of the interexchange between A_3 and A_4 is becoming at least as fast as initiation with A_4, the aggregation phenomena become of a minor importance. Such a situation takes place in L,L-lactide (LA) polymerization carried out above 100 °C [101].

These phenomena were surprisingly not recognized and have been clarified only in 1994 [102], when the difference in the rates of initiation with A_3 and A_4 have been measured for the first time.

The observed difference in reactivities of different aggregates of aluminum tris-isoproxide is not observed for some other aluminum alkoxides that bear larger alkoxy substituents. In such a case either the initiator aggregation could completely be prevented or the less reactive aggregate could be in a dynamic, fast equilibrium with other more reactive initiator form. Apparently, this is the case of polymerization of cyclic carbonates with aluminum tris-*sec*-butoxide studied by Wurm *et al.* [103].

Depending on a structure of the resulting active centers (mostly on the number of growing polyester chains located at one metal atom) propagation may also be accompanied by aggregation of the alkoxide species. In the A_3/CL system the macroalkoxide species assume exclusively the three arm unimeric structure [100], whereas for R_2AlOR'/CL dimeric and trimeric aggregates prevail at higher concentration of active centers [104–106]. Similar phenomena have earlier been observed for ionic centers [107].

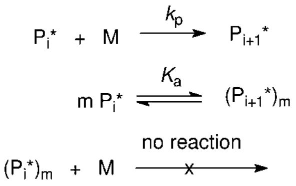
Aggregation may be diagnosed from the external kinetic order in active centers [101, 104–106] and from the NMR data, particularly ^{27}Al NMR [108]. In the majority of the reported cases aggregates are not reactive and the corresponding kinetic scheme reads as follows:

Thus, the $(P_i{}^*)_m$ species are dormant. Polymerization involving these species is living, providing that the aggregation and deaggregation rates are high enough when compared to that of propagation.

Solution of the kinetic Scheme 5.21 gives two useful dependences [104, 105]:

$$\ln r_p = \ln k_p (mK_a)^{-1/m} + \frac{1}{m} \ln [I]_0 \tag{5.2}$$

$$r_p^{1-m} = -mK_a k_p^{1-m} + k_p [I]_0 r_p^{-m} \tag{5.3}$$



P_i^*- non-aggregated, unimeric active centers
$(P_i^*)_m$ - aggregated species
m - aggregation degree
M - monomer molecule
k_p - rate constant of propagation
K_a - equilibrium constant of aggregation

Scheme 5.21 Kinetic scheme of propagation accompanied by the reversible aggregation of active centers.

where $r_p = d[M]/[M]dt = t^{-1} \cdot \ln([M]_0/[M])$, $[M]_0$ and $[M]$ denote the starting and instantaneous concentrations of monomer, $[I]_0$ – the starting concentration of initiator (equal at the properly chosen, living, conditions to the total concentration of active species – growing and dormant ones), and t is the polymerization time.

Fitting of the experimental data (i.e., r_p and $[I]_0$) available from the kinetic measurements to the Eq. (5.2) allows determination of the degree of aggregation (m). However, this approach does not allow determination of K_a and k_p, but merely their product.

The way of determining both k_p and K_a, is possible particularly when in the manner described above the degree of aggregation can be estimated [104, 105]. Equation (5.3) gives a direct access to both k_p and K_a and allows determination of k_p and K_a in several systems, that earlier were analyzed using numerical calculations [42]. In studies of CL polymerization, the kinetically determined proportion of the unimeric actually growing species $P_i{}^*$ was compared with the proportion of $P_i{}^*$ measured from the ^{27}Al NMR spectrum [108]. The corresponding spectrum is shown in Figure 5.2a. There are two peaks, for tetracoordinated [Al(4) in unimeric $P_i{}^*$ species] and pentacoordinated [Al(5) in $(P_i{}^*)_3$ aggregated species] aluminum atoms. The interconverting species can be depicted as in Scheme 5.22.

As estimated from the spectrum in Figure 5.2a, concentration of the Al(4) propagating species is equal to ≈10% of the total, thus comparable with that determined from kinetics (Figure 5.2b).

The rate of exchange between dormant and actually growing species can be analyzed using kinetic treatment in conjunction with MMD measurements developed by Kunkiel *et al.* [109].

$$M_w/M_n = 1 + k_p/\alpha k_a \tag{5.4}$$

where k_{ag} denotes the rate constant of aggregation and α – the molar fraction of deaggregated species.

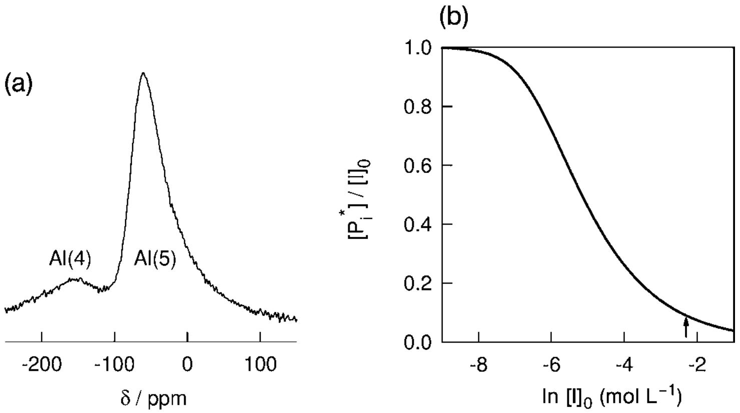
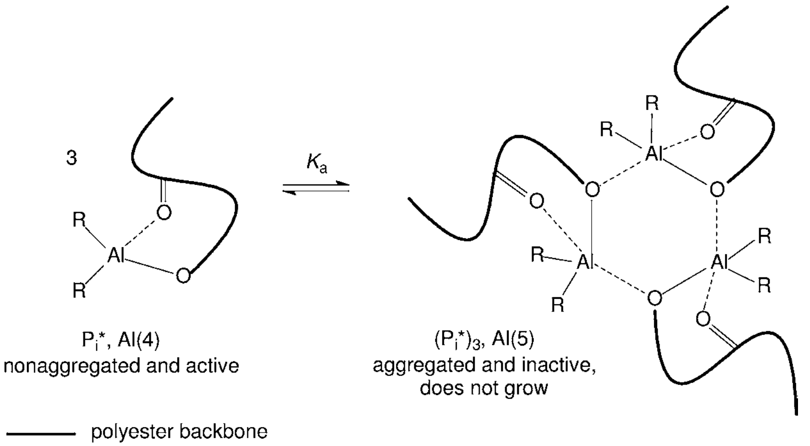


Figure 5.2 (a) ^{27}Al NMR spectrum of polymerizing mixture: CL/Et_2AlOEt/THF (+10 vol% of C_6D_6). Conditions: $[CL]_0 = 2$ mol l^{-1}, $[Et_2AlOEt]_0 = 0.1$ mol l^{-1}, 25 °C. (b) Dependencies of the mole fraction of the unimeric, nonaggregated active centers ($[P_n^*]/[I]_0$) on their total concentration ($[I]_0$) as determined from the kinetic measurements for the CL/Et_2AlOEt/THF system. Conditions: $[CL]_0 = 2$ mol l^{-1}, THF, 25 °C. Arrow indicates $[P_n^*]/[I]_0$ obtained for $[I]_0 = 0.1$ mol l^{-1} [108].



Scheme 5.22 Aggregation–deaggregation equilibrium in polymerization of ε-caprolactone initiated with Et_2AlOEt.

For example, in the ^{i}Bu$_2$AlOMe/CL system polycaprolactone (PCL) with $M_n = 6.5 \times 10^{-3}$ and $M_w/M_n = 1.11$ has been prepared [110]. Then, the kinetic measurements gave $k_p = 0.039$ l mol^{-1} s^{-1}, $K_a = 77$ l mol^{-1}, and $\alpha = 0.72$ [105]. This set of data analyzed in terms of Eq. (5.4) allows $k_a = 0.49$ l mol^{-1} s^{-1} and rate constant of deaggregation $k_d = 6.4 \times 10^{-3}$ s^{-1} to be

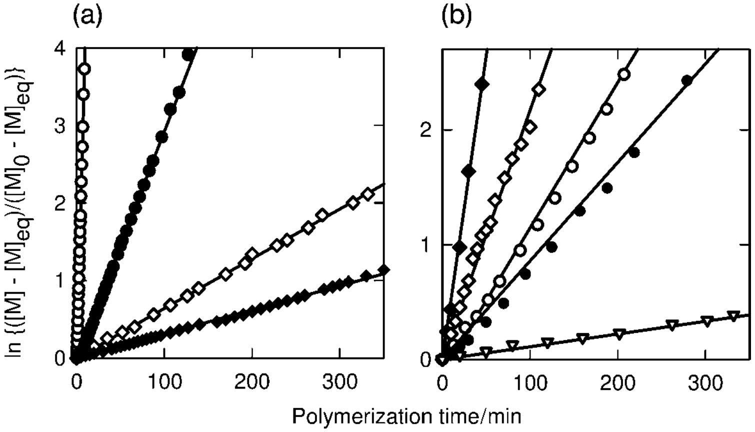


Figure 5.3 Kinetics of ε-caprolactone (a) and L,L-lactide (b) polymerization initiated with metal alkoxides ($R_nMt(OR')_{x-n}$). Conditions (concentrations in mol l^{-1}): (a, ○) $3[A_3]_0 = 3 \times 10^{-3}$, 25 °C; (a, ●) $[Sn(OBu)_2]_0 = 3.3 \times 10^{-3}$, 80 °C; (a, ◊) $[Et_2AlOEt]_0 = 8 \times 10^{-3}$, 25 °C; (a, ♦) $[Bu_3SnOEt]_0 = 9.9 \times 10^{-2}$, 80 °C; (b, ♦) $[Ti(O^iPr)_4]_0 = 10^{-2}$, 80 °C; (b, ◊) $[Fe(OEt)_3]_0 = 1.4 \times 10^{-3}$, 80 °C; (b, ○) $3[A_3]_0 = 2 \times 10^{-2}$, 80 °C; (b, ●) $[Sn(OBu)_2]_0 = 3 \times 10^{-3}$, 50 °C; (b, ▽) $[Bu_3SnOEt]_0 = 5 \times 10^{-2}$, 80 °C; $[CL]_0 = 2$, $[LA]_0 = 1.0$; THF solvent [111].

calculated. Thus, the rate of exchange has been found to be fast enough in comparison with that of propagation for controlled/living polymerization.

Polymerizations of CL, LA, and other cyclic esters initiated with a number of metal alkylalkoxide or metal alkoxide initiators, fulfill criteria required for the living process [91]. Figures 5.3 and 5.4 show the examples of CL and LA polymerizations initiated with $R_nAl(OR')_{3-n}$, $R_nSn(OR')_{3-n}$, $Fe(OR)_3$, and $Ti(OR)_4$ alkoxides, as well as the dependencies of $\ln\{([M]_0 - [M]_{eq})/([M] - [M]_{eq})\}$ on time and M_n on the monomer conversion, respectively [111].

Both dependences are linear. Thus, Figure 5.3 indicates that polymerization is devoid of termination whereas Figure 5.4 points to the absence of transfer. The lines in Figure 5.4 correspond to M_n – conversion dependences calculated assuming that each alkoxide group starts growth of one macromolecule, whereas points are experimental. Good agreement between the calculated and experimental plots means that for the multivalent metal alkoxide initiators their functionality is equal to the number of alkoxide groups. Some of these initiators, such as $Sn(OBu)_2$ allowed preparation of poly(L-lactide) (PLA) with M_n as high as $\approx 10^6$ in the controlled way [112]. Thus, $M_n \sim 10^6$ looks to be a limit of molar mass of the aliphatic polyesters prepared by the ROP, by using the usual techniques and this limit is, most probably, related to the concentration level of impurities. Close threshold value (measured from viscosity, $M_v \sim 9 \times 10^5$; hence M_n could be lower) has earlier been reported by Nijenhuis *et al.* some time ago [113]. It is not known whether there is a genuine termination reaction in these polymerizations.

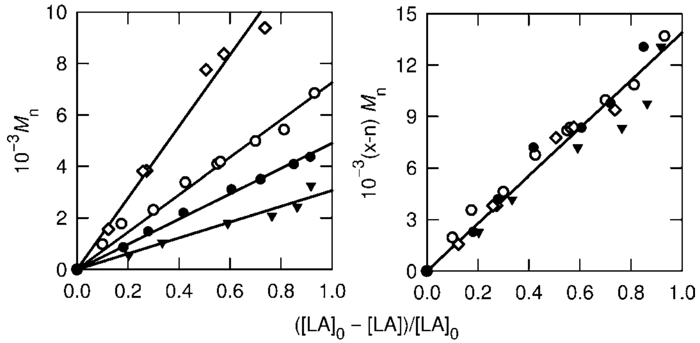


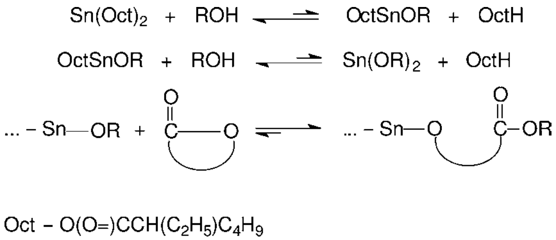
Figure 5.4 Dependence of M_n of poly(L-lactide) on the monomer conversion degree. Polymerization of L,L-lactide initiated with metal alkoxides ($R_nMt(OR')_{x-n}$): Bu_3SnOEt (◊), $Sn(OBu)_2$ (○), $Al(O^iPr)_3$ trimer (A_3) (●), and $Ti(O^iPr)_4$ (▼). Conditions: $[LA]_0 = 1.0$ mol l^{-1}, $[R_nMt(OR')_{x-n}]_0 = 10^{-2}$ mol l^{-1}, THF solvent, 80 °C (for $Sn(OBu)_2$ at 25 °C) [111].

In a discussion of the coordination polymerization of cyclic esters the rare earth metal (e.g., La, Sc, Sm, Y, Yb) alkoxides have also to be mentioned. These initiators applied first in DuPont [114–116] and then in other laboratories [117–123] provided much higher polymerization rates when compared with Sn or Al alkoxides. For example, in the polymerizing system $LA/Y(OAr)_3/{}^iPrOH$ (where Ar = 2,6-di-*tert*-butylphenyl group) the value of $k_p^{app} \geq 10\ \text{mol}^{-1}\ \text{l}\ \text{s}^{-1}$ (CH_2Cl_2 solvent, 22 °C) can be estimated [120]. This means that the polymerization proceeds with the rate more typical for the ionic polymerization of cyclic esters.

On the other hand, possibilities of the controlled polymerization initiated with rare earth metal alkoxides seem to be limited. For example, $Y(OCH_2CH_2NMe_2)_3$ taken in concentration 6.6×10^{-3} mol l^{-1} at 166 °C in the LA melt led to a final monomer consumption equal to 43%, suggesting the presence of the chain termination [116]. Moreover, MALDI TOF traces recorded for the La-alkoxide/LA polymerizing mixture reveal formation of the undesired cyclic oligomers fraction [118], which can be avoided in the kinetically controlled processes with some other initiators.

More recently, conditions of the controlled polymerization of cyclic esters, (co)initiated with tin octoate [$Sn(Oct)_2$] and tin(II) bis-2-ethylhexanoate ($Sn[O(O{=})CCH(C_2H_5)C_4H_9]_2$) have been elaborated. In a series of papers it has been shown that in the processes employing $Sn(Oct)_2$ the actual initiator–tin(II) alkoxide is formed in the alkoxide–carboxylate ligand interexchange reactions at the Sn atom (Scheme 5.23) [124–128].

Linearity of the first order kinetic plots pointed to the absence of termination. The polymerization degrees, being independent of the starting concentration of $Sn(Oct)_2$, were equal to the ratio of the molar concentrations of the consumed monomer and the hydroxy group containing compound (ROH) used. Results,



Scheme 5.23 Initiation with tin(II)–alkoxide formed via carboxylate–alkoxide ligand exchange reactions.

coming from other laboratories confirmed the formulated polymerization mechanism in the cyclic ester/$Sn(Oct)_2$/ROH system [129–135].

5.2.4
Organocatalytic ROP of Cyclic Esters

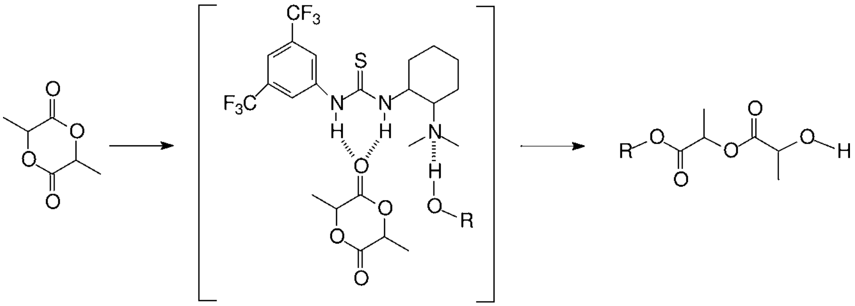
There are a number of papers on the so called "metal free", organocatalytic polymerization of lactones (see, e.g., Refs [39, 136–139] and the papers cited therein). Actually, this area has a longer history although it has been recently given a new life. Polymerization of β-lactones, initiated for example with amines, phosphines, or caboxylates with $(C_6H_5)_3PN^+P(C_6H_5)_3$ counterion was described already in early 1980s, including stereoselective polymerization of unsymmetrically substituted monomers [37, 38, 140] (and preceding papers cited there). It is surprising that 20 years later it is claimed that phosphines, for example were "discovered" as initiators of the polymerization of lactones [136]. In the new series of the organocatalytic polymerizations, usually the molar masses are limited and it is not convincing that polymerizations are living indeed, even if this expression is used throughout the papers. Initiation with strong "metal-free" bases leads, eventually in the case of lactones that do not propagate by carboxylate anions (six- and higher-membered monomers), to ionic structures. These ionic, actually initiating species, can be formed either by a direct proton abstraction from the monomer or from the alcohol molecule, which is usually a second component in the initiating system.

The anionic part, alkoxide anion can become the active species known to lead to the chain transfer in CL and lactides polymerization. The same may happen in polymerization initiated with carbenes, which provide alkoxide anions as well, at least according to the reaction scheme given by the authors of the pertinent papers (e.g., [137]). Also in this process molar masses are rather moderate and typically do not exceed $M_n = 3 \times 10^4$.

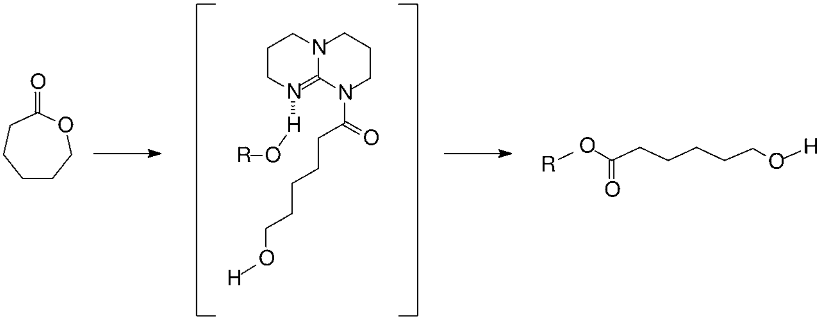
However, in the recently published papers of Waymouth, Hedrick, and their coworkers [138, 139] new, more effective organocatalytic systems are described. Kinetic and molar mass data show that for thiourea, guanidine or amidine based catalysts controlled polymerization could indeed result, although more data are still needed. Simultaneous linearity of the dependence of M_n on monomer conversion and first order kinetic plots has been reported. For at least one instance, M_n of the resulting polyester is equal to 8.5×10^4 (this is still much lower than ~10^6, as described above for Sn(II) initiators). In these papers, it is assumed, that polymerization proceeds either by nucleophilic attack of an activated alcohol on the AM (Scheme 5.24) or on the linear monomeric unit acylating a fragment of the catalyst (Scheme 5.25). Activation proceeds by H-bonding of monomer and alcohol used as an initiator. Thus, the proposed mechanism does not formally involve ions, although how far "activation" is from ionization is not yet clear. Analysis of the end groups could give an answer, informing on the extent of enolization, due to the presence of ions.

Presentation of the transient structure in Scheme 5.25 may raise some questions. For instance, what is the reason that the OH group from the linear unimer is not H-bonded in place of the OH group from an external alcohol? Neighboring group participation effect should rather help the intramolecular process.

Structures presented in the cited papers have not been observed by analytical means and have been proposed on the basis of the subjective choice as the most probable ones. It would be needed, however, to determine that the proposed "complexes" indeed do exist.



Scheme 5.24 ROP of lactide involving dual activation by a thiourea-tertiary amine catalyst.



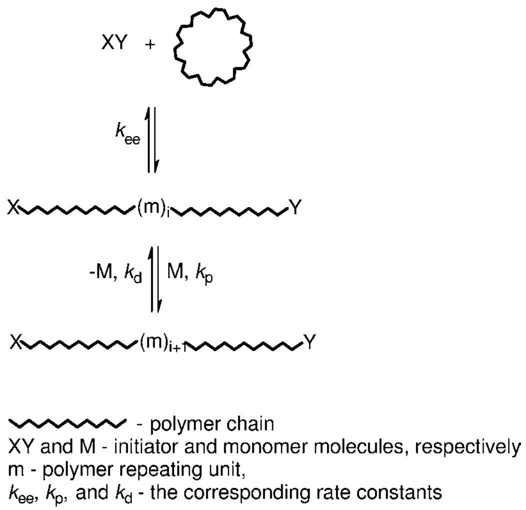
Scheme 5.25 ROP of ε-caprolactone involving dual activation by triazabicyclodecene.

5.2.5
Transfer Processes in the LROP

There are very few (in general) perfect definitions. Definition of controlled and living polymerizations, used throughout this paper to select and then describe these categories of processes, is not free from certain weaknesses. Indeed, living polymerizations encompass processes with reversible chain transfer. This means, that anionic polymerization of EO in the presence of an excess of a primary alcohol should be considered as a living process, as every chain transfer reaction to the alcohol molecule (realized via proton transfer) is producing an active species able to grow. Even, if the final result is addition of one molecule of an alcohol to one molecule of EO that is ethoxylation of an alcohol, it falls into the category of living polymerization, according to the existing definitions.

Chain transfer in the anionic or coordination LROP was particularly observed and studied for the polymerization of cyclic siloxanes [56–61] and cyclic esters [89, 92, 93, 107, 141–143]. Two different instances are known: kinetic enhancement in cyclics and kinetic enhancement in linear macromolecules. Thus, before the thermodynamic equilibrium in cyclics is reached, in the kinetically controlled period either cyclics or linear macromolecules are at concentrations exceeding these at the thermodynamic equilibrium. Scheme 5.26 explains the reason for the enhancement in rings, when the probability of reaction with the end group is higher than that of the reaction with the repeating units ($k_{ee} > k_p$).

With further growth, when the number of repeating units becomes large enough the end-to-end closure is loosing its importance and the almost exclusive source of rings is a random back biting. In the text below only this backbiting is taken into account.

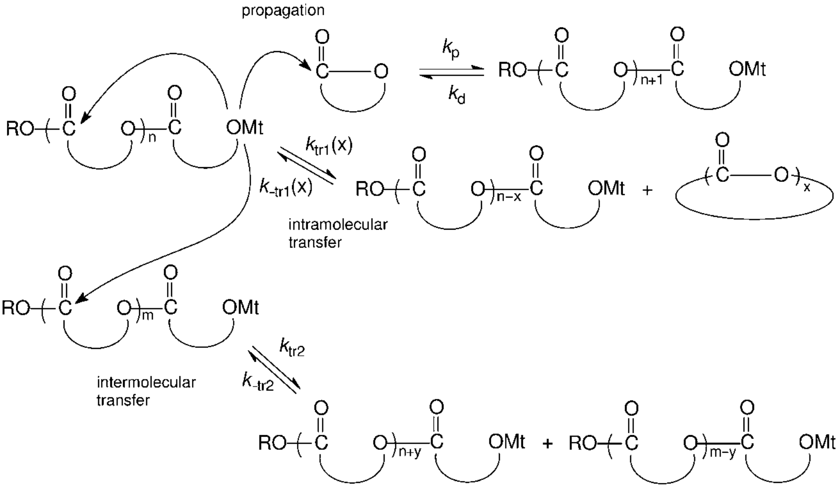


Scheme 5.26 Enhancement in cyclics vs. enhancement in linear macromolecules.

In the purely anionic polymerization of five- or higher-membered cyclic esters the monomer carbonyl carbon atom is attacked with subsequent acyl–oxygen bond scission and reformation of the alkoxide anion. In the coordination polymerization this is also carbonyl carbon that is first coordinated with alkoxide species and then the acyl–oxygen bond is broken with reforming of the covalent alkoxide chain end. In the already formed macromolecular chains the same ester bonds are present as those at the site of the nucleophilic attack in the monomer molecules. These processes are illustrated in Scheme 5.27, where the active centers are shown as . . .–OMt, for both anionic and covalent centers.

Investigations in this area started from the early work of the Nagoya group (Yamashita *et al.*) [142, 143] and have been further quantitatively developed in Lodz [92, 93, 107, 141]. Derivation of the corresponding kinetic equations giving access to the rate constant of transfer is based on the kinetic scheme shown in Scheme 5.28.

The intramolecular process is relatively easy to study quantitatively. This is because the products of the chain transfer are cyclic compounds and their concentration can be measured; for example, by the standard chromatographic methods. Thus, propagation and formation of cyclic oligomers are competitive reactions taking place simultaneously. Both reactions are reversible and result in thermodynamically determined concentrations of monomer and cyclic oligomers, which remain unconsumed in the polymerizing mixture, accompanying the polymer formed.



$k_{tr1}(x)$ - rate constant of intramolecular transfer
$k_{-tr1}(x)$ - rate constant of macrocycle propagation
k_{tr2}, k_{-tr2} - rate constants of intermolecular transfer

Scheme 5.27 Chain transfer reactions in the anionic and coordination ROP of cyclic esters.

$$P_n^* + M(1) \underset{k_d}{\overset{k_p}{\rightleftharpoons}} P_{n+1}^*$$

$$P_n^* \underset{k_{-tr}(x)}{\overset{k_{tr1}(x)}{\rightleftharpoons}} P_{n-x}^* + M(x)$$

$$P_n^* + P_m^* \underset{k_{-tr2}}{\overset{k_{tr2}}{\rightleftharpoons}} P_{n+y}^* + P_{m-y}^*$$

P_n^* - growing polyester chain with $DP = n$
M(1) - monomer, M(x) - macrocycle with $DP = x$

Scheme 5.28 Kinetic scheme of polymerization accompanied by intra- and intermolecular chain transfer.

Solution of the kinetic scheme (taking into account propagation and intramolecular transfer only) for some monomers (e.g., CL) for which propagation is practically irreversible gives Eq. (5.5) [141].

$$\beta = \frac{k_p}{k_{tr1}(x)} = \frac{\ln([M(1)]_0/[M(1)])}{[M(x)]_{eq} \cdot \ln\{[M(x)]_{eq}/([M(x)]_{eq} - [M(x)])\}} \tag{5.5}$$

where $\beta = k_p/k_{tr1}(x)$ is the selectivity parameter showing how many elementary acts of propagation (at $[M(1)] = 1\ \mathrm{mol\ l^{-1}}$) are accompanied by one macrocyclization step resulting in a given macrocycle. Thus, the value of β is a direct measure of selectivity of a given active species. In Figure 5.5, polymerizations proceeding on anionic and on covalent species are compared.

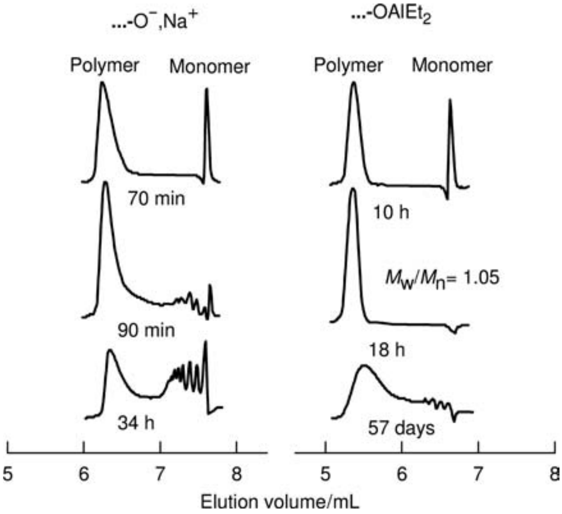


Figure 5.5 SEC traces showing formation of macrocycles in polymerization of CL initiated with ionic and covalent species. $[CL]_0 = 0.5\ \mathrm{mol\ l^{-1}}$, $[I]_0 = 5 \times 10^{-3}\ \mathrm{mol\ l^{-1}}$, THF, 25 °C. Polymerization times are indicated directly in the figure [141].

Table 5.2 Propagation rate constants (k_p) and the selectivity parameters ($\beta = k_p/k_{tr1}$) for the polymerization of ε-caprolactone [92][a].

Active species	k_p (l mol^{-1} s^{-1})	$\beta = k_p/k_{tr1}$ (l mol^{-1})
$\ldots-(CH_2)_5O^-Na^+$	≥ 1.70	1.6×10^3
$\ldots-(CH_2)_5O-Sm[O(CH_2)_5-\ldots]_2$	2.00	2.0×10^3
$\ldots-(CH_2)_5O-Al(C_2H_5)_2$	0.03	4.6×10^4
$\ldots-(CH_2)_5O-Al[CH_2CH(CH_3)_2]_2$	0.03	7.7×10^4
$\ldots-(CH_2)_5O-Al[O(CH_2)_5-\ldots]_2$	0.50	3.0×10^5

[a] Polymerization conditions: 20 °C, THF solvent.

With alkoxide anions, before the monomer is consumed there is already a large proportion of cyclics, whereas when the aluminum based covalent active species are used there are no detectable cyclics when full monomer conversion is reached. At equilibrium the composition of both systems should be the same, but it takes a long time in the covalent process to come to the equilibrium.

Using the described kinetic approach, these ratios of k_p/k_{tr1} were determined for a few initiating systems [92] and these ratios differed by a factor as large as 10^2. The corresponding data are collected in Table 5.2. There are two phenomena involved, namely, reactivity and steric hindrance. The higher the reactivity for species of comparable steric hindrance around growing species, such as Sm trialkoxide and Al trialkoxide, the lower the selectivity as it is often the case of other chemical reactions. If, on the other hand, the reactivity in propagation is the same but steric hindrance differs, for the more sterically hindered species the selectivity is higher. This is the case of dialkylaluminum alkoxides. For diisobutylaluminum alkoxides the selectivity is higher than for diethyl derivative because for more bulky substituents propagation is not affected, whereas in transfer chains they have more difficulties in achieving the conformation needed for the reaction to occur. Elimination of the intramolecular transfer in CL polymerization was also observed by Muraki *et al.* [144] when crowded dendrons were placed around Al atom in the active species, which led to increase of the entropy of activation for this side reaction.

The bimolecular transfer is a general problem of macromolecules with heteroatoms in the main chain, such as polyethers, polyesters, polyamides, and polyacetals (cf. also Section 5.3 on the cationic ROP). As far as aliphatic polyesters are concerned, when one active macromolecule reacts with another, also active, then two active ones are reproduced [93, 145, 146]. Thus, in the intermolecular transfer the only change that is observed is broadening of MMD. At a certain conversion bimodal MMD appears. This is a novel and general phenomenon which was not considered earlier in macromolecular chemistry. It is generally accepted, that in the polymerization process bimodality appears exclusively when there are two species propagating with different rate constants and that these species do not exchange fast enough.

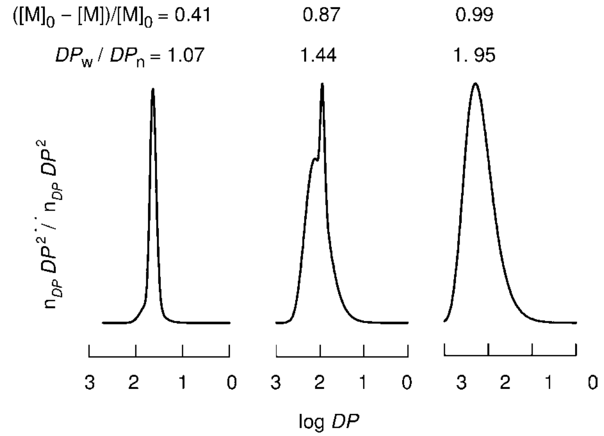


Figure 5.6 Computed (Monte–Carlo method) chain length distributions (DP_w/DP_n) as a function of monomer conversion degree $(([M]_0 - [M])/[M]_0)$. Conditions: $[M]_0/[I]_0 = 10^2$, $k_p \gg k_d$ [145].

The rate constant of intermolecular transfer (k_{tr2}) or the k_p/k_{tr2} ratio can be determined on the basis of the change of MMD as a function of monomer conversion $\{([M]_0 - [M])/[M]_0\}$. In Figure 5.6, the simulation of the MMD is shown for conditions when k_p/k_{tr2} is high, i.e., for a relatively slow transfer; numerical simulations are based on the kinetic Scheme 5.28 omitting the unimolecular transfer. Thus, chains are initiated at once and they grow, giving at the beginning close to Poissonian distribution.

Chains undergo transfer all of the time, but only approximately once for one hundred steps of propagation. A new population of macromolecules that participated in transfer adds slowly to the populations with Poisson distribution. The M_n of this population is the same, but M_w differs and this appears on the size exclusion chromatography (SEC) traces resulting in bimodal distribution. Numerical simulation was then applied, generating a number of nomograms (see lines in Figure 5.7a), giving finally the dependence of M_w/M_n on monomer conversion. Thus, if for a given ratio of starting concentrations of monomer to initiator, the dependence of M_w/M_n as a function of conversion is determined, the k_p/k_{tr2} can be found from the corresponding nomogram. This is shown in Figure 5.7b, for various covalent alkoxides. Lines were generated for a given ratio of k_p/k_{tr2} and points are experimental. On this basis, it was possible to determine k_p/k_{tr2} for a given system [93, 108, 145].

Another way to study the intermolecular transfer is possible when the monomer is already a dimer or a higher cyclic oligomer. This is the case of lactides (more precisely dilactides). Molar mass of LA monomer is 144.13 which is the same as for the repeating unit, although it is composed of two ester units (both of 77.013 molar mass). Thus, when there is no intermolecular (and in principle also no intramolecular) transfer, the repeating

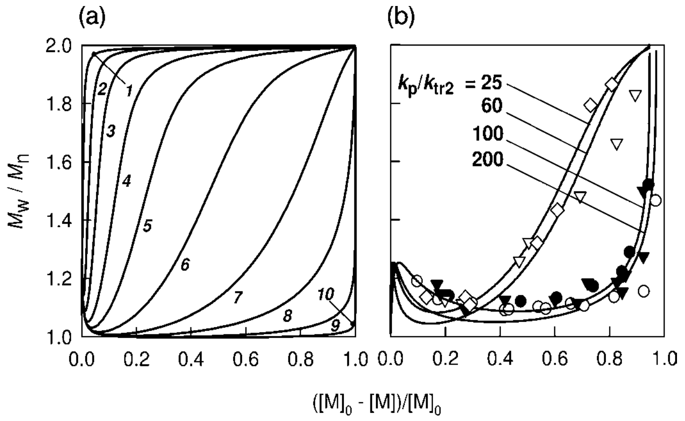


Figure 5.7 (a) Computed dependencies of M_w/M_n on degree of monomer conversion $(([M]_0 - [M])/[M]_0)$. Assumptions: $k_p/t_{tr2} = 10^{-2}$ (1), 2×10^{-1} (2), 5×10^{-1} (3), 2 (4), 10^1 (5), 5×10^1 (6), 2×10^2 (7), 10^3 (8), 5×10^3 (9), 2×10^4 (10). (b) Dependencies of M_w/M_n on $([M]_0 - [M])/[M]_0$ determined for L,L-lactide (LA) polymerization initiated with (in brackets are given $[M]_0/[I]_0$ ratios in which $[I]_0$ denotes starting concentration of the alkoxide group): (◊) Bu_3SnOEt, (▽) $Fe(OEt)_3$, (▼) $Al(O^iPr)_3$, (●) $Sn(Oct)_2$, (○) $Sn(OBu)_2$, THF solvent, 80 °C. Points experimental, lines computed assuming k_p/k_{tr2} = 200, 100, 60, and 25, respectively [108].

unit molar mass, observed by the MALDI TOF spectroscopy at the conditions excluding PLA chain fragmentation, is also equal to 144.13. Chain transfer, however, may lead to the PLA chains reshuffling that eventually results in mass spectra in which the neighboring signals are being apart by $m/z = 77.013$. In copolymerization of L,L-LA, for example, with a CL comonomer, extent of transesterification can be observed directly in the ^{13}C NMR spectra of the resulting copolymer on the basis of the intensity of the $\ldots{-}C({=}O)(CH_2)_5O{-}C({=}O)CH(CH_3)O{-}C({=}O)(CH_2)_5O{-}\ldots$ heterotriad [147]. Divalent tin-based active centers have particularly good selectivity [112]. Recently, even better selectivity was observed for aluminum alkoxides that bear the acetylacetonate [148] or bulky bidendate aryloxide-type ligands [149]. This is in agreement with the earlier findings in the back biting transfer (vide supra). Slowing down chain transfer is, however, important for the well controlled block copolymer synthesis when active centers of the second growing block may attack macromolecular fragments constituting the first comonomer block [150]. If this process is fast enough when compared with propagation, instead of block copolymer random copolymer results.

A very special case of the coordination living ROP employing aluminum porphyrins as initiators was elaborated by the Tokyo group. In their system reversible chain transfer is extended to such compounds as HCl (!) [151, 152]. Therefore, the expression "immortal" was introduced, to stress that this system is "better" than living. In our opinion the expression "immortal" is not needed. This system is just a case of the controlled/living polymerization accepting a larger number of chain transfer agents than usual, and it is not immortal. For instance HF would kill growing chain ends.

The reason to quote this structure is not only because this class of initiators give LROP, but also because "single site initiators" became recently popular in ROP without referring to the earlier developed similar systems.

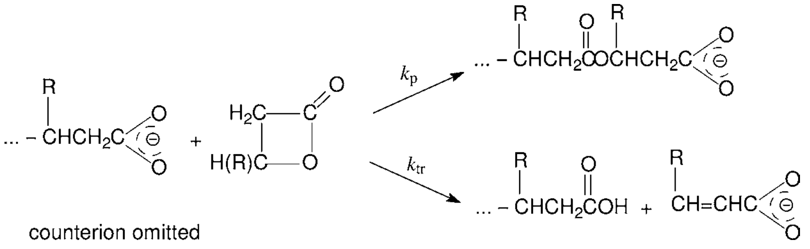
5.2.6
Departures from the Livingness

The above described anionic coordination ROP and particularly polymerization of cyclic esters show that the large majority of these systems behave not only as the living ones but also as fully controlled, i.e., with rates of initiation fast enough to allow control of M_n and MMD.

The most often observed departures from "livingness" are the already discussed chain transfers to monomer. Anionic polymerization of PL with carboxylate anions as growing species has measurable transfer (scheme, $R = H$) although macromolecules with M_n up to 10^5 can be formed even at room temperature [53].

Substituted PL (β-butyrolactone, Scheme 5.29, $R = CH_3$), like propylene oxide, is a much better proton donor and departure from livingness for these monomers is much more pronounced [26, 153]. This was observed for a substituted four membered lactone: indeed, the rate constant of proton abstraction k_{tr} (transfer to monomer) for β-butyrolactone was found to be relatively high, comparing with that of propagation and the resulting k_p/k_{tr} ratio was equal to 10^2 (measured in THF solvent at 25 °C). This ratio is equal to the maximal P_n that can be achieved at these conditions [26].

As already mentioned, coordination polymerization of LA initiated, for example, with $Sn(OBu)_2$ allows preparation of macromolecules of M_n up to almost 10^6 (i.e., P_n up to 6.7×10^3) [112]. This limit is most probably given by adventitious impurities present in the system. Nevertheless, in contrast to polyethers or polysulfides, polymerization of cyclic siloxanes and esters, with anionic or covalent active centers, proceeds with chain transfer to macromolecules (intra- and/or intermolecular). These processes should not be considered as departures from the living conditions. The proper choice of



Scheme 5.29 Polymerization of β-lactones accompanied by chain transfer to monomer.

initiator coupled with kinetic control can provide exclusively macromolecules retaining an ability to grow and eliminate formation of macrocyclics at the kinetically controlled conditions.

5.3
Cationic CROP and LROP

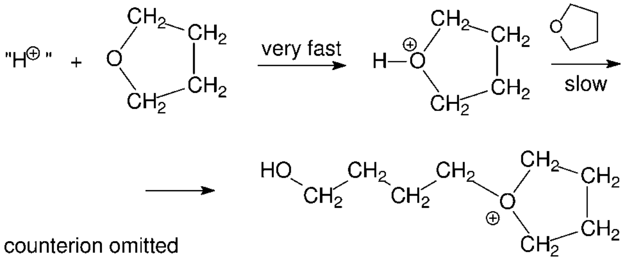
Cationic polymerization of THF is the only system studied in a sufficient depth. For this system, all involved rate constants are known and quantitative comparisons can be made. Thus, this section is almost exclusively on the basis of the data available for polymerization of THF with occasional comparison with other monomers. However, oxazolines, some N-substituted aziridines, and cyclic sulfides were also shown to polymerize under controlled or living conditions and several rate constants of propagation were determined. Although it is not known whether these rate constants describe propagation on ions or on ion pairs, it seems that in the cationic ring-opening polymerization the rate constants do not depend on the physical state of ions (discussed in the next sections). Polymerization of some cyclic acetals (formals) could not, however, be considered as a living process as the extensive chain transfer to polymer (transacetalization) [154] differs from the chain transfer in cyclic esters. In the latter, two living macromolecules involved in transfer reform two living ones, whereas in the polymerization of cyclic acetals (like 1,3-dioxolane but not trioxane) the transfer from one living to another living chain may result in two different macromolecules: one having two active sites and one not having any. It could, of course be argued, that this one, not having an active site in it may be hit by the living one and become living again, retaining the ability to grow, particularly because this transfer is at least as fast as the chain growth.

5.3.1
Cationic ROP of Tetrahydrofuran (THF)

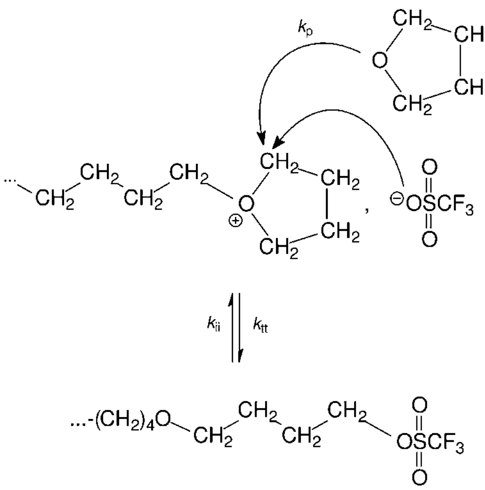
In the last two volumes published by Szwarc (one of them with van Beylen) polymerization of THF is discussed as an example of living ROP [34, 55]. For obvious reasons the treatment given there could not be as extensive as in the present review or other earlier reviews [14, 15, 155].

An initiator that is suitable for quantitative studies is trifluoromethanesulfonic acid [triflic acid, (CF_3SO_3H)] or its esters. The acid itself forms, during initiation, secondary onium ions that are usually less reactive than the propagating tertiary onium ions (Scheme 5.30).

Esters of triflic acid form directly onium ions of similar structure as propagating species, which are tertiary oxonium ions. The triflic anion of



Scheme 5.30 Initiation of THF polymerization with a strong acid.



Scheme 5.31 Ionic-covalent species equilibria in THF polymerization.

relatively high nucleophilicity may combine with cationic growing species forming the corresponding covalent species:

Propagation proceeds also as nucleophilic attack of the monomer molecule on the carbon atom in the cyclic oxonium ion with rate constant k_p, as shown in the scheme above for the temporary deactivation (Scheme 5.31).

The pertinent rate constants are k_{tt} and k_{ii} [tt = temporary deactivation and ii = internal (unimolecular) activation]. The importance of deactivation is governed by the nucleophilicity of the studied monomer and, therefore by the ratio of the rate constant of propagation to the rate constant of deactivation. On the other hand this importance would also depend on the position of equilibrium given in the scheme involving rate constants of deactivation and reactivation. In polymerization of THF the rate of temporary termination is comparable to the rate of propagation, as it will be shown in the next paragraphs.

There is also intermolecular chain transfer appearing at higher conversion. This process is neglected in the present treatment; therefore polymerization of THF fulfils requirements of CROP process, unless polymerization is conducted to high conversion, close to equilibrium conditions.

5.3.2
Propagation in the Cationic ROP

Direct information on the structure (and in some instances also on concentration) of active species may be obtained in several systems in ROP, from NMR studies (mostly ^{1}H NMR). The systems studied include polymerization of THF, oxepane, 3,3-dimethylthietane, 1,1,3-trimethylaziridine, 2-methoxy-2-oxo-l,3,2-dioxa-phosphorinane, and oxazolines [156–163].

Concentration of active species in cationic LROP of THF can be determined either directly from ^{1}H NMR spectra or after converting the oxonium ions into the phosphonium ions. In the ^{31}P NMR spectra only signals of groups containing phosphorus atoms are observed; thus the spectra are not affected by large signals from the chain units and the concentration of the chain ends can be determined down to 10^{-4} mol l^{-1}. In the same way concentration of active species was determined in polymerization of several other monomers [164, 165]. In some particular cases, when fluorine containing initiators were used ^{19}F NMR spectroscopy had successfully been applied for determination of the structure of active centers (see, e.g., Ref. [166]).

Ions and ion pairs cannot be observed independently by NMR because of fast exchange between those species; therefore, their relative proportions cannot be determined by this method. By combining kinetic and conductivity measurements it is, however, possible to determine propagation rate constants for both ions and ion pairs.

For a system with propagation exclusively on ions and ion pairs we have

$$\mathrm{d}\ln([M]-[M]_{\mathrm{eq}})/[P_\mathrm{i}{}^*]\mathrm{d}t = k_\mathrm{p}{}^{\mathrm{app}} = \alpha k_\mathrm{p}{}^{+} + (1-\alpha)k_\mathrm{p}{}^{\pm} \tag{5.6}$$

and

$$k_\mathrm{p}{}^{\mathrm{app}} = k_\mathrm{p}{}^{\pm} + \alpha(k_\mathrm{p}{}^{+} - k_\mathrm{p}{}^{\pm}) \tag{5.7}$$

where $[P_\mathrm{i}{}^*]$ denotes total concentration of ionic growing species (a sum of ions and ion pairs), α is proportion of ions (= [ions])/([ions] + [ion pairs]), and $k_\mathrm{p}{}^{+}$ and $k_\mathrm{p}{}^{\pm}$ are rate constants of propagation on ions and ion pairs, respectively.

Plotting $k_\mathrm{p}{}^{\mathrm{app}}$ as a function of α (Eq. 5.7), and knowing α from K_D (measured by conductivity), both $k_\mathrm{p}{}^{+}$ and $k_\mathrm{p}{}^{\pm}$ could be determined. Full analysis has only been performed for THF [167], oxepane [168], and conidine [169] polymerization.

In the systems discussed above and some other studied in less detail, it has clearly been shown that propagation on ions and ion pairs proceeds with the same rate constants. This is clearly demonstrated for polymerization of oxepane in CH_2Cl_2 and $C_6H_5NO_2$ (Figure 5.8) [168].

The $k_\mathrm{p}{}^{\mathrm{app}}$, encompassing both $k_\mathrm{p}{}^{+}$ and $\mathrm{k_p}{}^{\pm}$ does not depend on the degree of dissociation, that is on the proportions of ions and ion pairs. Therefore, these species have identical reactivities. The same dependence was observed for THF polymerization and even earlier in the polymerization of cyclic sulfides [170].

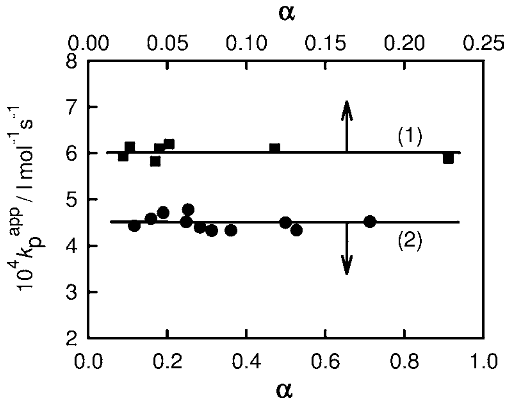


Figure 5.8 Determination of k_p^+ and $k_p^{\pm}$ in the polymerization of oxepane (OXP): k_p^{app} plotted as function of the degree of dissociation of macroion pairs; α: $[OXP]_0 = 5.0$ mol l^{-1}, 25 °C. (1) CH_2Cl_2 and (2) $C_6H_5NO_2$ as solvent [168].

Kinetic studies of propagation have shown, that $k_p^{\pm}$ does not depend on the anion structure; this result complements the earlier observation of $k_p^+ \approx k_p^{\pm}$. This has been an important result, as in the anionic polymerization of vinyl and cyclic compounds it has been found that ions were more reactive than ion pairs. The only exception was inversion of reactivities of these species, observed for cyclic esters.

Anions (counterions) used in cationic ROP can be divided into two groups. The first one consists of the complex ones, such as AsF_6^-, BF_4^-, SbF_6^-, that are not able to form covalent bonds, as their coordination sphere cannot be further enlarged. The other group comprises the noncomplex anions, such as $CH_3SO_3^-$, $CF_3SO_3^-$, and ClO_4^- that form covalent bonds, using two electrons of the oxygen atom to form a sigma bond. Therefore, whenever polymerization proceeds with these noncomplex anions, reversible ester formation may take place.

Reversible deactivation of growing species was studied in Lodz extensively, rate constants of propagation on covalent and ionic species were determined as well as the rate constants of their interconversion. Important observations were related to the NMR spectra in which signals of the covalent and ionic species were observed. This is illustrated in Figure 5.9, where ^1H NMR signals are shown for both ions and esters in three different solvents [156].

The relative concentrations of macroesters and macroion pairs in solvents of very different polarity, namely, CCl_4, CH_2Cl_2, and CH_3NO_2 vary dramatically. There are almost no ions in CCl_4, and almost no covalent species in CH_3NO_2 (the sum of concentrations of both species was kept constant).

As it has already been discussed, the basic feature of the cationic ring-opening polymerization is the equality of $k_p^{\pm}$ and k_p^+, that is the equal reactivities of the macroion pairs (independently of the anion structure) and macroions. Therefore, $k_p^{\pm}$ for macroion pairs with noncomplex anions (such as ClO_4^- or $CF_3SO_3^-$) should be the same as for the complex anions (BF_4^-, SbF_6^-, etc.). With such an assumption, k_p^{cov} can be determined from Eq. (5.8).

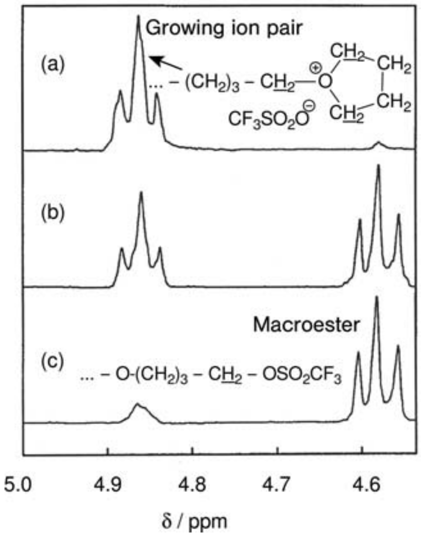


Figure 5.9 ^{1}H NMR spectra (the $\delta = 4.5–5.0$ ppm region only) of living poly(THF) with $CF_3SO_2O^-$ anion: (a) in CD_3NO_2, (b) in CH_2Cl_2, and (c) in CCl_4 solvent [156].

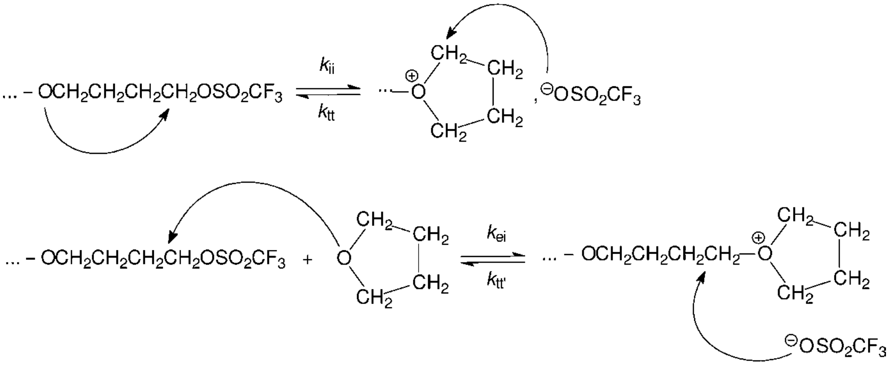
$$-\,\mathrm{d}t[M]/\mathrm{d}t = k_p{}^{\pm}[P_i{}^{\pm}][M] + k_p{}^{cov}[P_i{}^{cov}][M] \tag{5.8}$$

The rate is determined experimentally, concentrations of both kinds of active species, $[P_i{}^{cov}]$ and $[P_i{}^{\pm}]$, are known from ^{1}H NMR and if $k_p{}^{\pm}$ $(= k_p{}^{+})$ is also known, from any kinetic run $k_p{}^{cov}$ can directly be calculated. For example, in polymerization of THF carried out in solvents of different polarity the following $k_p^{\pm}$ $(= k_p{}^{+})$ and $k_p{}^{cov}$ (k_{ei}) values have been determined (in l mol^{-1} s^{-1}): 4×10^{-2} and 6×10^{-5} (CCl_4) and 2.4×10^{-2} and 5×10^{-4} (CH_3NO_2), respectively ($[THF]_0 = 8$ mol l^{-1}, 25 °C) [171].

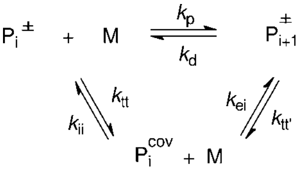
5.3.3
Macroion–Macroester Interconversions in the Cationic ROP

There are two possible ways of interconversions between the macroesters and the macroion pairs, namely the intramolecular (unimolecular) and the intermolecular (bimolecular, involving monomer) interconversions (Scheme 5.32).

In the intramolecular reaction, the back process involves attack on the endocyclic methylene group whereas in the intermolecular reaction the exocyclic group is attacked. It has been found that the intramolecular process is faster than the intermolecular one. Indeed, this was observed in the polymerization of THF indicating that the intramolecular process prevails. Within the accuracy of the ^{1}H NMR measurements concentrations of macroesters and macroions pairs were constant in the course of polymerization [156].



Scheme 5.32 Intramolecular and the intermolecular interconversions between the macroesters and the macroion pairs in THF polymerization.



Scheme 5.33 Kinetic scheme of cationic ROP involving ionic and covalent species.

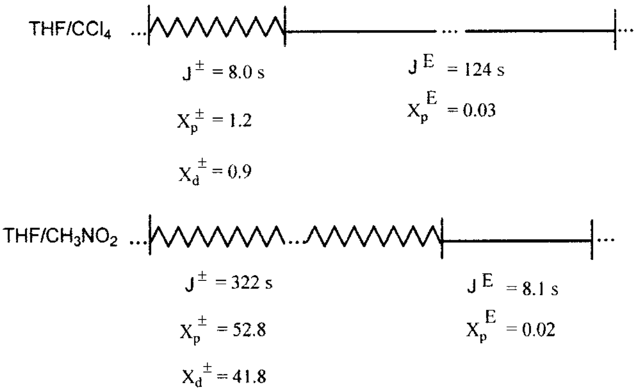
The complete scheme of cationic LROP of THF, involving ionic and covalent species is shown in Scheme 5.33 (the meaning of the super- and subscripts are self-explanatory in this scheme).

In a process with reversible deactivation shown in the scheme, like in the polymerization of THF with triflates or perchlorates, a given macromolecule propagates on its ionic species for a certain time, adding a certain number of monomer molecules; then the ion pair collapses into the covalent species. If these are much less reactive than ionic species ($k_p^{\mathrm{cov}} \ll k_p^{\mathrm{i}}$) this reaction is equivalent to the temporary deactivation. A macromolecule spends some time as an inactive one, until, as a result of internal ionization ($k_{ii} \gg k_{ei}[M]$) it reconverts into the active ionic form.

Scheme 5.34 shows how these periods oscillate in the polymerization of THF, carried out in two solvents, namely in CCl_4 and in CH_3NO_2 ($[THF]_0 = 8.0$ mol l^{-1}, 25 °C) [172].

This picture is a general one and applies (on a qualitative basis) to other polymerizations with a temporary deactivation, although it may require additional factors to be considered, depending on the mechanism of activation. Processes having a similar principle have been observed in controlled cationic [5] and controlled radical polymerization [6, 173] of unsaturated monomers.

An interesting article has recently appeared, treating similar problems in the polymerization of 2-methyloxazoline [174]. For the first time, in spite of a long history of studies of oxazolines, contribution of ions and covalent species to the chain growth as well as to the effective concentration has been determined.



$\tau^{\pm}$ and τ^{E} - lifetimes of the ion pair and an ester, respectively

$X_p^{\pm}$ and X_p^{E} - the number of monomer molecules added to the ionic and ester active species

$X_d^{\pm}$ - the number of monomer molecules that depropagate from ionic active species

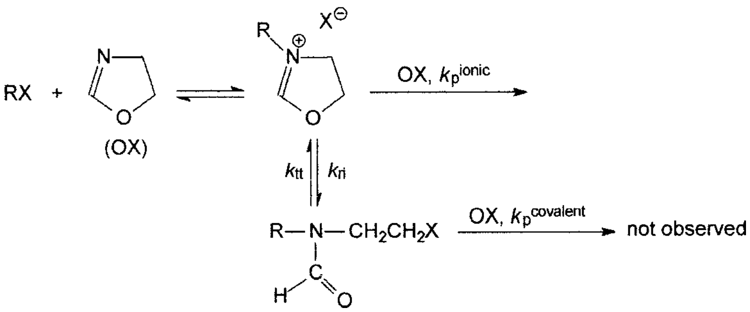
Scheme 5.34 Life records of poly(THF) macromolecules in cationic ROP of THF.

5.3.4
Cationic ROP of Cyclic Imino Ethers (Oxazolines) and Cyclic Thioesters

Polymerization of imino ethers, mostly 2-oxazolines, has been initially studied by Saegusa and Kobayashi [175]. This polymerization is an example of the isomerization polymerization and is important, as further reactions of polyoxazoline give linear poly(ethylene imine) that cannot be prepared directly by cationic polymerization of ethylene imine (aziridine). Recently a comprehensive review paper has been published by Kobayashi and Uyama [176]. This review with 98 references provides most authoritative discussion of the present state of the art in this field. Besides the analysis of the polymerization process itself, description of block copolymers, macromonomers, and telechelics as well as major applications of the resulting polymers are presented. Therefore, in the present chapter on LROP only the major phenomena are described.

In the polymerization of oxazolines, like in polymerization of THF, both ionic and covalent species (if counterions are able to form covalent bonds) could directly be observed by NMR. In the polymerization of THF it has conclusively been shown, that propagation on covalent species (e.g., esters, like triflates or perchlorates) practically does not contribute to the chain growth, even if these species prevail in the ester-ion equilibria. In the case of oxazoline this problem can be visualized by Scheme 5.35.

More recently, a paper was published giving the quantitative analysis of oxazoline polymerization at least for one system, in which it has been shown, that ionization proceeds mostly by reaction according to Scheme 5.35



Scheme 5.35 Cationic ROP of oxazoline involving ionic-covalent species equilibria.

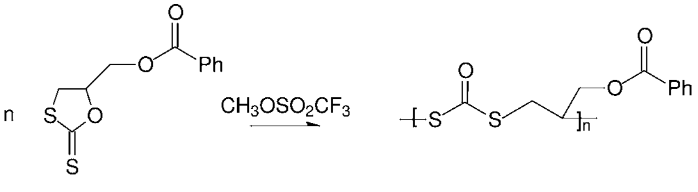
(i.e., unimolecularly) and not by the bimolecular reaction, namely, alkylation of the monomer by covalent species [174].

The ratio k_{ri}/k_p^{cov} [M] has been determined for polymerization of 2-methyl-2-oxazoline with Br^- counterion (thus $X = Br$ in the scheme above). The monomer concentration at which the rate of the intermolecular reinitiation (i.e., resembling covalent growth) would be equal to the rate of intramolecular reinitiation (i.e., giving back ionic growing species) is equal to $\approx 10^3$ mol l^{-1}, which exceeds, by almost two orders of magnitude, the monomer concentration in bulk. This leads to the conclusion that ionic centers (formed by unimolecular ionization) are almost exclusively responsible for the chain growth, even if their concentration is equal to only a few percent of the sum of the concentrations of the covalent and ionic species. In this way, the paper by Dworak [174] has clarified in more details the contribution of elementary reactions to the chain growth.

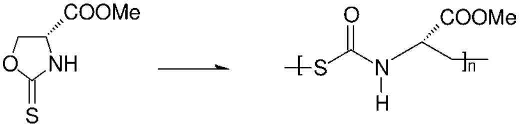
Polymerization of oxazolines is particularly slow, even if compared with polymerization of other heterocyclic monomers. For instance, k_p (the same for ions and ion pairs) is equal (in $l\,mol^{-1}\,s^{-1}$ at 0 °C) to $\approx 5 \times 10^{-3}$ (THF), $\approx 10^{-4}$ (oxepane), $\approx 10^{-3}$ (3,3-dimethylthietane), and to $\approx 10^{-5}$ (oxazoline).

In a series of papers, Choi *et al.* have shown that cationic polymerization of some cyclic thiocarbonates proceeds according to living polymerization scheme (degree of polymerization close to [monomer]$_0$/[initiator]$_0$ ratio, low dispersity, possibility of chain extension) (Scheme 5.36) [177].

Living character of polymerization of monomer shown in the scheme above is explained by the authors by neighboring (ester) group participation leading to stabilization of positive charge in the transition state.



Scheme 5.36 Cationic polymerization of thiocarbonate.



Scheme 5.37 Cationic polymerization of 1,3-oxazolidine-2-thione.

Also polymerization of related monomers, such as 1,3-oxazolidine-2-thione (cf. Scheme 5. 37) was shown to proceed as living process leading to chiral polythiourethanes [178].

MW of polymers increased linearly with $[\text{monomer}]_0/[\text{initiator}]_0$ ratio up to $M_n \sim 2.5 \times 10^4$ with dispersity in the range of 1.1–1.2.

5.3.5

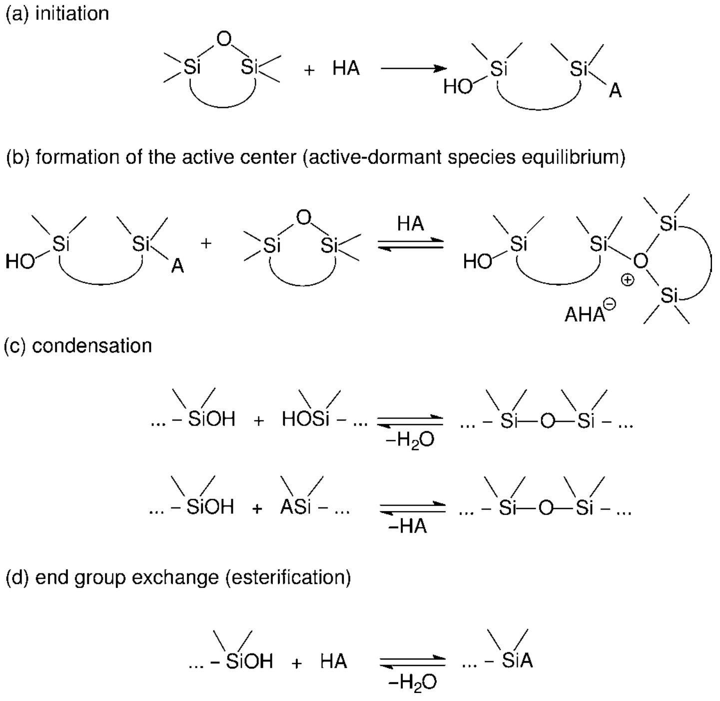
Cationic ROP of Cyclosiloxanes

'Cationic polymerization of cyclotrisiloxanes is a kinetically controlled process, in which there is neither termination nor irreversible transfer. On the other hand, the fast and reversible chain transfer and end-group exchange reactions taking place in the system effectively compete with propagation, so that the molar masses of the polymers, their distribution and the structure of end groups cannot be precisely controlled.

The most common initiators of the cationic ROP of cyclosiloxanes are strong protic acids. The most often used are H_2SO_4, CF_3SO_3H, $HClO_4$, CH_3SO_3H [56–61], and *tetrakis*-(pentafluorophenyl)boric acid hydrate [179]. Lewis acids, such as $FeCl_3$ and $SnCl_4$ are believed to initiate polymerization in cooperation with protic acids, which are common contaminations present in the system. However, some nonprotic systems, are able to initiate polymerization of hexamethylcyclotrisiloxane (D_3) in the presence of a proton trap [60, 61].

The mechanism of the cationic polymerization of cyclosiloxanes is very complex and has not been fully understood until now. The simplified picture is shown in Scheme 5.38 [60, 61, 180–183]. The most important features of the cationic polymerization of cyclosiloxanes are as follows:

- strong influence of the hydrogen bond association on the kinetics of the monomer conversion;
- in the kinetically controlled (nonequilibrium) stage of polymerization of cyclotrisiloxanes a considerable amount of macrocycles, the multiples of monomer, $(R_2SiO)_{3n}$, is formed;
- condensation of silanol groups and the end-group exchange contribute to the chain growth;
- stationary concentrations of water, acid, and ester are rapidly established at the early stage of the process.



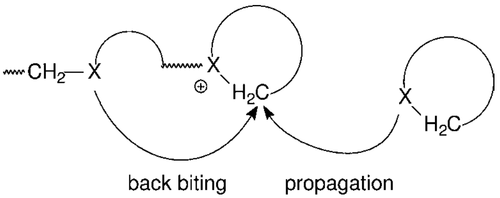
Scheme 5.38 Mechanism of the cationic polymerization of cyclosiloxanes.

As a consequence, the activity of initiator is maintained throughout the entire process resulting in a continuous initiation and in broadening of MW of the polymer (M_w/M_n in the range from 1.6 to 2).

5.3.6
Activated Monomer Cationic ROP of Cyclic Monomers

Many systems discussed till now could be described in terms of controlled and/or living polymerization because termination and irreversible transfer could be eliminated. However, in most ROP the chain transfer to polymer (intramolecular back biting and/or intermolecular) usually cannot be avoided, as described above for several systems. This is because nucleophilic site of monomer molecule (heteroatom) is still present along the chain and in some instances (cyclic acetals being an example) the nucleophilicity of an oxygen atom is higher in a polymer chain than in a monomer molecule (Scheme 5.39).

To what extent intramolecular chain transfer to polymer affects a course of polymerization depends on the relative rates of propagation and back biting that are mostly governed by the relative nucleophilicities of heteroatom in a monomer molecule and in polymer unit as well as steric factors.



Scheme 5.39 Propagation–macrocyclization competition in cationic ROP.

In the polymerization of THF backbiting and intramolecular transfer are slow as compared to propagation. Therefore, even after reaching the living polymer–monomer equilibrium, the amount of cyclic fraction is negligible. If, however, living (e.g., nonterminated) poly(THF) is kept for a period of time exceeding considerably the time needed for establishing the monomer–polymer equilibrium, cyclic oligomers are formed in measurable quantities [184]. On the other hand, when back biting proceeds with a rate similar to that of propagation, cyclic oligomers are formed simultaneously with the linear polymer. This is for example the case of cationic polymerization of cyclic acetals [185], and the cationic polymerization of the three-membered cyclic ethers – oxiranes. Thus, in the cationic polymerization of EO, typically the predominating product is a cyclic dimer: 1,4-dioxane [186] whereas in cationic polymerization of substituted oxiranes (propylene oxide, epichlorohydrin) other cyclic oligomers (trimers, tetramers) are formed in significant amounts. Therefore, although active centers in those systems were long living, the systems could hardly be described as living processes and no control could be achieved.

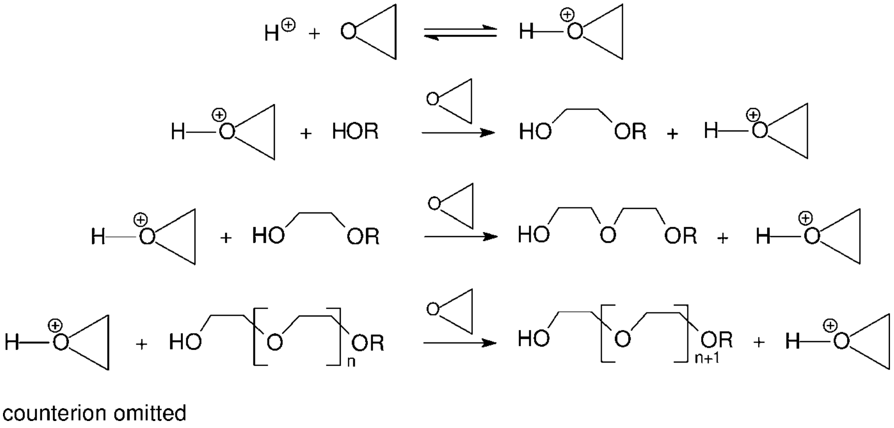
In the late 1980s, it was observed that in cationic polymerization of oxiranes carried out in the presence of compounds containing hydroxy groups (alcohols, diols) the amount of cyclic oligomers formed was substantially reduced [187]. An explanation has been proposed on the basis of the mechanism shown in Scheme 5.40 for which the expression "AM mechanism" has been applied. As already mentioned, the expression "AM" mechanism was introduced by Szwarc [73] to explain the NCAs polymerization course. The idea of the ionic chain polymerization proceeding with charges located at least temporarily on the monomer molecules, adding to the neutral macromolecules, was postulated also for the anionic polymerization of lactams. When strong base is used as initiator, the first reaction is formation of the monomeric anion and propagation proceeds by addition of this anion (AM) to the neutral chain end (see Section 5.2.2.2).

Results concerning cationic AM polymerization of heterocyclic monomers were summarized in an already published review [188].

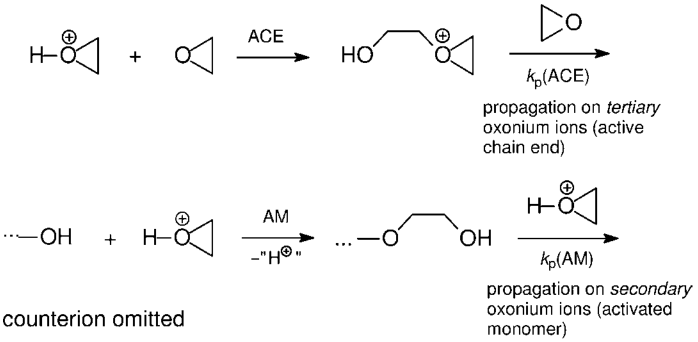
In polymerization proceeding by AM mechanism, active centers are located on the monomer molecule (thus becoming AM) and growing polymer chain is neutral although it is terminated with a reactive hydroxy group. Because in the cationic AM mechanism there is no active species at the chain end, backbiting is highly reduced (Scheme 5.40). At the final equilibrium state the total concentration of cyclics would be the same as in the ACE mechanism, but it may take unpredictably long time.

The scheme above is a simplified one. Because proton exchange is very fast, all nucleophilic sites are protonated. The only reactive species, however, are protonated monomer molecules. In the cationic polymerization of oxiranes in the presence of hydroxy groups the AM mechanism predominates, however, the possibility of contribution of the more conventional ACE mechanism is not eliminated. The competition between these two processes is illustrated in Scheme 5.41. As it follows directly from this scheme, in order for AM type propagation to prevail, the instantaneous concentration of monomer should be kept as low as possible.

Kinetic studies, based on the determination of monomer consumption, give only an apparent rate constant. This apparent rate constant may be determined



Scheme 5.40 Polymerization of oxirane according to the activated monomer mechanism.



Scheme 5.41 Competition between active chain end (ACE) and activated monomer (AM) mechanisms.

as

$$-\,\mathrm{d}[M]/\mathrm{d}t = k_{\mathrm{app}}[\mathrm{H{-}M^+}][\mathrm{HO{-}}\ldots]_0 \tag{5.9}$$

where $\mathrm{H{-}M^+}$ denotes protonated monomer, and $[\mathrm{HO{-}}\ldots]_0$ total concentration of the $\ldots{-}\mathrm{OH}$ groups.

Because not all of the protons participate in protonation of monomer (they are distributed among different nucleophilic sites), the concentration of protonated monomer is not known.

At low monomer conversion, however, when there is almost no polymer, it may be assumed that protons are distributed between oxygen atoms of monomer and hydroxy groups only:

$$[\mathrm{H{-}M^+}] = K_\mathrm{e}\frac{[\ldots{-}\mathrm{OH_2}^+][M]}{[\ldots{-}\mathrm{OH}]} \tag{5.10}$$

In such a case the sum of concentrations of protonated monomer and protonated hydroxy group is equal to the overall concentration of the protonic acid catalyst and the final equation, allowing determination of k_{app}, reads as follows:

$$\frac{[\mathrm{H^+}]}{\mathrm{d}[M]/\mathrm{d}t} = \frac{1}{k_{\mathrm{app}}} + \frac{K_\mathrm{e}}{k_{\mathrm{app}}}\cdot\frac{[\ldots{-}\mathrm{OH}]_0}{[M]} \tag{5.11}$$

A series of kinetic measurements at different $[-\mathrm{OH}]/[M]$ ratios allowed determination of both k_{app} and K_e from the intercept and a slope of the linear plots for AM polymerization of epichlorohydrin and propylene oxide [189, 190].

From the distribution of individual oligomers the ratio of rate constants $k_{\mathrm{AM}}/k_{\mathrm{ACE}}$ was determined [190]. In the AM polymerization of epichlorohydrin this ratio is about 5. Thus, although AM type propagation is preferred, this preference is not sufficient to ensure the high enough contribution of the AM mechanism. To enhance the contribution of AM propagation according to the AM the slow monomer addition process was applied, in which the overall ratio $[M]/[-\mathrm{OH}]$ was sufficiently high to ensure the required P_n ($P_n = [M]/[\mathrm{HO-}]$) while instantaneous concentration of monomer was low.

A series of telechelics and macromonomers were synthesized by AM polymerization of propylene oxide and epichlorohydrin using slow monomer addition approach [191, 192]. Resulting medium molar mass polymers had the required functionality,molar mass close to calculated, and narrow MMD. Thus, cationic AM polymerization of cyclic ethers shows features of a controlled and/or living process although it results in the limited molar mass range of the resulting polyethers. At high conversion, if P_n were large enough and subsequently the ratio [polymer unit]/[monomer] were sufficiently high, the rate of polymerization would be very low. Increasing the rate is possible by increasing $[\mathrm{H^+}]$. However at high $[\mathrm{H^+}]_0/[\mathrm{monomer}]_0$ ratio, higher P_n could not be achieved ($[\mathrm{H^+}]$ reacting with cyclic ether monomer generates additional HO–groups).

5.4
CROP and LROP Conducted in Dispersions

Dispersion polymerization, a process commonly used for synthesis of polymers by radical polymerization of vinyl monomers, recently was found also suitable for anionic and coordination ring-opening polymerization of CL and LA [193–199]. Polymerizations of these cyclic esters were carried out in 1,4-dioxane : heptane mixtures in presence of poly(dodecyl acrylate)-*g*-poly(CL) graft copolymers used as particle stabilizers.

There are also reports on heterogeneous polymerization and copolymerization processes of CL, LA, and glycolide (GL) carried out in supercritical carbon dioxide [134, 200–202], some leading to conveniently processable powders. However, for these polymerizations very little is known on the mechanism of particle formation, particle sizes, and distributions.

Polymerizations were initiated with tin(II) 2-ethylhexanoate (LA) [193, 194], diethylaluminumethoxide (CL) [193, 194], sodium trimethylsilanolate (CL) [196], and 2,2-dibutyl-2-stanna-1,3-dioxepane (LA) [198]. Spherical particles with diameters of 0.63 to 6.4 μm and with a narrow diameter distribution were obtained ($D_w/D_n < 1.1$ when particles were stabilized with poly(dodecyl acrylate)-*g*-poly(CL) with M_n of poly(CL) grafts close to 0.25 of M_n of the whole copolymer) [203].

Kinetics of polymerization, changes of number of particles in polymerizing system with time, dependence of diameters of particles on monomer conversion, and dependence of MW of polyesters in microparticles on monomer conversions and on initial concentration of initiator suggest the following polymerization mechanism [194, 196–198, 204]. Initially the polymerization mixture is homogeneous, as the monomer is soluble in the mixture of solvents. Initiation and first monomer additions to propagating centers occur in solution. When growing oligomers reach critical length (from 5 to 10 monomeric units) their conformation changes from coil to globule and collapsed oligomers aggregate into nanoparticles. The nanoparticles are stabilized by adsorption of polymeric stabilizer [poly(dodecyl acrylate)-*g*-poly(CL)] present in the system. Very quickly the number of particle seeds (primary nanoparticles) is so high that the probability that propagating oligomers (still present in solution) are adsorbed onto existing nanoparticles is much higher than probability of their aggregation into new particles. Subsequently, the whole polymerization process proceeds in monomer swollen microspheres until the equilibrium is reached. Particles are stabilized so efficiently that after initial period their aggregation does not occur.

Hypothesis that the above mentioned polymerizations of cyclic esters are living was based on following observations. Kinetic plots of $\ln([M]/[M]_0)$ vs. time are almost linear (up to ≈90% of monomer conversion) showing that termination up to the above mentioned polymerization stage could be neglected [194]. A good agreement between measured M_n of the synthesized polymers and that predicted, on the basis of the ratio of concentration of monomer converted into polymer to concentration of initiator, indicates that chain transfer also does not play an important role in these processes [198]. The highest M_n of poly(CL) synthesized by dispersion polymerization was 1.06×10^5 and M_w/M_n for this polymer was 1.15. [205].

The absence of termination in dispersion polymerization of LA initiated with tin(II) 2-ethylhexanoate was confirmed also in the classical experiment with sequential addition of new monomer portions after the monomer present in the system reaches an equilibrium [206, 207]. It has been found that the average volume of polylactide microspheres increases after each monomer addition and is proportional to the difference between concentration of monomer added to the system and monomer concentration at equilibrium.

Thus, the features of dispersion anionic and pseudoanionic polymerizations of cyclic esters indicate that these processes can be controlled. The term living has also in this instance an additional meaning. In addition to propagation without chain transfer and termination in these systems there is a fast particle nucleation followed by particle growth without any side processes (e.g., coalescence). Therefore, in dispersion polymerization of cyclic esters not only propagating macromolecules but also growing particles are living.

The above described mechanism of dispersion ROP has important kinetic consequences. As shortly after fast nucleation all active centers are located inside monomer swollen particles, the rates of propagation are proportional not to the product of concentrations of monomer and active centers averaged over the whole volume of reaction mixture but to the product of monomer and initiator concentrations in particles. It has been found that partition of CL monomer between continuous (liquid) and condensed phases (particles) favors the latter one (monomer concentration in particles is about 10 times higher than that in the liquid medium in which particles are suspended) [196]. As a result, the apparent propagation rate constants for polymerization in dispersed systems are several times higher (depending on the actual polymerization conditions) than the apparent propagation rate constants in polymerizations carried out in solution [197].

Dispersion polymerizations of cyclic esters require custom synthesized, commercially not available, copolymers that are used as surfactants. Quality of product strongly depends on proper mixing, keeping growing particles suspended in continuous phase and assuring efficient monomer transfer between continuous phase and particles. In majority of industrial applications dispersion polymerizations of cyclic esters cannot compete with similar processes in bulk or in solution but it is a method of choice when polymer in the form of particles with controlled diameter is needed.

These spherical particles are composed of the biodegradable polymers and could be used for the drug delivery systems, diagnostics, and some other medical applications.

5.5
Conclusion

ROP provides heterochain polymers. Some polymers of similar chain composition could be prepared by polycondensation. The scope of the related structures in ROP is very large, and the number of involved monomers that are being used in practice is most probably higher than the number of unsaturated monomers. Indeed, ROP leads to polyethers, polyacetals, polyesters (including polycarbonates), polyamines, polyamides, polyoxazolines, and polysiloxanes, to list only the best known classes of polymers.

The first living polymerization was ROP of EO studied by Flory, although Flory did not use this expression at that time. The presence of heteroatoms on the chains coupled with ionic processes, mostly used in ROP, allowed studying processes not existing in polymerization of other groups of monomers. These include kinetic chain transfer to macromolecules with material chain rupture and backbiting or end-to-end biting with formation of cyclic polymers. Cyclic polymers are also being prepared by end-to-end reaction in vinyl polymerization, however these processes are not spontaneous and special conditions have to be created (e.g., modification of the chain ends). Reversible deactivation of chain carriers have been first observed and described in ROP propagation, before this feature became the basis of controlled vinyl cationic and radical polymerizations.

The versatility of ROP has lead to two large families of novel applications: PEO in modification of polypeptides (in a process called *PEGylation*) and biodegradable polymers based on ROP. On the industrial scale the volume of polymer production by ROP is by far smaller than that of vinyl and olefin based polymers. Altogether, polylactide, polycaprolactone, polyamides (polycaprolactam), polyacetal, polysiloxanes, and numerous even smaller scale productions hardly reach 10^6 t/year at present. This is perhaps less than 1% of the total industrial production of all polymers. However, the ratio of the values of production may look differently, if it is remembered that the commodity polylactide is a few times more expensive than polyolefins (on the average) and that the total market for the products of PEGylation is reaching 4×10^9 USD/year [208]. Another large market is for polysiloxanes in cosmetics and biomedicine.

Therefore, ROP has its own place in polymer chemistry and technology that can not be replaced by polymers with exclusively C–C-based chains and products of polycondensation.

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6

Living Ring-Opening Metathesis Polymerization

Christopher W. Bielawski and Robert H. Grubbs

6.1

Overview of Ring-Opening Metathesis Polymerization (ROMP)

6.1.1

Introduction

Although a relatively new player in the field of polymer chemistry, ring-opening metathesis polymerization (ROMP) has emerged as a powerful and broadly applicable method for synthesizing macromolecular materials, particularly those with well-defined structures [1]. The origins of ROMP can be traced to the mid-1950s when various metals and reagents were combined to uncover new transformations and reactivities involving olefins. However, the rapid rise in popularity and utility of this polymerization technique is the result of extensive work on the identification and isolation of key intermediates involved in the general olefin metathesis reaction [2]. This led to the development of well-defined ROMP initiators, and ultimately enabled the synthesis of a wide range of polymers with complex architectures and useful functions. The aim of this review is to provide the reader with a ''user's manual'' to living ROMP so that they may readily begin applying this unique and powerful polymerization method. Beginning with a concise overview of ROMP chemistry, the chapter will provide the reader with a historical account of the polymerization technique. Particular emphasis will be placed on the transition-metal complexes used to initiate and mediate the polymerization and will include a description of their current status in contemporary polymer chemistry. Following a discussion of current and potential applications of ROMP, the review will conclude with some current challenges and predictions for the future.

6.1.2

ROMP Essentials: Mechanism and Thermodynamics

ROMP is a chain growth polymerization process where a mixture of cyclic olefins is converted to a polymeric material (see Figure 6.1 for an illustrative

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example) [3]. The mechanism of the polymerization is based on olefin metathesis, a unique metal-mediated carbon–carbon double bond exchange process [4]. As a result, any unsaturation associated with the monomer is conserved as it is converted to polymer. This is an important feature that distinguishes ROMP from typical olefin addition polymerizations (e.g., ethylene → polyethylene).

A general mechanism for ROMP, based on Chauvin's original proposal [5] is shown in Figure 6.2. Initiation begins with coordination of a transition-metal alkylidene complex to a cyclic olefin. Subsequent [2 + 2]-cycloaddition affords a four-membered metallacyclobutane intermediate, a process that effectively forms the beginning of a growing polymer chain. This strained intermediate undergoes a cycloreversion reaction to afford a new metal alkylidene. Although the resulting complex has increased in size (because of the incorporated monomer), its chemical characteristics toward cyclic olefins are similar to those of the initiator. Analogous steps are repeated during the propagation stage until the polymerization reaction ceases (i.e., all of the monomer is consumed, a reaction equilibrium is reached, or the reaction is inadvertently or deliberately terminated). Living ROMPs are commonly quenched deliberately through the addition of a specialized chemical reagent. The function of this reagent is to (i) selectively remove and deactivate the transition-metal from the end of the growing polymer chain and (ii) install a known functional group (FG) in place of the metal.[1]

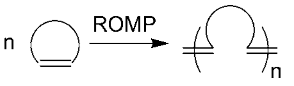

Figure 6.1 A generalized example of a ring-opening metathesis polymerization (ROMP) reaction.

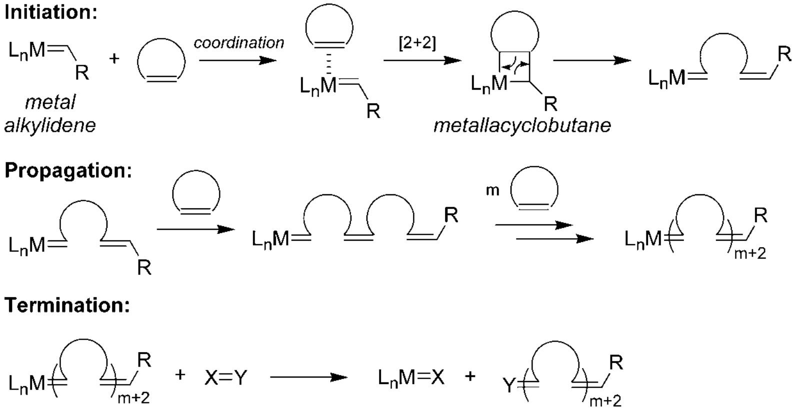

Figure 6.2 The generally-accepted mechanism of contemporary metal catalyzed ROMP reactions. Note that in this example, the metal alkylidene functions as the polymerization initiator.

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[1] For most Ru-mediated polymerizations this reagent is ethyl vinyl ether, which provides a [Ru] = CHOEt type complex and a methylidene end-functionalized polymer; For Mo-mediated polymerizations, this reagent is benzaldehyde, which provides a [Mo] = O type complex and a benzylidene end-capped polymer.

There are three important features regarding metal-mediated ROMP reactions. First, it is important to note that the propagating metal centers on the growing polymer chains may exist in either the metallacyclobutane or metal alkylidene form. This difference depends on the transition metal and its associated ligands, as well as on the reaction conditions. Second, like most olefin metathesis reactions, ROMP is generally reversible. Thus, the basic mechanism illustrated in Figure 6.2 can proceed in the opposite direction as shown. As most ROMP reactions are reversible, they are equilibrium-controlled reactions and the position of the equilibrium (products versus reactants) can be predicted by considering the thermodynamics of the polymerization reaction. As with other ring-opening polymerizations, the reaction is driven from monomer to polymer by the release of strain associated with the cyclic olefin (so-called ''ring strain'') and balanced by entropic penalties. The most common monomers used in ROMP are cyclic olefins, which possess a considerable degree of strain ($>5\,\mathrm{kcal\,mol^{-1}}$), such as cyclobutene, cis-cyclooctene, norbornene, and their derivatives; as a result, polymerization generally proceeds to very high conversions and depolymerization processes are often not significant [6]. One notable exception is cyclohexene. With low ring strain, this cyclic olefin has very little enthalpic driving force to be polymerized using ROMP. At any rate, the temperature and concentration at which the polymerization is conducted has strong influences over the outcome of the reaction. Using the Gibbs free energy equation, one can derive a ''ceiling temperature'' and a related concentration at which polymerization (for any cyclic olefin) will not occur [7]. At this concentration/temperature juncture the entropic penalty is essentially too high to be compensated by the enthalpic contribution associated with the release of ring strain. These considerations are important when attempting the polymerization of any new cyclic olefin. Generally, the most favorable conditions for a successful ROMP reaction are high monomer concentrations and low temperatures. (Another key consideration is the chemical functionality present on the monomer, which often defines the initiator to be used. Additional discussion on this important point will be given below.)

In addition to the general ROMP mechanism illustrated in Figure 6.2 (and its related depolymerization mechanism), the equilibria noted above can be established via other metathetical pathways, including intermolecular chain-transfer and intramolecular chain-transfer (so-called ''backbiting'') reactions. Examples of these types of secondary metathesis reactions are shown in Figure 6.3. In an intermolecular chain-transfer reaction, one polymer chain containing an active metal alkylidene on its terminus can react with any olefin along the backbone of a different polymer chain in the same reaction vessel. Although the total number of polymer chains remains the same, the molecular weights of the individual polymers will increase or decrease accordingly. In a backbiting reaction, the active terminus of a polymer chain reacts with itself to release a cyclic species and a polymer chain of reduced molecular weight. Collectively, these chain-transfer reactions

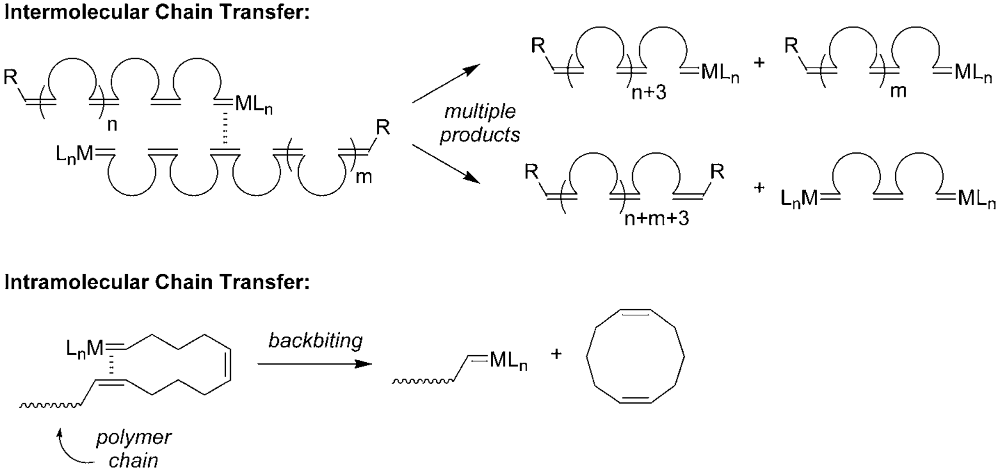


Figure 6.3 Generalized examples of intermolecular (top) and intramolecular (bottom) chain transfer rections that may happen during a ROMP reaction. These reactions typically lead to polymers with reduced molecular weights and increased polydispersities.

effectively broaden the molecular weight distribution (or polydispersity) of the system.

Another implication of equilibrium-controlled polymerizations such as ROMP is the propensity to form cyclic oligomers. According to the Jacobson–Stockmayer theory of ring–chain equilibria, the formation of cyclic oligomers will always accompany the formation of high molecular weight polymer [8]. The total amount of cyclic species present will depend on factors such as solvent, cis/trans ratio of the polymer backbone, rigidity of the monomer, reaction time, and concentration. Formation of cyclic species is favored at higher temperatures and lower concentrations with a critical value dependent on the factors noted above. While these side reactions are certainly disadvantageous when considering a living polymerization, they have been exploited to synthesize materials consisting almost entirely of cyclic species by simply conducting the reaction under relatively dilute conditions [9].

6.1.3
Living Ring-Opening Metathesis Polymerization

In 1956, Swarzc defined a “living polymerization” as one that proceeds “without chain transfer or termination” [10, 11]. Under certain conditions (defined below), living polymerizations afford polymeric materials that generally have very narrow molecular weight distributions. These distributions are usually quantified through determination of the sample's polydispersity index (PDI), which follows the equation: $\mathrm{PDI} = M_\mathrm{w}/M_\mathrm{n} = 1 + 1/\mathrm{DP}$, where M_w is the weight-averaged molecular weight, M_n is the number-averaged molecular weight, and DP is the degree of polymerization (i.e., the average number of monomer units per polymer chain). Living polymerizations can often be distinguished from kinetically controlled (i.e., free radical) or condensation-type polymerizations by analyzing the evolution of the polymer's molecular weight as a function of time and/or monomer conversion. Condensation polymerizations generally provide high molecular weight polymer only at very high conversions while kinetically controlled polymerizations provide high polymer at relatively early stages. In contrast, molecular weight is directly proportional to monomer conversion in living polymerizations as all polymer chains are growing at essentially the same rate. Gold demonstrated that even when the rate of propagation is orders of magnitude greater than the rate of initiation, a living polymerization can lead to polymers with low polydispersities [12]. However, in systems where the rate of initiation is faster or similar to the rate of propagation, control over the polymerization is obtained at an earlier stage of the reaction. Under these conditions, access to well-defined, monodispersed materials of low molecular weight is possible.

Thus, in addition to Swarzc's original constraint, we will require a ROMP reaction to exhibit the following characteristics to be considered ''living and controlled'': (i) fast and complete initiation, (ii) exhibits a linear relationship between the degree of polymerization (typically measured as the number-average molecular weight of the polymer, M_n) and monomer consumption (or conversion to polymer), (iii) PDIs < 1.5, and (iv) at the conclusion of the polymerization reaction, the polymer chains possess active species at their termini that are capable of further reaction or transformation [13]. Assuming complete conversion of monomer to polymer, ROMP reactions with these characteristics enable the synthesis of well-defined polymers with narrow distributions and predictable molecular weights specified by the initial monomer to initiator ratio (M/I). Under a broader context, such ROMP reactions facilitate the preparation of well-defined block-, graft-, and other types of copolymers, end-functionalized polymers, and various other polymeric materials with complex architectures and useful functions [14].

When considering the metal-mediated and equilibrium nature of most ROMP reactions, it quickly becomes apparent that very special olefin metathesis complexes are needed to satisfy all these requirements. The complex must (i) convert to growing polymer chains quantitatively and rapidly (i.e., exhibit fast initiation kinetics), (ii) mediate a polymerization without a significant amount of (intramolecular or intermolecular) chain transfer or premature termination, (iii) be readily modified and react with accessible terminating agents to facilitate selective end-functionalization or end-transformation, (iv) display good solubililities in common organic solvents (and/or aqueous media for certain applications), and (v) for convenience, broad usability and practicality, show high stability toward moisture, air, and common organic FGs. To avoid confusion, these complexes will be often referred to as *initiators* for the remainder of the review with the notion that each initiator will produce one growing polymer chain (via an active propagating species that remains at the end of the chain facilitating further growth until the polymerization reaction terminates).

6.2
Initiators for Living ROMP

6.2.1
Historical Aspects

The advances in ROMP can be attributed to the tremendous efforts of a large number of researchers dedicated to the development of well-defined, FG tolerant initiators capable of facilitating olefin metathesis reactions. Early initiator systems were often heterogeneous mixtures that were extremely sensitive toward air and moisture, difficult to characterize, and almost impossible to systematically study and optimize. It was immediately recognized that the development of an initiator with a well-defined structure was essential for olefin metathesis to reach its full potential. This was especially true for the development of a living ROMP initiator where knowledge and precise control over polymerization kinetics is critical. It is beyond the scope of this review to give an in-depth analysis of this rich and fascinating history; however, this section includes selected milestones in the historical development of initiators suitable for living ROMP. The aim is to provide the reader with an appreciation for the origin and progression of this field, which may lead to insight into how challenges in the future may be addressed and overcome.

6.2.2
Ill-Defined Initiators

Although the use of olefin metathesis in synthetic organic chemistry (e.g., ring-closing metathesis, cross metathesis, ring-opening cross metathesis, etc.) has gained in prominence [15], its roots were founded in the field of polyolefin and petroleum chemistry. In fact, because of their similar beginnings, there were considerable misunderstandings regarding the relationships and respective mechanisms of Ziegler–Natta type olefin addition polymerizations and ROMP reactions.

While studying the oligomerization of ethylene using alkyl aluminum catalysts, Ziegler isolated butenes rather than oligomeric materials [16], a reaction that was ultimately discovered to be catalyzed by Ni salts (contaminants from the reaction vessel). Subsequent exploration of other metal salts by Ziegler and Natta resulted in the finding that titanium salts resulted in the formation of high polymers; it was a work that served as the basis for much of the present polyolefin industry and culminated in the 1963 Nobel Prize in Chemistry [17].

The olefin metathesis reaction was discovered serendipitously by groups searching for new transition-metal catalysts, cocatalysts, and additives to facilitate the polymerization of other olefins. Interestingly, these results remained relatively obscure for a number of years. However, this changed dramatically after Phillips Petroleum informed the chemical community that they commercialized a variant of the olefin metathesis reaction as the "triolefin process" in the 1960s [18]. As a result, massive efforts toward understanding, optimizing, and applying olefin metathesis chemistry were launched. Particular attention was directed toward the isolation and characterization of metal–carbene complexes, metallacyclobutanes, and other key intermediates in olefin metathesis reactions (Figure 6.2) [19].

The potential of olefin metathesis in the synthesis of polymeric materials was borne out from reports by Truett and coworkers at DuPont and Natta at almost the same time the reaction was discovered [20]. They independently found that a polymer could be obtained from norbornene using heterogeneous mixtures of various Ti, W, or Mo halides that were often enhanced with strongly Lewis acidic Al cocatalysts. Importantly, the polymer was unsaturated with a repeating unit that was essentially 1,3-dimethylidenecyclopentane (Figure 6.4). This suggested that the norbornene ring had somehow opened during the polymerization. As the carbon–carbon double bonds along the backbones of the polynorbornenes were mostly of cis geometry, the mechanism of the polymerization was believed to occur through a ring-opening reaction that originated at the bridgehead carbon.

Soon after, similar reports on the conversion of norbornene and other cyclic olefins into unsaturated polymers began to emerge. Calderon and coworkers at Goodyear reported a new system for initiating metathesis polymerizations that was prepared from a mixture of WCl_6, $AlEt_2Cl$, and ethanol [21]. Importantly, this mixture resulted in a homogeneous initiator

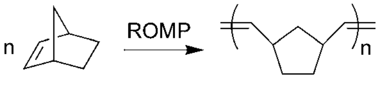


Figure 6.4 The ROMP of norbornene affords polynorbornene, a polymer that contains 1,3-methylidenecyclopentane as its repeating unit.

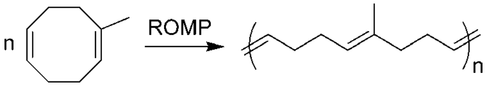
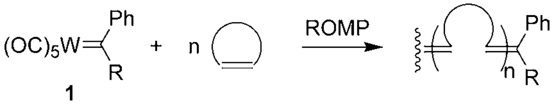


Figure 6.5 The ROMP of 1-methyl-1,5-cyclooctadiene affords a perfectly alternating copolymer of 1,4-butadiene and isoprene.



1

Figure 6.6 A generalized example of a ROMP reaction using a well-defined W initiator. Note that upon initiation of the polymerization reaction, one end-group of the polymer chain contains the alkylidene that was formerly on the initiator.

that showed reproducible activities and opened the potential of creating commercially important materials. The initiator also helped in demonstrating the potential of ROMP in creating new types of polymers. For example, in the late 1960s, Calderon and coworkers reported that polymerization of 1-methyl-1,5-cyclooctadiene afforded a material that was essentially a perfectly alternating copolymer of 1,4-butadiene and isoprene (Figure 6.5) [22].

A large number of other initiators based on a wide range of transition metals were also discovered by Natta, Michelotti, Dall'Asta, Banks, Rinehart, and other researchers from around the world [23]. Detailed studies on the performance of many of these initiators in ROMP can be found in reports by Osborn, Rooney, Ivin, Feast, and others [24]. Although ROMP reactions using these initiators (heterogeneous or homogeneous) were not living and many required extremely dry and air-free conditions, they collectively provided insight into the mechanism of olefin metathesis and built a solid foundation for the development of well-defined initiators.

One of the first reports of a well-defined initiator that was capable of mediating ROMP was from Katz in 1976. He reported a series of tungsten complexes $(CO)_5W{=}CPhR$ (**1**, R = Ph or OCH_3), which were previously prepared by Casey and Fischer [25], that were found to facilitate the polymerization of a variety of cyclic olefins, including cyclobutene, cycloheptene, cyclooctene, and norbornene, without the need for any cocatalyst or additive (Figure 6.6). Although there was little molecular weight control over these polymerizations and the polydispersities of the resultant polymers were relatively broad (PDI > 1.85), the disubstituted methylidene moiety of **1** was found on the ends of the polymer chains [26]. Thus, the complex appeared to suffer from poor initiation characteristics or extensive secondary metathesis reactions (or both). Regardless, the contribution provided tremendous credence to the feasibility of a creating a well-defined complex that was capable of initiating and mediating a living ROMP reaction.

6.2.3
Titanium

The first examples of single-component, well-defined initiators capable of mediating living ROMP reactions were based on Ti. As shown in Figure 6.7,

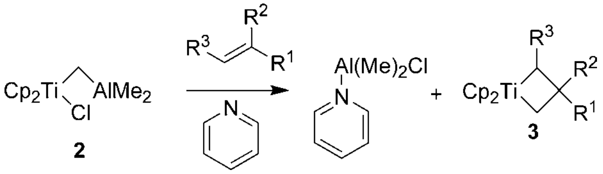


Figure 6.7 Treatment of the Tebbe reagent (**2**) with an olefin in the presence pyridine (which sequesters the aluminium reagent) affords a well-defined ROMP initiator, bis(cyclopentadienyl) titanacyclobutane comples (**3**).

by reacting the Tebbe reagent (**2**) [27] with various olefins in the presence of pyridines (to sequester the aluminum), a variety of well-defined, metathesis-active bis(cyclopentadienyl) titanacyclobutanes (**3**) were obtained [28]. Although these complexes were not extremely active, they did mediate the ROMP of norbornene without any evidence of chain-transfer reactions [29]. Subsequent attention focused on the synthesis of a well-defined Ti complex that exhibited rapid initiation kinetics at practical temperatures through modification of the substitution pattern on the metallacyclobutane ring [30]. For example, complex **4**, prepared via reaction of **2** with 3,3-dimethyl-1-butene, was found to mediate the ROMP of norbornene at a convenient 60 °C (Figure 6.8). At elevated temperatures, the titanacyclobutane **4** is believed to undergo a cycloreversion reaction which affords a reactive Ti methylidene and a volatile alkene. The resulting coordinatively unsaturated Ti methylidene quickly binds norbornene and undergoes another [2 + 2] cycloaddition reaction to afford **5**. At this point, the reaction vessel can be cooled to room temperature and the complex can be isolated. However, in the presence of excess norbornene at elevated temperatures (>60 °C), a polynorbornene with a Ti alkylidene end-group (**6**) is obtained.

Notably, these Ti initiators provide polymers with narrow polydispersities (PDI < 1.2) and with molecular weights that scale linearly with the amount of monomer consumed divided by the number of active metal centers. As the

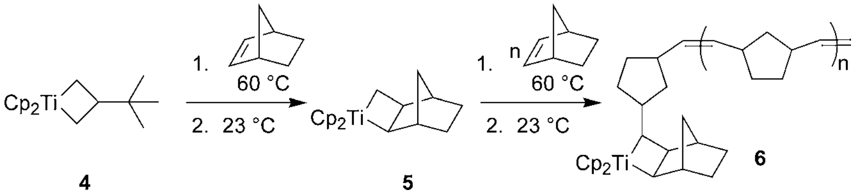


Figure 6.8 Representative example of a ROMP of norbornene using a Ti-based initiator. At 60 °C, the titanacyclobutane **4** is believed to undergo a cycloreversion reaction, affording a Ti methylidene that ultimately initiates the polymerization reaction. At the conclusion of the reaction, a polymer with a Ti titanacyclobutane may be isolated.

rate-determining step of the ROMP is the unimolecular cycloreversion of the titanacycle noted above, the rate of the polymerization is proportional to the concentration of the initiator (i.e., the rate equation is zero order in monomer). This provides an extremely convenient method to modify molecular weight of the polymer chains. The complexes can simply be heated in a large excess of monomer until the desired molecular weight is reached.

Like the Tebbe reagent, these Ti-based ROMP initiators react with carbonyl containing compounds in a Wittig-type fashion to form substituted olefins and deactivated Ti oxide species. This reactivity pattern provides a convenient method to not only terminate the polymerization but also to install FGs on the ends of polymer chains. For example, addition of benzaldehyde to the reaction vessel at the conclusion of a polymerization affords a polymer chain with a benzylidene moiety on its terminus (Figure 6.9). One can envision using a variety of functionalized aldehydes as a means for installing reactive groups on the ends of polymers chains. Although, depending on the tolerance of the initiator employed, the FGs may have to be protected and subsequently deprotected after the polymerization reaction is complete. Regardless, this overall process provides a method for elaborating or utilizing the end-groups of polymer chains produced via ROMP.

The ability of these Ti complexes to initiate living ROMP reactions enabled the synthesis of macromolecular materials with advanced architectures as well as functional materials. An early example of preparing block copolymers using living ROMP is shown in Figure 6.10. By sequentially adding various norbornene derivatives to Ti-based initiator **7**, di- and triblock copolymers were prepared with very low polydispersities [31, 32]. Subsequently, a variety of bifunctional and multifunctional initiators based on these Ti initiators were also developed and used in the construction of macromolecular materials with advanced topologies [33]. Although the low activity of the Ti-based initiators limited their use in living polymerizations, their advantages included a flexible design to control initiation, a means to install functional and well-defined end-groups, and the ability to form block copolymers, which were first demonstrated with these systems.

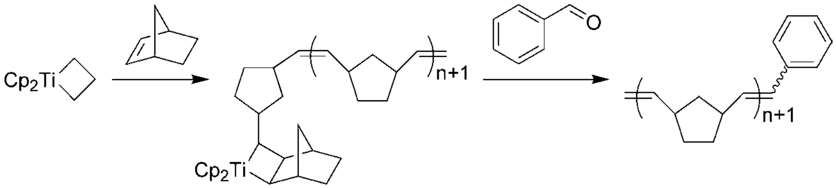


Figure 6.9 Example of terminating a ROMP reaction, initiated with a titanacyclobutane complex, with benzaldehyde. Notably, this reaction sequence affords a polymer with a benzylidene moiety on one terminus of the polymer chain (stemming from the added benzaldehyde) and a methylidene on the other (stemming from the initiator).

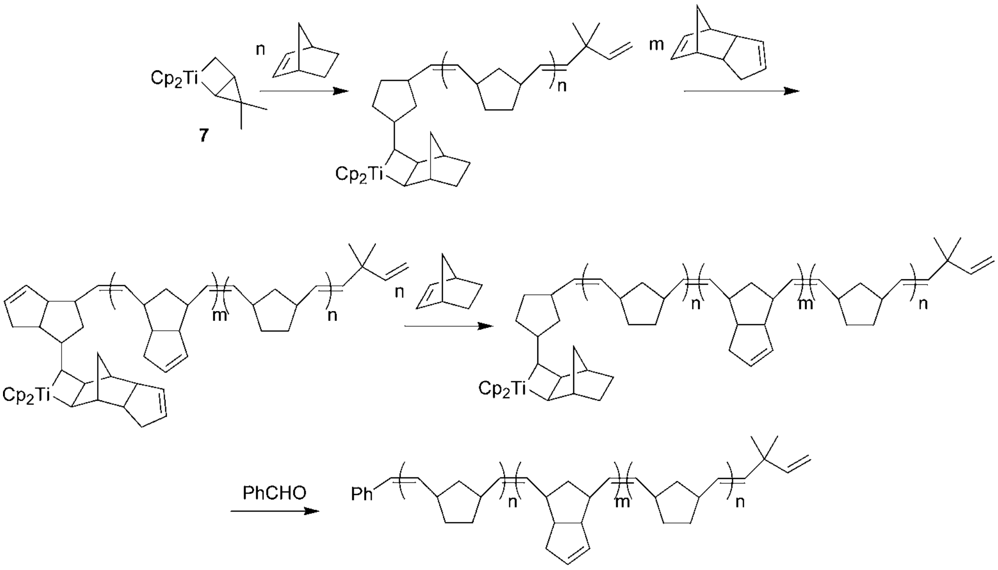


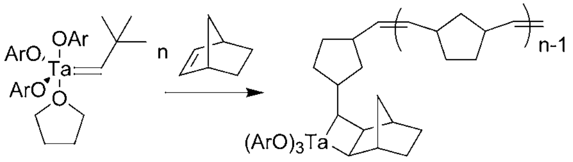
Figure 6.10 Example of preparing a well-defined triblock coploymer using ROMP. Note that the end-groups of the copolymer stem from the Ti-based initiator and the added benzaldehyde.

6.2.4
Tantalum

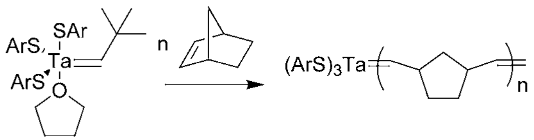
Shortly after the Ti complexes were reported, a new series of well-defined complexes (**8**) based on tantalum were introduced by Schrock and coworkers (Figure 6.11) and were shown to function as ROMP initiators [34]. These complexes were prepared in three steps from commercially available $TaCl_5$, by sequential treatment with $Zn(CH_2CMe_3)_2$, tetrahydrofuran (THF), and the requisite aryloxide ligand, in excellent overall yields. While these complexes have been shown to polymerize norbornene in a well-controlled fashion, they possessed higher activities than their Ti predecessors. As a result, it was found to be necessary to monitor the ROMP reactions if materials with low polydispersities were desired [35]. For example, stopping a polymerization of norbornene ($M/I = 200$) at 75% monomer conversion provided a polynorbornene with a molecular weight of 32 100 Da and a $PDI = 1.04$. However, if this same polymerization was taken to completion (i.e., complete consumption of monomer), polymers with increased molecular weights were observed, but their polydispersities were significantly broader ($PDIs > 1.6$). The discrepancy has been attributed to secondary metathesis reactions as a result of the high activity of the propagating species combined with slow initiation kinetics. Thus, while the rates of secondary metathesis reactions are slower than chain propagation, they appear to become competitive as the polymerization approaches completion. The mechanism of the ROMP using these initiators is believed to proceed similarly as their Ti predecessors. For example, the rates of polymerization are first-order with respect to the Ta complex and independent of the concentration of norbornene, suggesting that the metallacyclobutane reversion is again the rate-determining step of the polymerization.

The propensity of these Ta-based initiators to facilitate secondary metathesis reactions was successfully reduced through the incorporation of bulky, electron rich diisopropylphenoxide ligands [36] which essentially decreased their electrophilic character (Figure 6.11). As a result, norbornene was successfully polymerized to completion using this initiator and the resultant polymers obtained at the conclusion of the reaction exhibited very narrow polydispersities (PDI > 1.1). One feature that distinguishes Ta-based **8a** (and the aforementioned Ti complexes) from **8b** is that propagating chains from the latter appear to have alkylidene end-groups as opposed to metallacyclobutane end-groups in the former. Thus, the rates of polymerization with initiators like **8b** are second-order and dependent on the initiator and monomer concentration. Regardless, both complexes **8a** and **8b** react with aldehydes and ketones in a Wittig-type fashion, which provides a convenient method for terminating ROMP reaction and installing FGs on the termini of polymer chains.

The Ti and Ta complexes mentioned above are extremely Lewis acidic as a result of their high oxidation states. In addition to carbonyls, they react rapidly with most heteroatom-containing FGs (hydroxyl, amino, etc.), placing limitations on their utility in living ROMP reactions. However, more



8a, Ar = 2,6-diisopropylbenzene



8b, Ar = 2,4,6-triisopropylbenzene

Figure 6.11 Two representative Ta-based ROMP initiators. Note that the aryloxy-containing initiator (top) prefers to exist in a metallacyclobutane resting state during a ROMP whereas the thiolate analog (bottom) prefers to remain as an alkylidene.

importantly, they were an outstanding testament to the power of initiator design in tailoring activity. Attention soon turned toward the discovery of new initiators that not only maintained this tunability but were also tolerant of a broader range of FGs.

6.2.5
Tungsten

Olefin metathesis catalysts containing tungsten have been employed for almost a half century. In fact, several commercial processes utilize various tungsten-based complexes, and will be described in more detail in a following section of this review. However, for most of this time, the catalysts were ill-defined and/or comprised of heterogeneous mixtures. While many of these systems were successful in initiating ROMP reactions, the respective polymerizations did not show living characteristics. Furthermore, many of these initiators were highly Lewis acidic and were sensitive to most heteroatom-containing FGs.

As noted above, Fischer and Casey prepared the first well-defined initiators based on tungsten. While these systems were capable of initiating the polymerization of strained cyclic olefins, they did not do so in a living fashion. In the late 1970s, Schrock and Osborn developed new classes of well-defined, tungsten-based complexes with the general structures of $W(=CHC(CH_3)_3)(OCH_2\text{-}t\text{-}Bu)_2Br_2$ (**9**) [37]. As shown in Figure 6.12, they were found to polymerize a variety of derivatized norbornenes in a living manner at low temperatures and were also subsequently used to make block

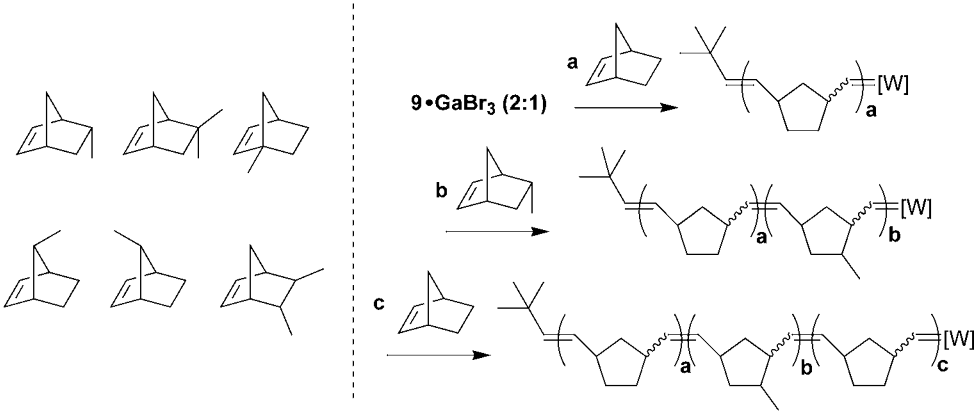


Figure 6.12 (left) The structures of various derivatized norbornenes that have been successfully polymerized using W-based ROMP initiators. (right) Synthesis of a norbornene-based triblock coploymer using initiator **9** in the presence of a Lewis acid activator ($GaBr_3$).

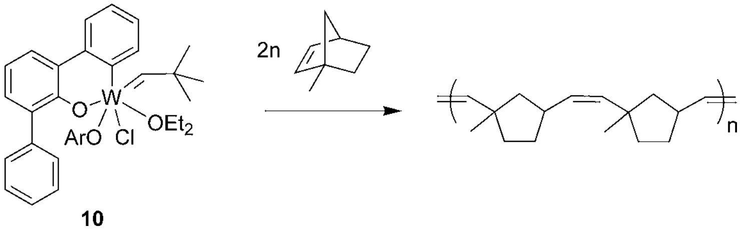
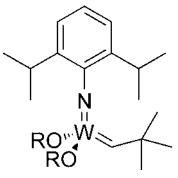


Figure 6.13 Romp of a sterically-hindered norbornene derivatives using the W-based initiator **10** produces a polymer with high stereoregularity.

copolymers when a Lewis acid (such as $GaBr_3$) was included during the ROMP reactions [38, 39].

A variety of Lewis acid-free initiators based on the structure $W(OAr)_2Cl(CHCMe_3)(CH_2CMe_3)(OR_2)$ (Ar = 2,6-disubstituted phenyl; R=Et or ^{i}Pr) were reported by Basset and coworkers [40]. These single-component complexes showed exceptional FG tolerance and were reported to initiate the polymerization of a variety of functionalized norbornenes, including those which contained ester and nitrile function groups. Notably, complex $W(=C(CH_2)_4)(OCH_2\text{-}t\text{-}Bu)_2Cl_2$ was reported to polymerize *exo*-norborn-5-ene-2,3-dicarboxylic anhydride, which was a testament to its relatively high FG tolerance [41]. As shown in Figure 6.13, complex **10**, which possessed a bulky aryloxy substituent, was shown to facilitate stereocontrol over the polymerization of 1-methylnorbornene and provided high cis polymers with a strong head-to-tail preference [42]. The high activity of these complexes promoted secondary olefin metathesis reactions which ultimately prevented the corresponding ROMP reactions from showing living characteristics. However, these results were an important demonstration that initiators with increased FG tolerance could be made and designed to exert stereochemical control over ROMP reactions.

Schrock and coworkers modified the design of the complex described above to arrive at a new single-component, Lewis acid-free, imido-alkoxy based system (**11**) that showed outstanding activities in ROMP reactions [43]. A particularly useful feature of these complexes is their modular alkoxide ligands which were shown to vary the activity of the corresponding initiators over a considerable range, depending on their structures. For example, addition of an excess of norbornene to **11a** resulted in a living ROMP and afforded polymers with predictable molecular weights and polydispersities as low as 1.03 after quenching with benzaldehyde [44]. Increasing the electrophilic character of the initiator via replacement of the hydrogenated alkoxy ligands with fluorinated analogs substantially increased their activity in olefin metathesis reactions. For example, complexes **11b** and **11c** (structures shown in Figure 6.14) were found to readily scramble cis-2-pentene (whereas **11a** does not); as a result, the ROMP of norbornene using these initiators results in secondary metathesis reactions as well as slow initiation relative to propagation.



11a, R = *t*Bu
11b, R = $C(CH_3)_2(CF_3)$
11c, R = $C(CH_3)(CF_3)_2$

Figure 6.14 Structures of various tungsten alkylidenes that have been successfully employed as ROMP initiators.

Initiators with similar activities but increased FG tolerance were obtained using oxo-tungsten based alkylidene complexes W(=CH-*t*-Bu)(O)(PR_3)($OAr)_2$. These initiators were found to mediate the living ROMP of 2,3-dicarbomethoxynorbornadiene and 2,3-bis(trifluoromethyl)norbornadienes[45] to give polymers with high number of cis olefins in their backbones (>95%) and high isotacticities (>95%). There was also an excellent linear relationship between the molecular weight of the polymer and the initial monomer to initiator ratio. Notably, the initiators appear to show very little propensity to facilitate secondary metathesis reactions as there is no change in the PDI (which can often be as low as 1.01) of the polymer even after prolonged reaction in solution. The polymerizations are extremely rapid as more than 100 equivalents of monomer can be polymerized within minutes. These W complexes were also found to display Wittig-type reactivity in analogy to their Ti and Ta precursors. As such, the addition of ketones or aldehydes can be used to terminate the polymerization and install functionalized and/or reactive end-groups.

The aforementioned W complexes have also been shown to initiate the living ROMP of other classes of cyclic olefins. As discussed in the introduction, cyclopentene is considerably less strained than norbornene, which increases opportunities for various types of backbiting reactions. Thus, this monomer is considerably more difficult to polymerize in a living fashion and generally requires low temperatures. For example, a living polymerization of cyclopentene was conducted at −40 °C with **11a** and afforded a polypentenamer with a PDI of 1.08 [46]. It was important to monitor the ROMP reaction as extended exposure to the initiator caused molecular weight broadening over time. In contrast to cyclopentene, cyclobutene is considerably strained and readily polymerizes. As a result, the rates of initiation are often slower than the rates of propagation, which limits control over the ROMP reaction and often leads to polydispersed materials. To enable living ROMP reactions of cyclobutenes, a donor ligand such as trimethylphosphine (PMe_3) must be included in the polymerization reaction [47]. This ligand reversibly binds to the active propagating species and reduces its propensity to mediate olefin metathesis chemistry. The rate of the polymerization reaction is therefore reduced relative to initiation and the ROMP adopts living characteristics. Other donors such as dimethylphenylphosphine, phenyldimethylphosphine, pyridine, quinuclidine, and THF may also be used, although, as a result of their weaker binding affinities, larger amounts are often required.

The advantages and high activities of W-based initiators were manifested in the synthesis of organic materials with promise in electronic applications.

A key requirement for application of these materials in any electronic device is conductivity, which necessitates an extensively unsaturated or conjugated polymeric backbone. The prototypical example is polyacetylene which, interestingly, may have been discovered in the Natta group. As shown in Figure 6.15, exposing acetylene to typical classical olefin addition polymerization initiators (trialkylaluminum reagents mixed with titanium alkoxides) at elevated temperatures produced polyacetylene as a red powder, later identified as the trans isomer. Performing the polymerization at low temperatures afforded the cis isomer. Unfortunately, these materials were insoluble and sensitive toward oxidation, which curtailed further efforts toward studying these materials. The area was revitalized in the early 1970s when Shirakawa reported a modification of Natta's original procedure that allowed for the synthesis of a usable thin film of the polymeric material. In conjunction with Heeger and MacDiarmid, it was discovered that the electrical conductivity of this film could be drastically enhanced through the introduction of various dopants and oxidants. This outstanding discovery opened the field of organic electronics and ultimately resulted in the 2000 Nobel Prize in Chemistry [48].

As shown in Figure 6.16, a wide variety of routes to prepare polyacetylene using ROMP have been developed. To solve the problem of intractability, a

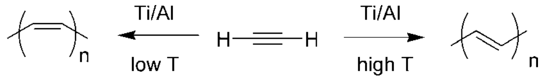


Figure 6.15 Synthesis cis and trans polyacetylene.

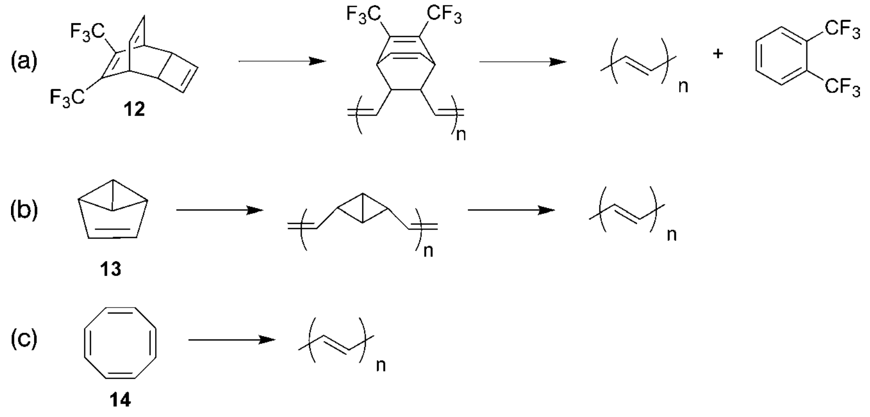
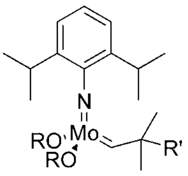


Figure 6.16 Various ROMP-based methods used to synthesize polyacetylene. (A) In this method, which is ofetn called the Durham route, ortho-di(trifluoromethyl)benzene is liberated from the polymer obtained from **12** to afford polyacetylene. (B) ROMP of benzvyalene (**13**) followed by rearrangement affords polyacetylene. (C) Cyclooctatetraene possesses enough ring-strain to undergo ROMP and can be poymerized directly to afford polyacetylene.



15a, R = *t*Bu
15b, R = $C(CH_3)_2(CF_3)$
15c, R = $C(CH_3)(CF_3)_2$
(R' = CH_3 or Ph)

Figure 6.17 Structures of various molybdenum alkylidenes that have been successfully employed as ROMP initiators.

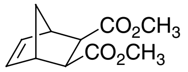
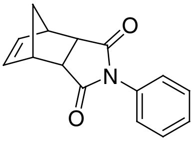
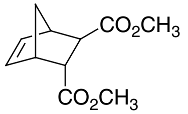
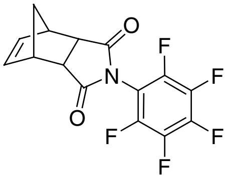
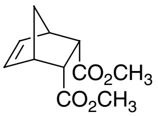
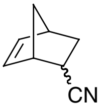
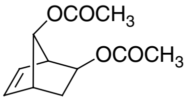
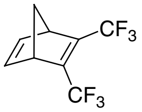
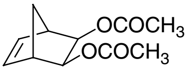
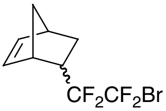
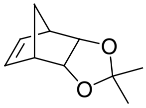
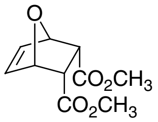
new monomer (**12**) was developed that upon polymerization would provide a soluble and processable precursor to polyacetylene [49]. Subsequent thermal or chemical treatment of the polymer obtained from the ROMP of **12** would eliminate a volatile small molecule and liberate polyacetylene. This process is often called the *Durham route to polyacetylene*. As a means to limit mass loss associated with this approach, benzvalene (**13**) was synthesized and polymerized using ROMP [50]. Rearrangement of the resulting polymer produced polyacetylene. In a third approach, the ROMP of cyclooctatetraene (COT) (**14**) using various W initiators provided a "one-step" synthesis of polyacetylene from a liquid monomer, which after doping, provided a highly conductive material [51]. Limitations of the latter approach included a nonliving nature of the ROMP reaction due to competing secondary metathesis reactions (e.g., benzene is one possible product that forms upon intramolecular cyclization) and the difficulties associated with processing and handling the resultant films.

6.2.6
Molybdenum

As noted in the introduction, initiators that tolerate a broad range of organic FGs have been (and still are) highly desired since the inception of the olefin metathesis reaction. While the well-defined W initiators noted above were a strong testament of progress toward this goal, a significant advance was Schrock's introduction of well-defined Mo-based alkylidenes (**15**) (Figure 6.17) [52]. Although structurally similar to W-based alkylidenes **11**, these initiators tolerated a much broader range of functionality including monomers containing ester, amide, imide, ketal, ether, cyano, trifluoromethyl, and primary halogen-containing FGs. The increased FG compliance also facilitated their synthesis and use when compared to their W analogs, as they exhibited a greater tolerance toward oxygen, water, and other impurities. These complexes were also found to be more stable toward decomposition and other side reactions.

A representative sample of functionalized norbornene-based monomers that are amenable to living ROMP using **15a** is shown in Table 6.1 [53]. In general, the resultant polymers showed narrow polydispersities and good control over molecular weight was achieved by adjusting the initial monomer to initiator ratio. It is particularly noteworthy that monomers with strong electron

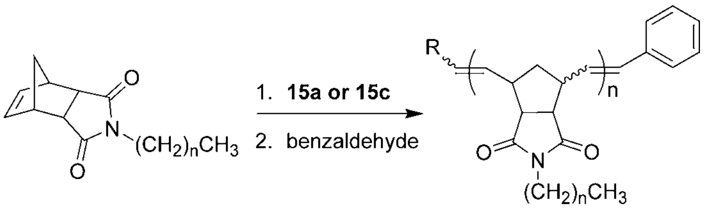
Table 6.1 ROMP of various monomers using **15a**. Unless otherwise noted, [M/**15a**] = 100.

Functional group	Monomer structure	PDI	Functional group	Monomer structure	PDI
Ester		1.07	Imide		1.07
		1.04	Imide		1.05 (M/I = 50)
		1.12	Cyano		1.07
Carbonate		1.11	Halo		1.05
		1.19			1.06
Ether		1.07	Ether/ester		1.17

withdrawing groups (i.e., fluorinated moieties) and norbornene derivatives with functionalized endo substituents were amenable to living ROMP. Previously, these monomers were either reluctant to undergo polymerization or coordinated to the ROMP initiators in a nonproductive manner.

One common feature that these initiators shared with their W precursors is that their activity could be tuned through modification of the alkoxide ligand. In general, complex **15a** does not readily react with acyclic olefins, limiting its ability to mediate secondary metathesis reactions when used in a ROMP reaction. In contrast, its fluorinated derivatives **15b** and **15c** showed markedly increased activities and were found to rapidly isomerize 2-pentene and other acyclic olefins. The difference in activities of these initiators in ROMP was demonstrated in a comparative study using various n-alkyl exo- and endo-norbornene dicarboximides [54]. As shown in Figure 6.18, various ROMP reactions initiated by **15a** afforded polynorbornenes with lower polydispersities than analogous reactions initiated with **15c**. The differences were ultimately attributed to not only the higher activity of the latter, but also to its relatively poor initiation characteristics. Thus, when used in ROMP applications it is important to monitor the polymerization to find timescales that maximize the rate of polymerization with respect to the rates of chain-transfer reactions. Notably, the endo-5-norbornene-2,3-dicarboximides were obtained from the methyl esters of amino acids and the resultant polymers were designed as synthetic analogs to biological polymers [55]. Star polymers have also been prepared using the aforementioned initiators [56].

Another advantage of the Mo initiators is their ability to provide stereoregular polymers. While certain conventional initiators were well known to produce substituted polymer chains with high stereoregularity, it was discovered that well-defined Mo alkylidenes could also exert control over polymer stereochemistry [57]. For example, Schrock, Feast, and Gibson found that polymers obtained from the living ROMP of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene initiated by **15a** were highly tactic, possessing >98% trans olefins along their backbones. Interestingly, when the same ROMP reaction was initiated with **15c**, the resultant polymer was also highly tactic, but featured >98% cis olefin content. Furthermore, they found that alkoxy ligand exchange was rapid on the timescale of the polymerization (Figure 6.19), enabling the synthesis of polymers with predetermined amounts of cis/trans contents by initiating the ROMP with varying mixtures of **15a** and **15c**. Notably, these ROMP reactions were living and provided materials with tunable molecular weights and low polydispersities. A kinetically controlled mechanism that balances the rates of interconversion of



catalyst	monomer	polymer PDI
15a	exo (n = 6-11)	1.05 - 1.1
15c	exo (n = 6-11)	1.3 - 2.1
15a	endo (n = 8)	1.3
15c	endo (n = 8)	1.8

Figure 6.18 Comparison of representative ROMP reactions initiated by **15a** and **15c**. Notably, the former leads to polymers with significantly lower polydispersities than the latter.

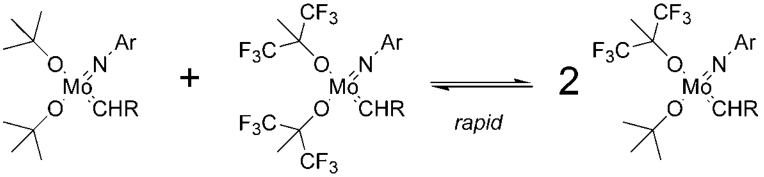


Figure 6.19 The exchange of the alkoxy ligands in the Mo-based alkylidenes shown is rapid. Since each initiator has its own unique set of steroselectivities, polymers with predetermined cis/trans ratios can be prepared by using combinations of these two complexes.

cis and trans rotamers of the alkylidene moiety with the rate of polymerization has been proposed to describe the origin of the stereochemical control in these systems [58]. This mechanistic knowledge was later used to create Mo-based initiators containing C_2-symmetric diolate ligands, which ultimately provided highly isotactic polymers via an enantiomorphic site-control mechanism [59].

In addition to norbornene-derived architectures, Mo-based initiators were found to polymerize a range of cyclic olefins with varying degrees of ring strain and functionality [60]. For example, polycyclopentene with controllable molecular weights and narrow polydispersities (PDI < 1.1) was obtained using initiator **15a** [61]. As with the ROMP reactions initiated with the various W initiators noted above, a strong donor ligand (e.g., trimethylphosphine) was required. However, the Mo complex initiated the ROMP reaction in a living fashion at room temperature whereas use of the W complex required low temperatures. This feature enabled estimation of the equilibrium monomer concentration (at room temperature) for cyclopentene (1.3 M). Thus, performing the ROMP reactions at relatively high monomer concentrations ($>$2.8 M) and low initiator loadings (initial monomer to initiator ratios of up to 10 000) enabled the synthesis of polycyclopentenes with molecular weights up to 67 800 Da with PDIs as low as 1.04. In addition, the living nature of these ROMP reactions facilitated access to well-defined diblock copolymers comprised of polycyclopentene and polyethylidenenorbornene which, after hydrogenation, afforded a new diblock copolymer with crystalline and amorphous regions (Figure 6.20).

While this sequential monomer addition method was found to be useful for preparing diblock copolymers, both monomers must be amenable to the same polymerization method. If two (or more) desired monomers cannot be polymerized by the same polymerization mechanism, then multiple steps are required. For example, poly(styrene)-*b*-poly(norbornene) and poly(methyl acrylate)-*b*-poly(norbornene) diblock copolymers have been prepared by combining atom-transfer radical polymerization (ATRP), a metal-mediated method for controlling radical polymerizations [62], with ROMP [63]. Norbornene was polymerized using ROMP and capped with an agent that was subsequently used as an initiator for the ATRP of styrene or methyl acrylate (Figure 6.21).

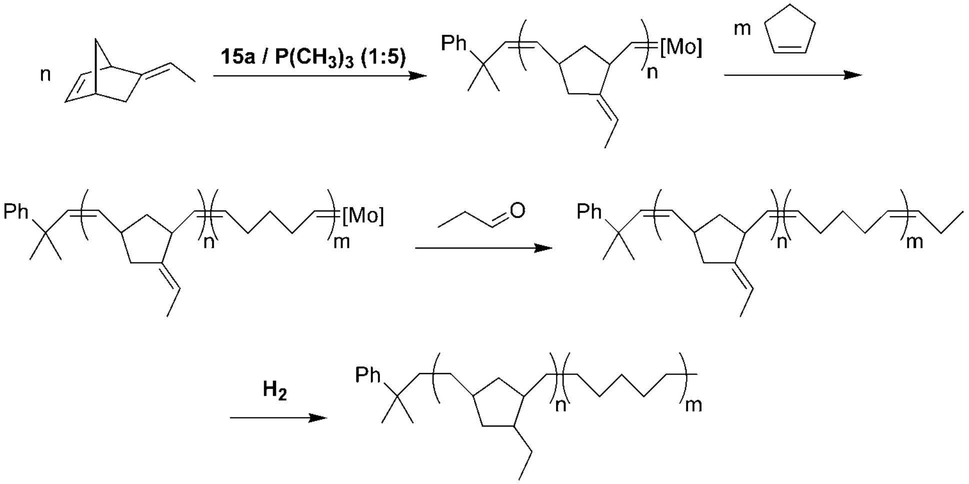


Figure 6.20 Synthesis of a diblock copolymer that possesses crystalline and amorphous segments using ROMP followed by hydrogenation.

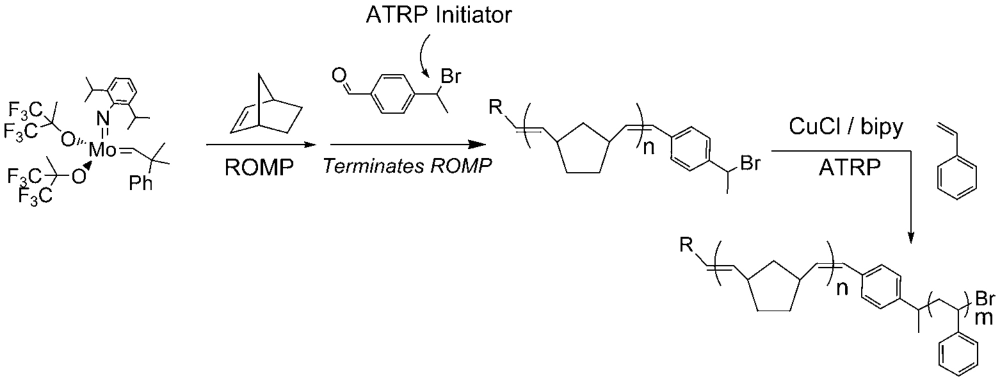


Figure 6.21 Synthesis of polynorbornene-*b*-polystyrene copolymers through the combination of ROMP and ATRP.

The Mo-based initiators have also been used to polymerize a variety of 3-substituted cyclobutenes [64]. For example, 3-methylcyclobutene and 3,3-dimethylcyclobutene were independently polymerized using **15a–c**. After hydrogenation, these materials are effectively poly(ethylene-*alt*-propylene) and poly(ethylene-*alt*-isobutylene) copolymers, respectively. Unfortunately, the high degree of ring strain associated with this monomer prevented control over the ROMP and materials with relatively broad polydispersities were obtained. As with the W initiators, the rate of propagation was found to be generally faster than the rate of initiation. In contrast, the ROMP of 3,4-disubstituted cyclobutenes using Mo-based initiators has been reported

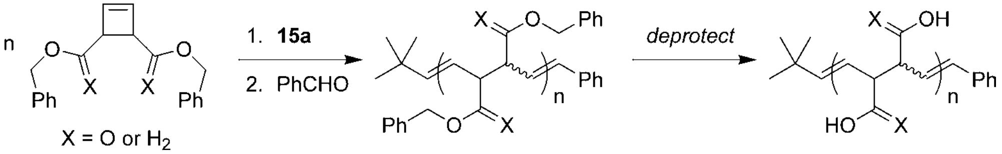


Figure 6.22 example of synthesizing a polymer with a high degree of fuctionality through the ROMP of a protected monomer, followed by deprotection.

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to be living and provides polymeric materials with well-defined structures [65]. For example, cis-cyclobutene-3,4-dicarboxylate and cis-3,4-bis(2-oxa-3-phenylpropyl)cyclobutene were polymerized using **15a**. Excellent control over the polymerization was observed and materials with low polydispersities (PDI < 1.15) were obtained. However, to obtain living character, it was found essential to use **15a** in these polymerizations as the more active derivatives (e.g., **15c**) lead to extensive chain transfer and ultimately materials with relatively broad polydispersities. As shown in Figure 6.22, these polymers were deprotected to provide a variety of high-strength adhesives.

More recently, the living ROMP of cyclopropenes was reported using various Mo-based initiators [66]. As shown in Figure 6.23, addition of a 3,3-disubstitutedcyclopropene to **15a–c** afforded the corresponding polycyclopropenamers in excellent yields ($>94\%$) after quenching the ROMP with benzaldehyde. Polymers obtained from these ROMP reactions exhibited molecular weights over 1000 Da with extremely narrow polydispersities (PDIs < 1.05). Analysis of the materials produced from these reactions by ^{1}H NMR spectroscopy suggested that the geometry of the olefins along the polymer backbones was predominately trans. Considering the paucity of examples reported in the literature on the polymerization of cyclopropenes, this result should provide a method for studying the thermodynamics of a new class of cyclic olefin amenable to ROMP and may lead to new elastomeric materials. Notably, reaction of 3,3-disubstitutedcyclopropenes with W alkylidenes **11** did not afford polymer and instead resulted in the corresponding W allylidenes (W=CH–CH=CHR) [67].

6.2.7
Ruthenium

Like most late transition metals, Ru shows low oxophilicity, which makes it inherently stable toward many polar FGs. However, Ru also readily forms

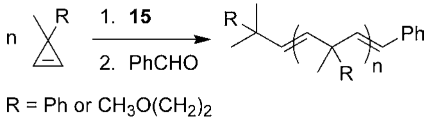


Figure 6.23 Synthesis of various polyalkenamers through the ROMP of cyclopropenes using a Mo-based initiator.

bonds with carbon which opens opportunities for mediating olefin metathesis reactions. Despite these advantages, the popularity and extensive utility of ruthenium in olefin metathesis have risen only relatively recently [68]. Early reports on the use of Ru stem from the 1960s when it was discovered that $RuCl_3$ salts in protic media facilitated the polymerization of various norbornene derivatives [23, 69]. Over two decades later, the use of this metal was reinvestigated for preparing charged polymers via ROMP [70]. During these studies, it was discovered that the hydrates of $RuCl_3$ or Ru(*p*-toluenesulfonate)$_2$ were successful in initiating the nonliving ROMP of various oxanorbornenes in aqueous or protic media. In organic solvents or when anhydrous conditions were employed, long initiation periods were required when the reactions were performed [71]. Regardless, these systems were found to initiate the ROMP of functionalized norbornenes, 7-oxanorbornenes, and norbornadienes. More importantly, the ability to conduct these polymerizations in aqueous or protic media exemplified their extraordinary tolerance toward polar FGs. Attention soon shifted toward isolating a well-defined Ru alkylidene, as it was assumed that Ru-based ROMP reactions proceeded by the same mechanism as for early metals [72]. For example, it was found that including various acyclic olefins during ROMP reactions resulted in polymeric materials with end-groups containing FGs from the added olefins [73]. Additional evidence stemmed from detailed NMR spectroscopic analyses, indicating that the microstructure of the polymers produced from Ru initiators were similar to those produced from well-defined metal alkylidenes (ruling out radical, ionic, and other types of chain addition polymerizations processes).

The first well-defined, single-component Ru-based ROMP initiator was $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ (**16**) [74]. The synthesis of this complex was facilitated by adopting synthetic methodology used to prepare some of the W-based alkylidene complexes mentioned above. Specifically, treatment of $(PPh_3)_2RuCl_2$ or $(PPh_3)_4RuCl_2$ with 3,3-diphenylcyclopropene afforded **16** in nearly quantitative yield. The complex was found to be stable in degassed and dry organic solvents (benzene, dichloromethane, etc.) for extended periods of time (>weeks). It is stable indefinitely in the solid state. The complex also does not show appreciable decomposition after exposure to water, various alcohols, or ethers and does not react with aldehydes and ketones in a Wittig-type fashion. Complex **16** was found to initiate the ROMP of norbornene in a living fashion with outstanding activity. For example, as shown in Figure 6.24, addition of norbornene to **16** resulted in a polymer chain with a propagating alkylidene species observable by ^{1}H NMR spectroscopy ($\delta = 17.79$ ppm). However, upon the addition of 2,3-dideuterionorbornene, the signal disappeared. Introduction of additional norbornene restored the signal and effectively produced a triblock copolymer of the two monomers. The polymerizations were effectively terminated through the addition of ethyl vinyl ether which replaced the Ru alkylidenes on the termini of the polymer chains with a methylidene and formed a metathesis inactive Fischer carbene complex ([Ru]=CHOR) [75]. Although the rate of initiation was found to be slower

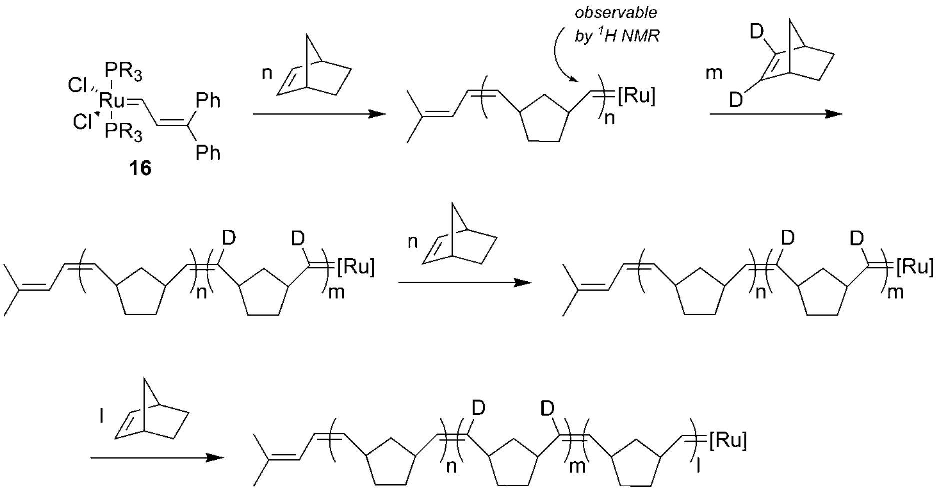


Figure 6.24 Synthesis of a triblock copolymer containing norbornene and 2,3-dideuterionorbornene. This reaction was monitored by NMR spectroscopy and used to evaluate the fidelity of the Ru-based initiator **16**.

than the rate of propagation, quantitative initiation was accomplished through the addition of excess monomer. Importantly, secondary metathesis reactions were minimal. Initiator **16** was also found to mediate the living ROMP of bicyclo[3.2.0]heptane and trans cyclooctene as well as block copolymers of these monomers with norbornene [76].

While **16** showed an impressive tolerance to a broad array of functionalities and was capable of mediating living ROMP reactions of norbornene and cyclobutene derivatives, the initiator did not show appreciable activity toward other olefins. In accord with the studies on other systems mentioned above, attention soon shifted toward optimizing the ligand environment of the Ru center. The most convenient method to optimize activity was to vary the nature of the phosphine ligand. Ultimately, it was discovered that the use of bulky and electron rich phosphines (e.g., PCy_3) lead to highly active initiators. This trend is in direct contrast with the Schrock initiator which shows higher activities when electron withdrawing ligands are employed. The aforementioned phosphine exchange reaction is relatively straightforward to perform and may be accomplished by adding an excess of PCy_3 (or $P(i\text{Pr})_3$) to **16** (Figure 6.25) [77]. The resultant complexes $(PPCy_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ (**17**) were found to be more stable and exhibited a broader range of tolerance toward FGs than their precursors. For example, in addition to water and alcohols, these complexes were found to be stable toward organic acids (acetic acid) as well as solutions of strong inorganic acids (diethyl ether solutions of hydrogen chloride). While these complexes were found to initiate the ROMP of norbornene, they did not show significant control over the reaction.

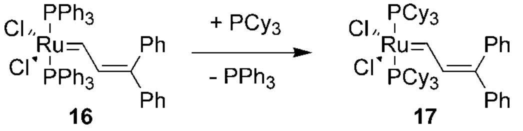


Figure 6.25 Addition of triclohexylphosphine to **16** results in ligand exchange and affords a derivative (**17**) that displays higher stabilities and increased activities in ROMP reactions.

Their highly active nature exasperated the differential between their rates of initiation and propagation. In addition, there was some evidence that chain-transfer reactions were occurring [78]. Thus, polynorbornenes obtained from the ROMP of norbornene using initiator **17** generally exhibited high molecular weights ($M_n > 10^5$ Da) with broad polydispersities (PDI > 2). However, these initiators opened new opportunities in the living ROMP of functionalized monomers that were less reactive than norbornene. For example, as shown in Figure 6.26, block copolymers of monomers containing silicon functionalities were successfully prepared [79].

Large quantities of metathesis-active Ru alkylidenes were soon available once an alternative synthesis involving the treatment of $(PPh_3)_2RuCl_2$ with diazobenzylidene was developed (Figure 6.27). The resulting complex **18** can be readily converted into its more active derivative **19** via phosphine exchange. Likewise, it can also be converted to other alkylidene complexes by adding the corresponding terminal olefin. Like the phosphine ligand, it was determined that the structure of the alkylidene affects the initiation characteristics of these complexes in ROMP reactions although a comprehensive study of complexes possessing various benzylidene derivatives revealed that the parent compound (**19**) has the most favorable initiation kinetics in ROMP reactions

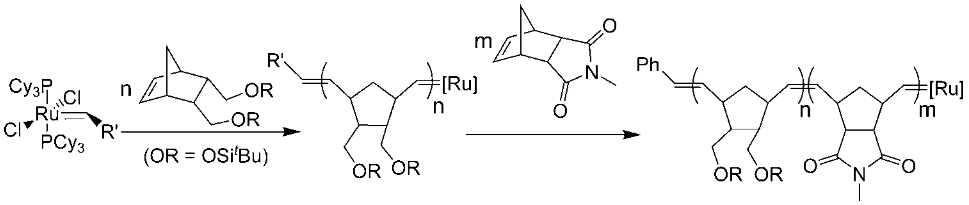


Figure 6.26 Synthesis of a block coploymer containing a high degree of silicon via ROMP.

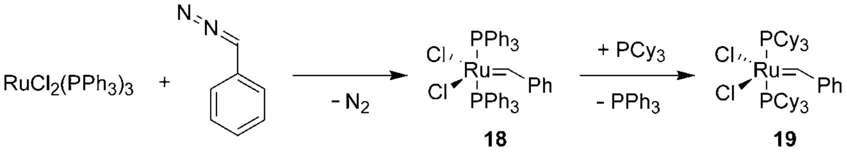


Figure 6.27 Two step synthesis of the Ru benzylidene initiator **19**.

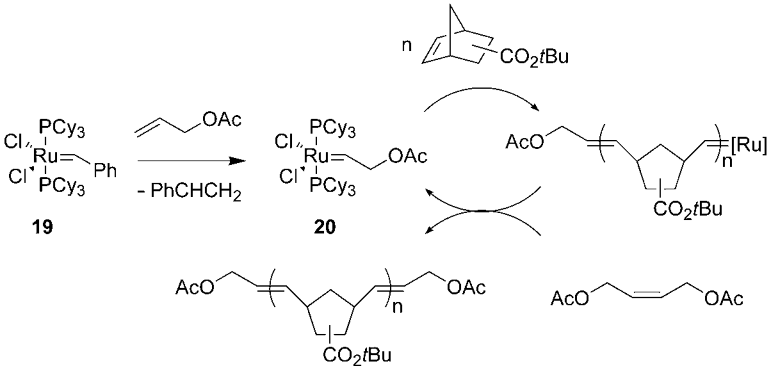


Figure 6.28 The addition of a functionalized norbornene followed by a chain transfer agent (1,4-diacetoxy-2-cis-butene) in an alternating fashion to a living ROMP reaction results in the formation of telechelic polymers.

[80]. Regardless, the ability to vary the alkylidene initiator provides a convenient method for functionalizing the end-groups of polymer chains. For example, as shown in Figure 6.28, Gibson prepared a series of end-functionalized polymers using Ru complex **20** (prepared by reacting **19** with allyl acetate). This ROMP initiator effectively placed an acetoxy group on one terminus of the polynorbornene chain and an active Ru alkylidene at the other end. Upon the conclusion of the polymerization (i.e., after all the monomer was consumed), 1,4-diacetoxy-2-butene was added, effectively installing an acetoxy group on the growing end of the polymer chain and re-forming the functionalized initiator. Ultimately, this produced a polymer with acetoxy groups on both ends of the polymer chains (a so-called "telechelic polymer") [81].

Complex **19** was also found to initiate the ROMP of a wide variety of functionalized norbornenes and cyclobutenes, many of which contained pendant alcohol, amino, ester, amido, and keto FGs, in a living manner and in protic media [82]. In addition to exhibiting a high tolerance for most FGs, **19** was also found to be relatively thermally stable with a half-life of over a week at 55 °C [83].

The ability to prepare designer Ru initiators was used to address a fundamental problem in the synthesis of block copolymers composed of segments that cannot be prepared by the same polymerization mechanism. While a variety of coupling or chain-transfer strategies have been put forth, from a practical standpoint it would be ideal to use a single-component complex to initiate multiple mechanistically distinct reactions and form block copolymers more succinctly. As shown in Figure 6.29, this was effectively accomplished through the synthesis of a difunctional initiator that effectively mediated the ROMP of cyclooctadiene and the ATRP of methyl methacrylate, facilitating access to a variety of poly(butadiene)-*b*-poly(methyl methacrylate) block copolymers in a single step [84].

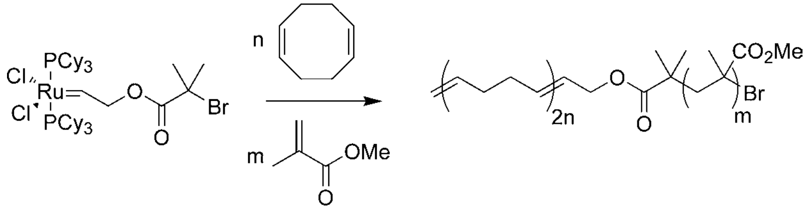
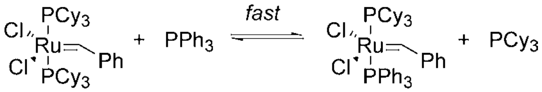


Figure 6.29 Using a complex that contains both ROMP and ATRP initiators, a diblock copolymer containing mechanistically-incompatible segments can be synthesized in one step.



19 **21**

Figure 6.30 Phosphine exchange in Ru alkylidenes (such as **19**) is fast, a feature that can be used to increase control over ROMP reactions (see text).

As noted above, the more active Ru alkylidenes possessing trialkylphosphine groups were unable to polymerize norbornene and many of its derivatives in a highly controlled manner because of poor initiation characteristics and (slow) secondary metathesis reactions. One solution to this problem was reported by Gibson who capitalized on the ability to readily exchange the ligands on these complexes and produced an initiator with increased initiation characteristics [85]. However, as a direct result of extensive mechanistic analyses, it was determined that the rate of phosphine exchange was significantly faster than the rates of reactions with olefins in the bisphosphine Ru alkylidene complexes, offering an alternative solution to this problem. In addition, the triphenylphosphine derivatives of these complexes exhibit elevated rates of initiation. It was determined that addition of relatively labile phosphines such as PPh_3 to **19** during a ROMP would enhance its initiation efficiency. As phosphine exchange is fast, mixed phosphine complex **21** forms *in situ*, which was found to exhibit better initiation characteristics than **19** (Figure 6.30). In essence, phosphine competes with monomer for the propagating species and effectively lowers the rates of propagation. Indeed, inclusion of triphenylphosphine (1–5 equivalents) in the ROMP of various norbornene derivatives reduced the PDIs from 1.25 to as low as 1.04 [86].

In parallel with studies involving their use in various polymerization reactions, tremendous effort was directed toward gaining a greater understanding of how these initiators facilitated olefin metathesis reactions [87]. Ultimately, it was determined that Ru complexes such as **19** initiated ROMP and other metathesis reactions via a process that involved ligand dissociation. In other

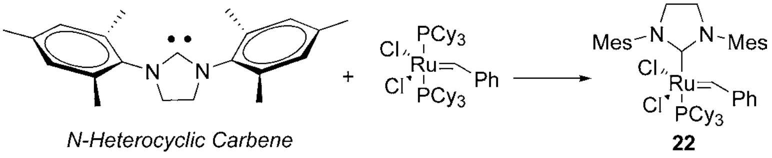


Figure 6.31 Synthesis of Ru based ROMP initiator containing an N-heterocyclic carbene.

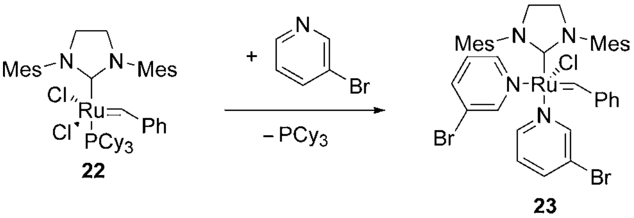
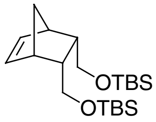
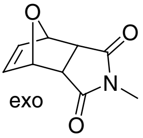
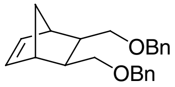
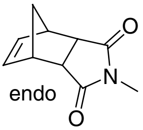
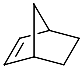


Figure 6.32 Treatment of **22** with 3-bromopyridine results in the formation of **23**, a complex that initiates a broad range of ROMP reactions relatively quickly. This initiator often affords polymers with very low polydispersities; see Table 2 for representative examples.

words, a phosphine ligand must separate from the complex before olefin coordination (and subsequent reaction) may occur. Stabilization of these coordinately unsaturated intermediates was also necessary to prevent premature decomposition. N-heterocyclic carbenes (NHCs) were known to be strong σ-donors yet less labile than phosphines [88]. Hence, they are not only less likely to dissociate from the Ru metal center but also provide increased electron density to stabilize intermediates. Ultimately, as shown in Figure 6.31, a mixed-ligand system (**22**) was designed and synthesized through a phosphine exchange type reaction [89].

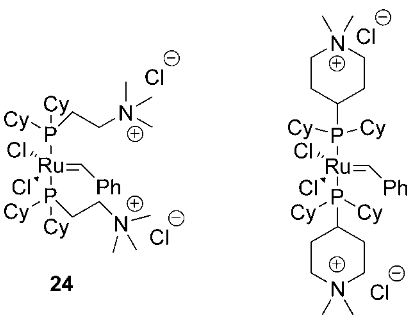
Complex **22** was shown to possess exceptional activity in a large number of ROMP reactions [90]. For example, it was found to polymerize cis-cyclooctadiene at higher rates than Schrock's Mo-based initiators and could also initiate the ROMP of 1,5-dimethylcyclooctadiene, as well as 1,3,5,7-cyclooctatetraene [91]. However, this initiator generally provides polymers with high (uncontrolled) molecular weights and broad polydispersities. This has been attributed to relatively slow rates of initiation coupled with competing secondary chain-transfer reactions. By tuning the ligand environment, a new class of Ru-based metathesis initiators (**23**) containing strongly ligating NHCs with weakly coordinating pyridines were developed (Figure 6.32) [92]. These initiators displayed not only extremely high activities in ROMP but also exhibited fast initiation kinetics as a result of the labile nature of the pyridine ligands. As a result, living ROMP reactions were achieved with Ru initiators ligated to NHCs. As shown in Table 6.2, a wide range of monomers were polymerized using this initiator. Notably the PDIs of the resultant polymers

Table 6.2 ROMP of a variety of cyclic olefins mediated by catalyst **23**. In all cases below, the initial monomer to catalyst ratio was 100:1. The theoretical molecular weights assume quantitative conversion. The last example (norbornene) was performed at −20 °C.

Monomer	M_n (GPC)	M_n (theo)	PDI
	24 500	38 300	1.06
	29 100	18 000	1.05
	30 400	33 500	1.05
	22 900	17 800	1.08
	28 700	19 900	1.10
	9 000	9 500	1.09

were extremely low. It is also notable that a polynorbornene was prepared with a PDI as low as 1.06. However, it was important that in this case the ROMP was conducted at −20 °C to suppress secondary chain-transfer reactions. As a testament to the living nature of these polymerizations, a variety of diblock copolymers were also prepared using this initiator.

The ability to readily replace the ligands on the aforementioned Ru complexes also led to the development of water-soluble derivatives for aqueous ROMP applications. By incorporating charged phosphines, for example, water-soluble Ru complexes **24** and **25** were obtained (Figure 6.33) [93]. While both of these complexes are metathesis active, they do not initiate living ROMP reactions because the propagating species is unstable and rapidly decomposes. However, it was later determined that decomposition was enhanced in the presence of a base which prompted the notion that the observed instability was due to



24

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Figure 6.33 Representative examples of water soluble Ru-based ROMP initiators.

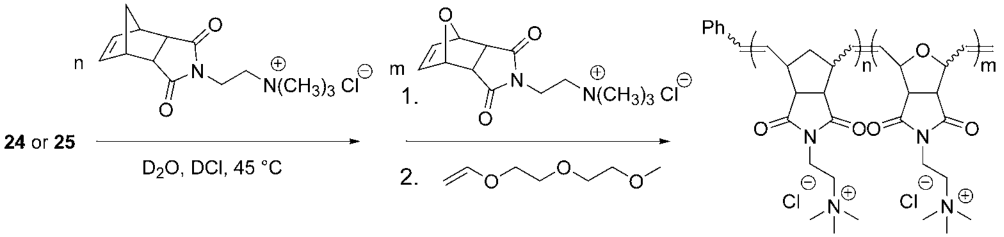


Figure 6.34 Synthesis of water soluble block copolymers via ROMP in aqueous media.

the presence of a small amount of hydroxide in solution. This limitation was readily resolved by adding a strong Brønsted acid (e.g., HCl) during the ROMP reaction. Interestingly, the acid not only sequesters any hydroxide that may be present in solution, but it has the added effect of promoting initiation through phosphine protonation. Ultimately, this led to living aqueous ROMP reactions. In particular, as shown in Figure 6.34, the living ROMP of water-soluble norbornene derivatives afforded homopolymers with PDIs of <1.24 as well as block copolymers of these two monomers. Water-soluble quenching agents such as triethyleneglycol methyl vinyl ether were found to effectively terminate these polymerizations. More recently, water-soluble initiators bearing NHC ligands have been prepared and were found to show extremely high activities in aqueous ROMP reactions [94].

6.3
Applications of Polymers Synthesized Using ROMP: From Novel Materials to Commercial Products

As detailed above, olefin metathesis chemistry, and particularly ROMP, has witnessed tremendous growth since its discovery. The number of features and advantages inherent to these reactions has created a number of new applications across a range of scientific and engineering disciplines. In particular, the high FG tolerance exhibited by the well-defined initiators mentioned above, as well as their abilities to facilitate living polymerizations, has enabled the synthesis of a myriad of well-defined homopolymers as well as various diblock, triblock, and other advanced copolymers with advanced structures and functions. Described below are selected applications, including those that have been commercialized, that have been realized as a result of developments in ROMP.

6.3.1
Selected Applications for Polymers Synthesized Using ROMP

One area in which polymers prepared using ROMP has had a remarkable impact is biomedicine. Because of the living nature inherent to ROMP using well-defined initiators described above, polymers with predetermined lengths, low polydispersities, and high degrees of chemical functionality can be conveniently synthesized. Collectively, these features offer a number of advantages for creating polymeric materials to probe or exploit biological processes. This is particularly true for those that exhibit multivalent effects and is a highly effective strategy that has been extensively explored and developed by Kiessling [95]. The basic idea behind this approach is to use a polymer that contains many recognition elements along its backbone as a means to significantly increase binding affinities on a target (relative to monofunctional species). In addition to any potential chelation-type effects, the local concentrations of the recognition elements around a target are particularly high which inherently increases the chance for association between the two.

One of the most common ROMP polymer scaffolds that has been used to study multivalency effects is based on polynorbornene. As shown in Figure 6.35, polynorbornenes containing pendant FGs can be prepared via (i) homopolymerization of a functionalized norbornene, (ii) copolymerization when a living system is employed (generally to prepare amphiphilic block copolymers that are capable of forming micelles to maximize presentation of the multivalent array), or (iii) via subsequent modification of a preformed polymer that is capable of further reaction. Polymers with functionalized end-groups have also proven utility in many regards and can be prepared by using functionalized initiator and/or terminating agent, or via postpolymerization modification [96]. Hydrogenation as a postpolymerization reaction has also shown to be beneficial as it reduces the chances for cross-linking or other degradative side reactions (through saturation of the alkenes positioned along the polymer backbone) and, in some cases, can be accomplished in tandem with the ROMP using the same initiator [97]. In many cases, the aforementioned materials are functionalized with various carbohydrates and have been explored in applications ranging from preventing cell agglutination to inhibiting biological interactions in the inflammatory response to the

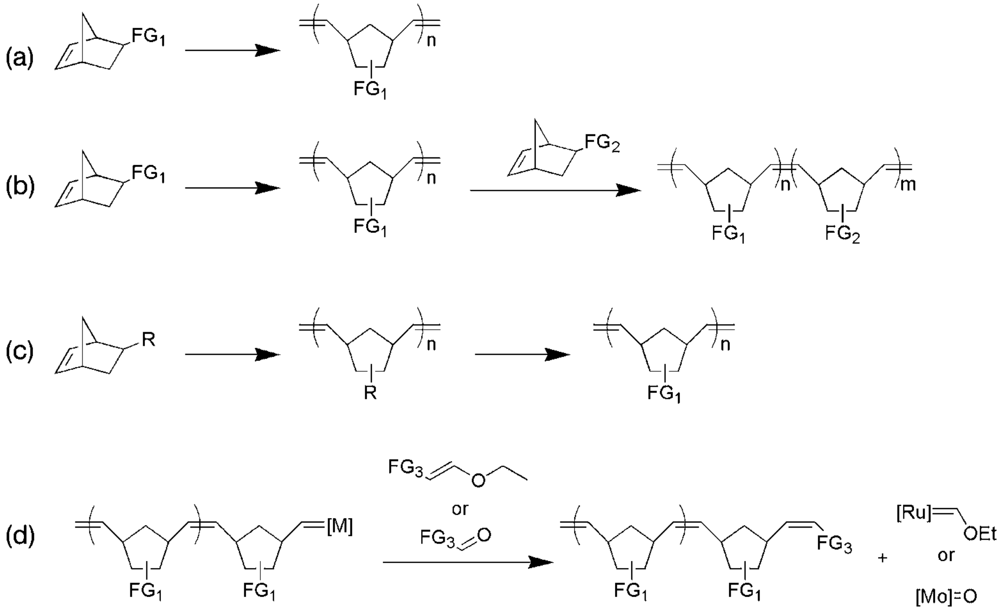


Figure 6.35 Polynorbornenes containing pendent functional groups can be prepared via (A) homopolymerization of a functionalized norbornene, (B) copolymerization, or (C) postpolymerization modification. (D) Polynorbornenes with functionalized endgroups have also been prepared by using functionalized initiator and/or terminating agent. Many of these polymer scaffolds have been used to study multi-valency effects *in vitro* and *in vivo* (see text).

development of novel antibiotics [95]. Specific examples of monomers and polymers that have been synthesized and in some cases explored under this context are shown in Figure 6.36. The impressive range of structure and functionality can be attributed to the robustness and tolerance of the initiators used to synthesize these materials.

In addition to carbohydrate-containing polymeric displays, ROMP has also been used to prepare polymers which contain peptides [98] and nucleic acids [99], as well as drug/polymer conjugates and delivery systems (e.g.,Figure 6.37). For example, Nguyen synthesized a series of copolymers that contained anti-inflammatory agents, such as indomethacin, as well as agents used to treat lymphatic leukemia and malignant melanomas, such as chlorambucil [100]. An amphiphilic copolymer containing the former afforded micelles in water with the drug concentrated in the core surrounded by a hydrophilic corona. Drug release (approximately 20% over 48 h) was found to occur at pH 3 and 37 °C *in vitro* via hydrolysis of the amide group that links drug molecule to the polymer backbone. Another example includes an indomethacin-containing block copolymer that was successfully used to introduce DNA and antibodies that target cancer cells (Figure 6.37) [101].

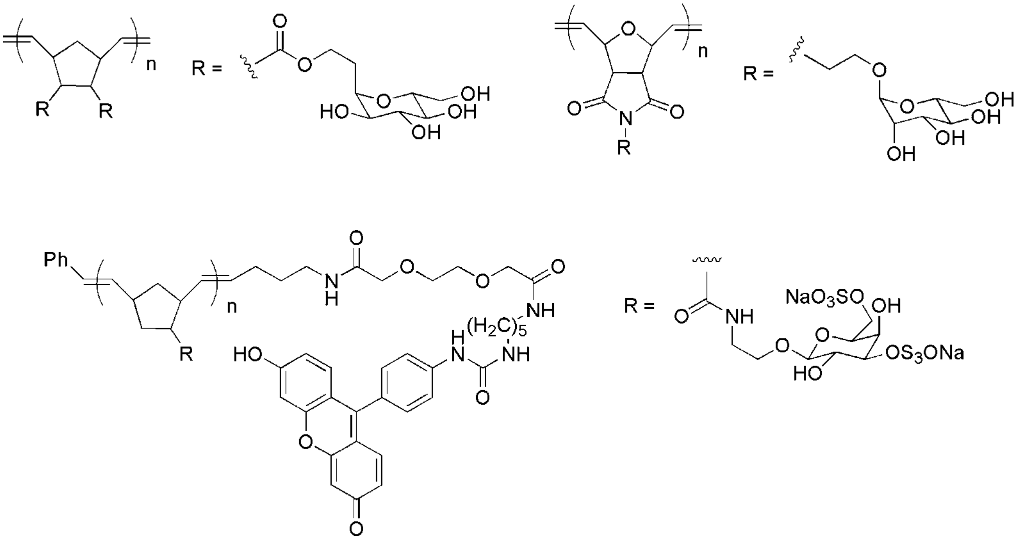


Figure 6.36 Representative examples of functionalized polynorbornenes that have been synthesized and explored in biological systems or for related applications.

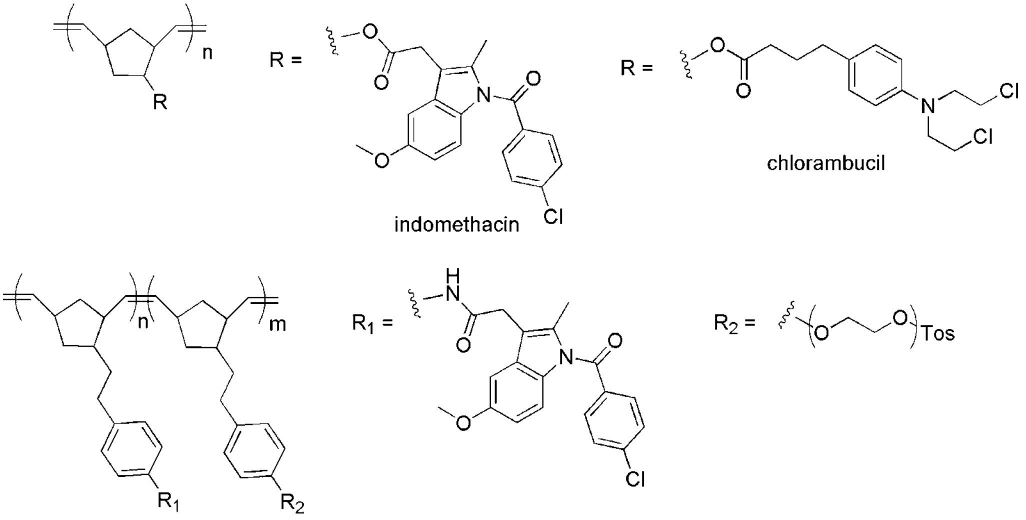


Figure 6.37 Representative examples of functionalized polynorbornenes prepared via ROMP which contain various drugs appended to tha polymer's backbones.

Tangential to materials with biological relevance, researchers at the University of Illinois demonstrated that ROMP can be used to create what are known as *self-healing materials*. The team showed that stress-induced microcracks could be autonomously repaired through the incorporation of capsules containing dicyclopentadiene (DCPD), as well as a ROMP initiator, i.e., $(PCy_3)_2Cl_2Ru{=}CHPh$ (**19**), into an epoxy matrix [102]. The self-healing composite is believed to function through a series of events. First, the propagating crack ruptures embedded capsules, causing the monomer, which is a liquid, to be released. When the monomer comes in contact with the initiator, which is also embedded throughout the epoxy, a ROMP reaction begins. Ultimately, the crack becomes filled with a cross-linked material that restores a significant portion of the epoxy's mechanical properties. Notably, healing efficiencies of up to 75% were confirmed through various fracture analyses. This unique feature has attracted a number of companies who are interested in using self-healing materials in a variety of sporting goods, coatings, adhesives, and many other applications.

As a testament to the versatility of ROMP, the technique has also been used as an aid in the purification of organic reactions [103]. For example, Barrett has developed a variety of ROMP-derived materials, often termed *ROMPgels*, which have been used as reagents and scavengers in solution-phase reactions, particularly in those employed in combinatorial chemistry [104]. These polymers have two key design features: (i) they contain either reagents or scavengers pendant to their main chains and (ii) they generally show low solubilities in common organic solvents which facilitates their removal. One example of how such materials have been used is shown in Figure 6.38 [105]. The polynorbornene bearing pendant phosphonates (Horner–Emmons reagents) were synthesized from their respective monomers via ROMP and found to swell in a range of organic solvents. Under basic conditions, these gels were found to convert various aldehydes to their respective α,β-unsaturated esters and nitriles in excellent yields and in high purities. Notably, the purification protocol involves simple filtration through a plug of silica gel, followed by evaporation of the residual solvent. The ROMP-derived materials used to facilitate and to aid in the purification have been greatly expanded over the past several years to include, for example, the conversion of terminal aldehydes to alkynes using a homologation reaction, benzylation of amines, nucleophile scavengers as well as various types of coupling chemistries among many others types of contemporary synthetic reactions and transformations [103].

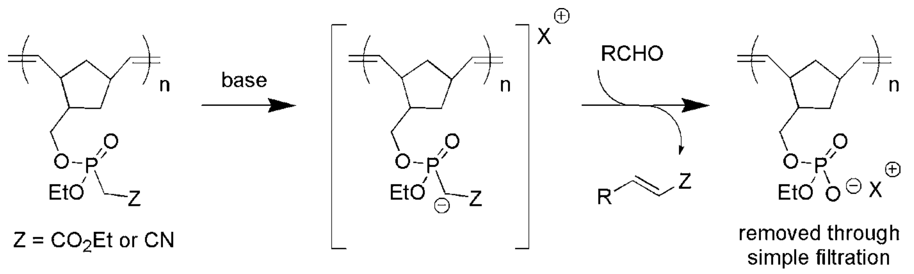


Figure 6.38 Representative example of using ROMP to purify a synthetic organic reaction.

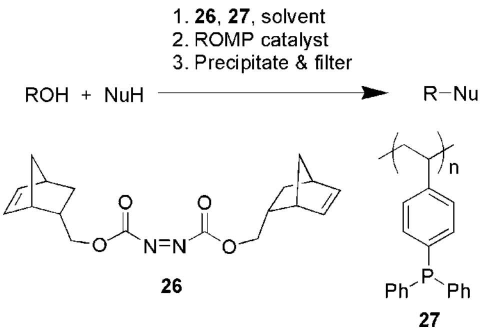


Figure 6.39 Example of using ROMP to purify a Mitsunobu reaction. Over the course of the coupling reaction, the diazocarboxylate **26** converts to a hydrazine derivative, which can be polymerized by adding a ROMP initiator and easily removed through filtration.

In parallel with the development of ROMPgels, Barrett also introduced another approach for using ROMP to purify solution-phase reactions. In this method, termed *reagent annihilation*, a functionalized cyclic olefin (generally norbornene) is added to a synthetic reaction to scavenge byproducts and impurities produced. Thus, at the conclusion of the reaction, a ROMP initiator is added which results in the formation of a polymer (containing the byproducts and impurities) that is either insoluble or can be easily removed through precipitation. As an example, norbornene-derived azodicarboxylate **26** and polystyrene-bound triphenylphosphine **27** were used to aid in the purification of Mitsunobu reactions (Figure 6.39) [106]. At the conclusion of the reaction, the resulting mixture was filtered through charcoal and Celite (facilitating removal of the hydrazine dicarboxylate byproducts), and then washed. Removal of solvent afforded the desired esters and amides in high yields and purities.

Other methods that utilize ROMP for purifying solution phases have also been reported. For example, Hanson has developed "scavenge-ROMP-filter" [107] and "capture-ROMP-release" [108] methods where various functionalized cyclic olefins (which are also generally based on norbornene) are used to scavenge or capture byproducts or desired products, respectively, from a reaction mixture. Subsequent polymerization of these derivatized monomers using a ROMP initiator produces a polymer that can be easily isolated through precipitation or extraction. The materials can then be discarded (byproduct removal) or subsequently treated to remove the desired products. Examples of these methods are illustrated in Figure 6.40 for the synthesis of esters and amines, respectively. A variety of solid- and surface-supported initiators prepared using ROMP have also been reported as a means for purifying organic reactions, as well as recycling catalysts. In a similar vein, ROMP has also been used to create a variety of supports that have been used for catalyst recovery, purification, and other applications [109].

6.3.2
Commercial Polymers Synthesized Using ROMP

Commercial interest in olefin metathesis chemistry began in the 1960s, mainly for producing high value olefins from hydrocarbon feedstocks using cross

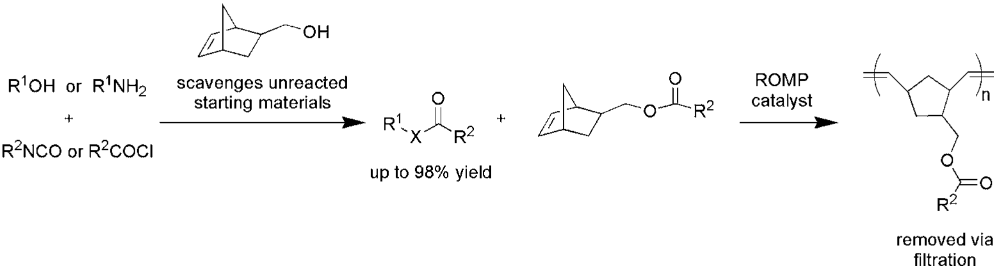


Figure 6.40 An example of the "scavange-ROMP-filter" methodology used to purify organic reactions.

metathesis reactions. As noted above, the first example was the Phillips triolefin process for converting propylene into more valuable 2-butene (and ethylene). Soon thereafter, commercial polymers prepared from the ROMP of common cyclic olefins began to emerge. For example, polynorbornene (e.g., Norsorex®), polycyclooctene (e.g., Vestenamer®), and polycyclopentene are produced industrially using ROMP chemistry. (Norsorex® is a registered trademark of Elf Atochem S.A. Vestenamer® is a registered trademark of Degussa AG. These materials have been produced using heterogeneous initiators based on tungsten, molybdenum, or ruthenium salts in conjunction with various cocatalysts and additives. For instance, polynorbornene can be prepared via the ROMP of norbornene using $RuCl_3$ in acidified alcoholic solvents.

Because of their unique structures, the aforementioned polymers are typically elastomeric, which makes them suitable for using in shock absorbers or insulators and other applications that require viscoelastic damping. For example, polynorbornene is commonly utilized in the various automotive parts to dampen vibration and noise. [Notably, this polymer can also absorb large amounts of oil and other hydrocarbons (up to 10 times its weight), which makes it especially useful in oil-spill recovery applications.] As noted in an early section of this review, polymers produced from ROMP reactions are unsaturated. As such, they can and often are further cross-linked (vulcanized) to enhance their mechanical and thermal properties, and to increase their chemical and oxidative stability. For instance, polycyclooctene is commonly used as a covulcanizable processing aid in the rubber industry. Alternatively, many of these polymers can be hydrogenated to afford to high-performance polyolefins. Zeonex®, Zeonor® and Topas® are a few examples of hydrogenated polynorbornenes that are produced industrially [110].

Polydicyclopentadiene, which is prepared via the ROMP of DCPD, has different properties than the polycycloolefins described above. Because DCPD possesses two strained olefins (i.e., norbornene and cyclopentene), ROMP can occur in two locations which ultimately results in the formation of cross-linked materials that are mechanically robust and exhibit excellent resistance to corrosion and oxidation (Figure 6.41). Hence, a primary interest

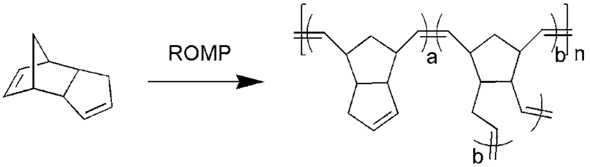


Figure 6.41 As a result of the two strained cyclic olefins present in dicyclopentadiene, ring-opening metathesis polymerization of this monomer often leads to crosslinked materials.

of polydicyclopentadiene has been in direct reaction injection molding (ROMP) applications that range from automotive parts (bumpers, moldings, etc.) to pipes and other chemical processing equipment. Metton®, Telene®, and Pentam™ are a few examples of commercially available materials that are prepared through the ROMP of DCPD. (Metton® is a registered trademark of Metton America, Inc. Telene is a registered trademark of APT, LLC. Pentam™ is a trademark of Zeon Corporation.) Also included are a range of composites and resins for use in applications such as corrosion resistance piping [111], flame retardant materials [112], bathroom fixtures and septic tanks, various types of sports equipment and accessories, and, more recently, materials for various electronics applications [113].

6.4
Challenges and Perspectives for the Future

The ability to provide exquisite control over macromolecular structure and function remains a central aim in polymer chemistry. As noted in the introduction, the advent of living polymerizations has resulted in a significant step toward the realization of this goal by providing a method to tune the size and polydispersity of many types of macromolecular materials. However, advancement of the field will continually require the development of new synthetic methodologies. The introduction of well-defined complexes that initiate living ROMP reactions has pushed the frontier of living polymerization even further. As a result of the development of these initiators, an impressively broad range of monomers, many of which are densely functionalized, may now be polymerized to nearly any shape or size. Another advantage of living ROMP reactions is an ability to prepare a wide range of copolymers as well as materials with advanced topologies. Indeed, many of these materials have found utility in biological and electronic applications. However, living ROMP is not a solved problem. Several remaining challenges are listed below.

6.4.1
Development of New Initiators

Nearly every advance in ROMP can be traced to an advance in catalysis. As such, the future of living ROMP is critically dependent on the development of new

Ti / Ta	W	Mo	Ru
acids	acids	acids	olefins
alcohols	alcohols	alcohols	acids
aldehydes	aldehydes	aldehydes	alcohols
ketones	ketones	olefins	aldehydes
esters/amides	olefins	ketones	ketones
olefins	esters/amides	esters/amides	esters/amides

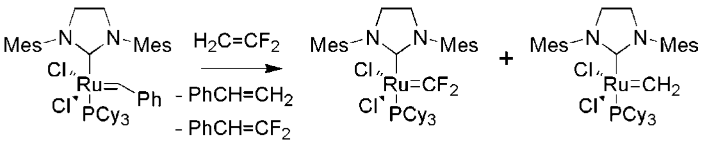
increasing reactivity

Figure 6.42 Comparison of the functional group tolerance of various early and late transition metal complexes that have been successfully employed as ROMP initiators.

initiators, which is likely to involve new transition metals and the development of new ligands. It has been shown that late transition metals are inherently more stable toward polar FGs (for a summary, see Figure 6.42) and, through proper ligand choice, can often exhibit activity in ROMP reactions comparable to their predecessors based on early transition metals. This trend suggests that future generations should look toward other late transition metals such as Fe or Re. However, this will be challenging as Fe alkylidenes generally prefer to cyclopropanate olefins and there are only a handful of examples demonstrating that Re catalyzes metathetical reactions [114]. For Ru-based initiators, it is clear that highly donating ligands enhance activity. Efforts will continue to focus on finding new ligands showing higher electron donating properties than NHCs. Ultimately, the ideal initiator for living ROMP reactions will react with cyclic olefins exclusively (i.e., in the presence of a broad range of FGs). This is a challenging task as high activity often equates to increased chances for secondary metathesis reactions, which limit their potential for use in living ROMP reactions.

6.4.2
Polymerization of "New" and "Old" Monomers

The field of living ROMP will also be dependent on an ability to polymerize new monomers. For example, one area that has been underdeveloped is the ROMP of highly halogenated cyclic olefins. It has been shown that Ru complex **22** reacts with 1,1-difluoroethylene to afford a Ru difluoromethylidene complex **28** that was subsequently found to be active in initiating the ROMP of 1,5-cyclooctadiene (Figure 6.43) [115]. With the right ligand environment (or transition metal), ROMP may one day be used to polymerize highly halogenated olefins such as perfluorocyclobutene. Another challenging area is the polymerization of tri- and tetrasubstituted olefins. The synthesis of



22 **28**

Figure 6.43 Examples of olefin metathesis reactions involving halogenated alkenes.

tetrasubstituted olefins has recently experienced considerable utility in ring-closing and cross metathesis reactions, poising the exploration of analogous cyclic olefins in ROMP reactions.

Another means to push the frontier of living ROMP is to develop new initiators to obtain new polymeric materials with interesting topological features from "old" monomers. The Ru initiators discussed above are particularly suited for such application as both the alkylidene and the phosphine/NHC ligands can be extensively modified. This concept was demonstrated in the synthesis of water-soluble complexes through the incorporation of water-soluble phosphine ligands which enabled living ROMP in aqueous media. More recently, this concept was used to design an initiator that provided cyclic polymers [116]. As shown in Figure 6.44, the addition of cis-cyclooctene to complex **29** affords a propagating species where both ends of the polymer chains remain attached to the metal center. At some point later in time, an intramolecular cyclization reaction occurs and effectively provides a cyclic polymer and complex **29**. This approach effectively eliminated the need for linear polymeric precursors and high dilution that were drawbacks of traditional strategies for preparing these materials.

6.5
Conclusion

Fifty years ago, Szwarc introduced the concept of "living" polymerizations. This technique changed the way polymer chemists think about preparing well-defined macromolecular materials and has resulted in numerous scientific advances, many of which can be found in contemporary society. Coincidentally, the olefin metathesis reaction was also introduced about 50 years ago. In some ways, this reaction also changed the way polymer chemists think about preparing macromolecular materials. The original metathesis initiators were ill-defined mixtures consisting of several metals, additives, and specialized conditions. As the direct result of advances in the field of catalysis, a series of well-defined initiators based on a range of metals including titanium, tantalum, tungsten, molybdenum, and ruthenium have been prepared. Through subsequent optimization and modification, living ROMP initiators based on each of these metals have been synthesized. These initiators have found utility

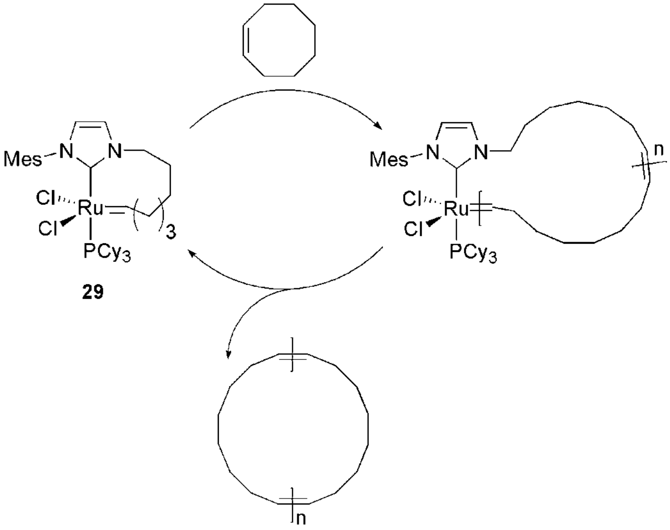


Figure 6.44 Synthesis of cyclic polymers via ROMP using a specially designed initiator.

in a wide range of applications including the synthesis of macromolecular materials with interesting biological, electronic, and mechanical properties. Finally, it is important to note that a "universal" initiator does not exist; each of the initiators described in this review possesses its own inherent advantages and disadvantages. Considering the broad range of initiators known, it should be possible to find an application to meet nearly any specific need. If not, the synthetic diversity available should facilitate the necessary modifications.

Acknowledgments

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7

Macromolecular Architectures by Living and Controlled/Living Polymerizations

Nikos Hadjichristidis, Marinos Pitsikalis, Hermis Iatrou, and Georgios Sakellariou

7.1

Introduction

Homo- and copolymers, with high molecular weight (MW) as well as structural and compositional homogeneity, can be synthesized exclusively by living or controlled/living polymerizations. The way to living polymerization was opened in 1955 when the seminal work of Szwarc proved the livingness of macroanions and the term *living* was coined [1]. Szwarc's initial experiments, carried out under high vacuum conditions, proved the livingness of the anionic polymerization of styrene in an elegant but relatively simple way, i.e., the increase in viscosity (falling ball) by addition of new quantities of monomer. Furthermore, the critical contributions from Morton [2] and Bywater [3], to mention a few, propelled the field to its current state. New methods of controlled/living polymerizations were subsequently developed and led to the synthesis of well-defined materials composed of monomers noncompatible with anionic polymerization.

About 30 years after Szwarc's seminal work, the controlled/living routes for cationic polymerization were discovered. The highlights of the living cationic polymerization are presented in an elegant review by Kennedy, whose fundamental contributions to the field led to novel structures based on monomers not susceptible to anionic polymerization [4]. Simultaneously, the living/controlled group transfer polymerization of (meth)acrylates was developed by Webster [5].

Recently, several groups introduced controlled/living radical polymerization, and reviews on these new methods have been written by leading scientists in the field [6, 7]. The ground-breaking discovery of Szwarc together with subsequent developments inspired many researchers to apply the concept of livingness to other monomers such as ethylene, propylene, norbonene, etc. [8]. These methods and their combinations, together with a wide selection of monomers, serve as an arsenal for the synthesis of well-defined polymeric materials with predetermined properties and a rich variety of applications.

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Representative syntheses of polymers with different macromolecular architectures (star, comb, cyclic, dendritic, hyperbranched, and other complex-branched), resulting from living and controlled/living methodologies and, in a few cases, with appropriate post-polymerization linking chemistry (e.g., chlorosilanes, "click") are presented in this chapter.

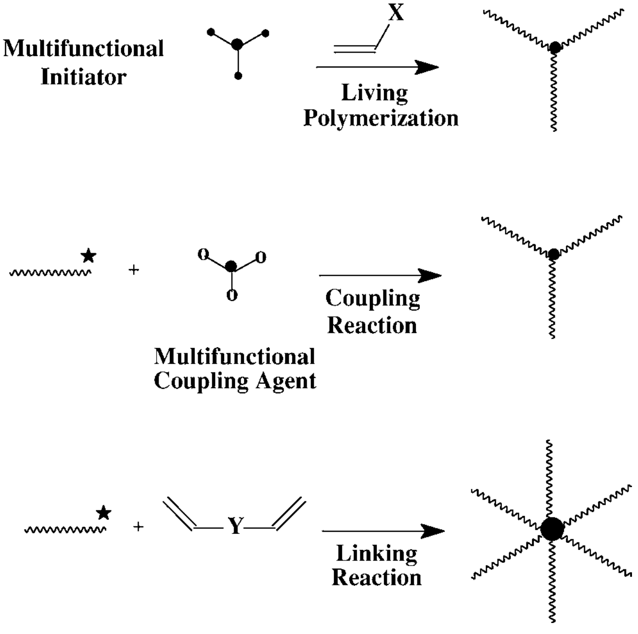
7.2
Star Polymers

7.2.1
Symmetric Stars

Symmetric star polymers are branched polymers consisting of several identical linear chains linked to a central core. The synthesis of well-defined star polymers has been the subject of numerous studies to date [9–12]. Three general synthetic methods have been developed, as outlined in Scheme 7.1.

7.2.1.1 Multifunctional Initiators (MFIs)

Multifunctional initiators (MFIs) are compounds capable of simultaneously initiating several polymerizations to form the arms of the star polymer, while



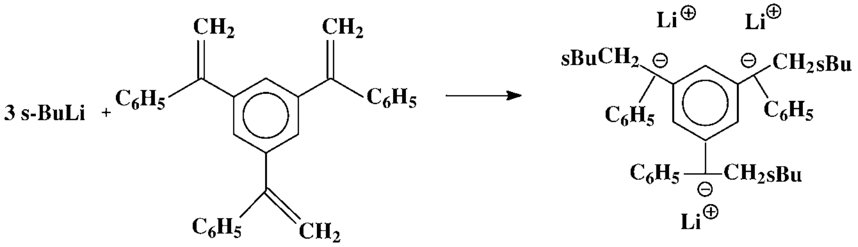
Scheme 7.1

the remaining moiety composes the core of the star. An MFI has to fulfill the following requirements to produce well-defined star polymers with uniform arms, low MW distribution, and controllable MWs: (i) all the initiation sites must be equally reactive and (ii) the initiation rate must be higher than the propagation rate.

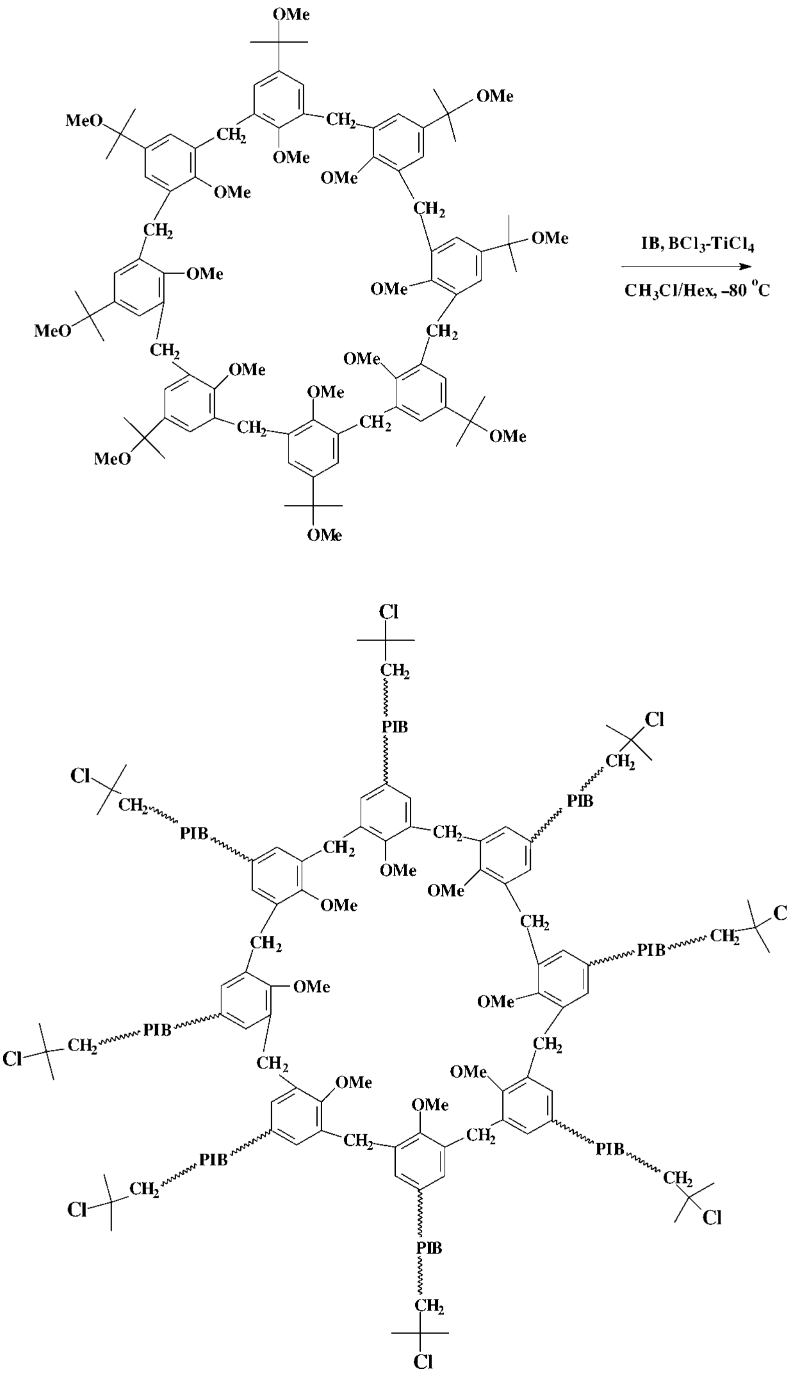
Burchard and colleagues [13, 14] first, and later Rempp and colleagues [15, 16] demonstrated that the reaction of divinyl benzene (DVB) with *n*-butyl lithium (*n*-BuLi) in dilute benzene solutions leads to MFIs (microgels) capable of polymerizing styrene, isoprene, and butadiene to produce star polymers. A slight variation was adopted by Funke [17, 18], where the polymerization of DVB was realized by low MW living poly(*t*-butylstyryl) lithium chains, instead of *n*-BuLi, to avoid the solubility problems arising from the strong association of the carbon-lithium functions in the nonpolar solvent.

A novel hydrocarbon-soluble trifunctional initiator was proposed by Quirk *et al.* [19] and was prepared by the reaction of 3 mol of *sec*-butyllithium (*s*-BuLi) with 1,3,5-tris(1-phenylethenyl)benzene (tri-DPE), as presented in Scheme 7.2. This initiator was found to be efficient for the polymerization of styrene only when tetrahydrofuran (THF) was added to the reaction mixture ([THF]/[*s*-BuLi] = 20). The same initiator was also used to produce a three-arm polybutadiene (PBd) star [20] in the presence of *sec*-lithium butoxide (*s*-BuOLi) in a ratio [*s*-BuLi]/[*s*-BuOLi] = 2 to disrupt the association of the initiator. The limitations of the method include the extreme care necessary to maintain the stoichiometry of the reaction between *s*-BuLi and tri-DPE and the fact that a minimum arm MW of approximately 6×10^3 is required for a successful synthesis. For arm MWs lower than 6×10^3, incomplete initiation was observed. If these requirements are fulfilled, well-defined three-arm stars can be prepared.

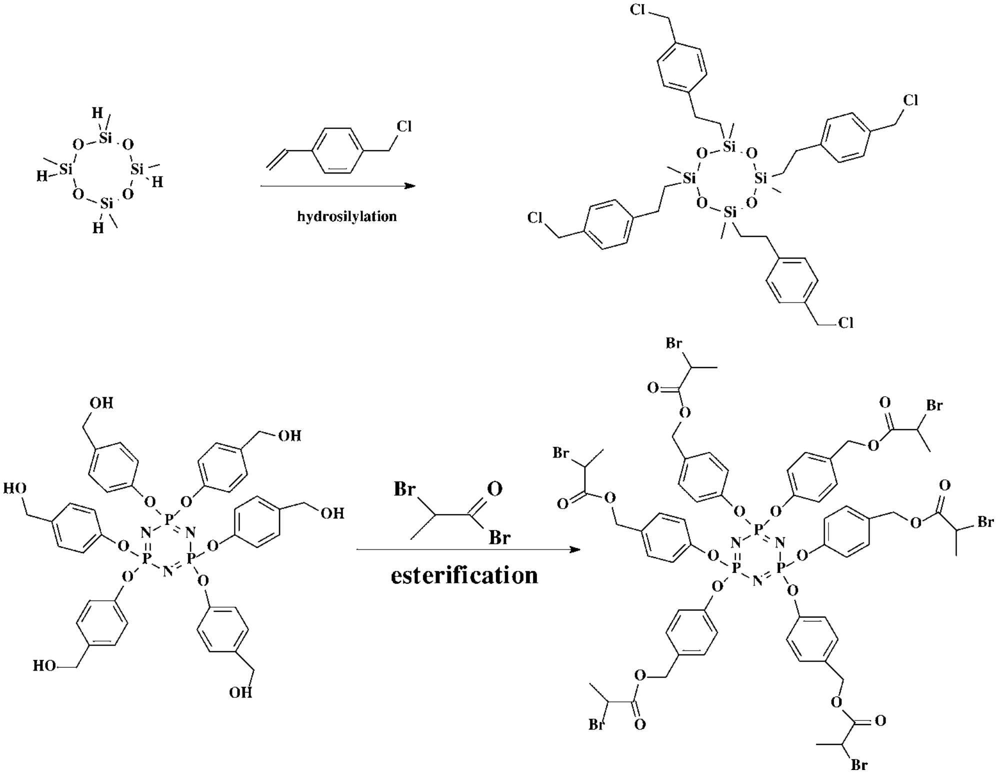
Well-defined eight-arm polyisobutylene (PIB) stars were synthesized using the *tert*-hydroxy and *tert*-methoxy derivatives of 5,11,17,23,29,35,41,47-octaacetyl-49,50,51,52,53,54,55,56-octamethoxycalix[8]arene as octafunctional initiator and cationic polymerization (Scheme 7.3) [21]. The polymerization was performed in two steps in the same reactor. In the first step, the initiator along with BCl_3 and 25% of the IB monomer were added in CH_3Cl at −80 °C, followed by the second step in which hexane, $TiCl_4$, and the rest of the monomer were added. Size exclusion chromatography (SEC) with on-line refractive index



Scheme 7.2



Scheme 7.3

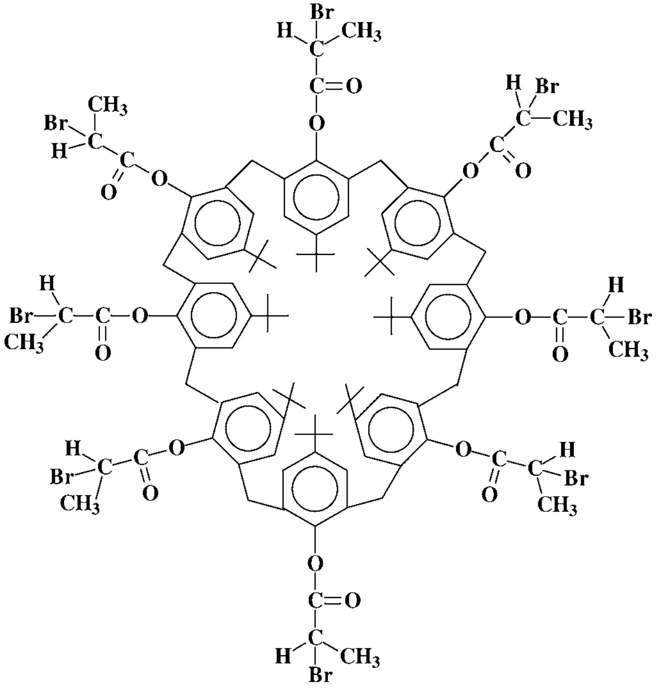


Scheme 7.4

(RI), ultraviolet (UV), and low angle laser light scattering (LALLS) detectors was used for the determination of the MWs and composition of the stars. The MWs obtained were close to the theoretically expected values.

Tetra- and hexafunctional initiators shown in Scheme 7.4 have been used for the polymerization of styrene and acrylates by atom transfer radical polymerization (ATRP) [22]. The resulting stars had low polydispersity indices, and the MWs obtained by SEC equipped with the LALLS detector and viscometry showed good agreement with the theoretical values. In addition, a six-armed star-block copolymer composed of poly(methyl methacrylate) (PMMA) internal and poly(isobornyl acrylate) external blocks was synthesized in this work.

A novel octafunctional calixarene derivative (Scheme 7.5) was prepared and utilized as an MFI for the bulk ATRP of styrene at 100 °C in the presence of CuBr/2,2-bipyridyl, leading to the synthesis of eight-arm star polymers [23]. Well-defined stars could be observed only at low polymerization conversion (up to 20%) since the irreversible coupling reactions that take place at higher concentrations are avoided.



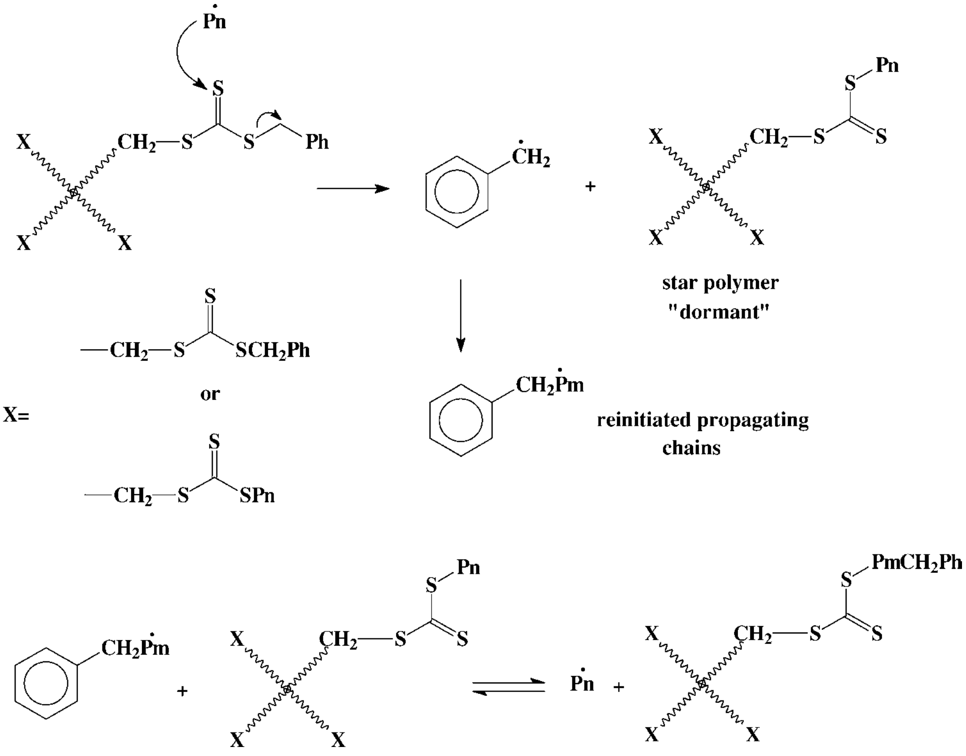
Scheme 7.5

The synthesis of dendritic multifunctional reversible addition-fragmentation chain transfer (RAFT) initiators carrying 6 and 12 external 3-benzylsulfanylthiocarbonylsulfanylpropionic acid groups has been reported [24]. These compounds, in combination with azo-α,α'-diisobutylnitrile (AIBN), have been used to polymerize *n*-butyl acrylate (*n*BA), in bulk at 60 °C, leading to star poly(*n*-butyl acrylate) (P*n*BuA) with moderate polydispersity (1.1–1.5). The star-shaped structure of the synthesized polymers has been confirmed through the cleavage of the arms from the core and characterization.

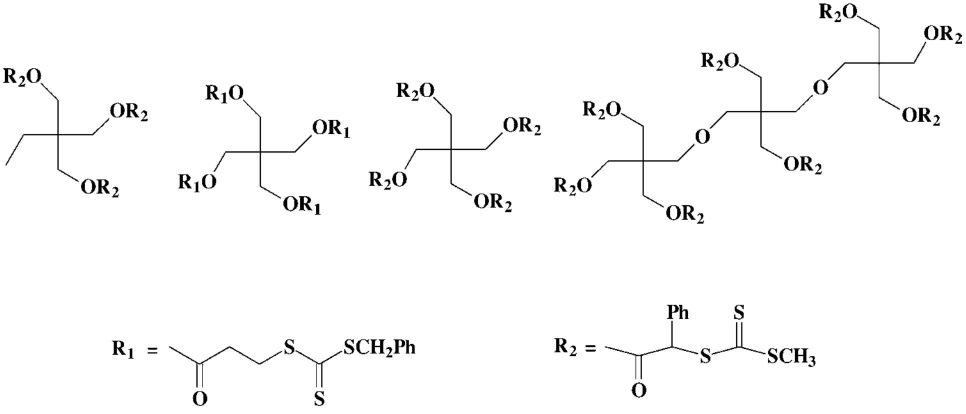
In the "arm-first" approach presented in Scheme 7.6, the fragmentation results in the formation of benzyl radicals, which are able to reinitiate polymerization of linear chains. The arms of the star polymer are dormant, and the growth of the arms always occurs away from the core. Using this methodology, four-arm polystyrene (PS) and PMMA stars were prepared [25].

A series of multi-thiocarbonyl thio compounds with three, four, six, or eight functional groups were prepared (Scheme 7.7) [26] and were subsequently employed as chain transfer agents for the synthesis of star polymers using the RAFT technique [27].

Four-arm hydroxyl-terminated poly(ε-caprolactone) (PCL) stars were synthesized by ring-opening polymerization (ROP) of ε-caprolactone (ε-CL), using pentaerythritol as the MF initiator [28] (Scheme 7.8). The terminal

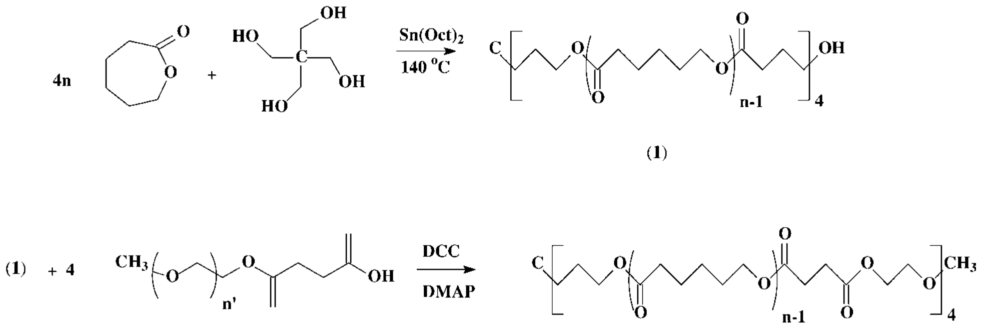


Scheme 7.6



Scheme 7.7

hydroxyl groups of the star were then reacted with an α-carboxy-functionalized poly(ethylene oxide) (PEO) to afford the four-arm PCL-*b*-PEO star-block copolymer. The linking efficiency was high (~95%). The PCL star



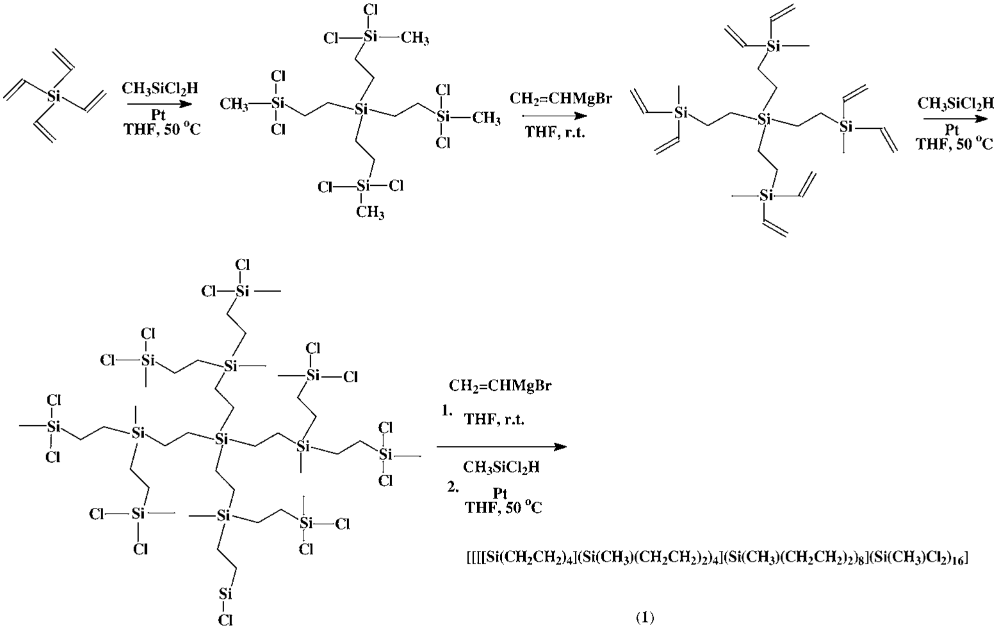
Scheme 7.8

homopolymer precursors along with the final star-blocks were characterized by nuclear magnetic resonance (NMR) spectroscopy and SEC. The star precursors exhibited higher MWs than those theoretically expected and the polydispersities were rather high (1.42–1.56). After reaction with the carboxy-PEO, the polydispersity indices of the star-block copolymers decreased (1.16–1.36).

7.2.1.2 **Multifunctional Linking Agents (MFLAs)**

Multifunctional linking agents (MFLAs) are compounds with several reactive sites that can react with living chains and represent the most efficient way to synthesize well-defined star polymers due to the absolute control afforded in all the synthetic steps. The functionality of the linking agent (LA) determines the number of the arms of the star polymer, provided that the linking reaction is quantitative. The living arms can be isolated and characterized independently along with the final star product. Consequently, the functionality of the star can be measured directly and accurately. Disadvantages of the method include the extensive amount of time often required for the linking reaction as well as the need to perform fractionation to obtain the pure star polymer since a small excess of the living arm is used, in almost all cases, to ensure complete linking.

Several LAs have been used for the synthesis of star polymers from living precursors synthesized by anionic polymerization [9]. The most important are the chlorosilanes [29] and the chloromethyl or bromomethyl benzenes [30, 31]. The linking reactions of the macroanions with the chlorosilanes proceed without any side reactions. However, the efficiency of the linking reaction depends on the steric-hindered character of the LA and the living macromolecular chain end. It was shown that the higher the steric hindrance of the reactants the lower the linking efficiency. The linking efficiency can be improved by separating the Si–Cl groups by spacers, such as methylene groups, and/or by end-capping the living chains with a few units of butadiene to reduce the steric hindrance and facilitate the linking reaction. Under these conditions, well-defined stars have been prepared with functionalities ranging



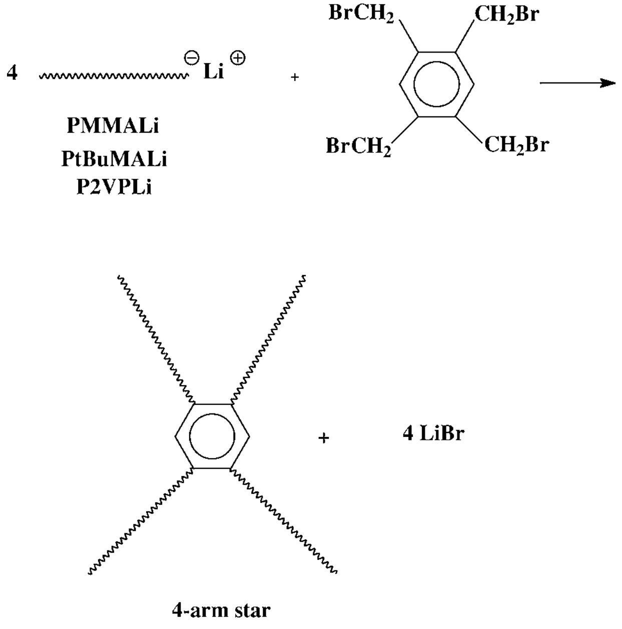
(1)

Scheme 7.9

from 3 up to 18 [32–38]. Recent advances in the synthesis of pure carbosilane dendrimers led to the preparation of LAs with functionalities as high as 128 [39]. These dendrimers were successfully used for the synthesis of PBd stars having 32, 64, and 128 branches [40, 41] (Scheme 7.9). The products were characterized by SEC, membrane osmometry (MO), vapor pressure osmometry, and light scattering (LS), and their dilute solution properties were extensively studied; low MW distribution polymers with functionalities close to the theoretical value were obtained in all cases. The validity of the chlorosilane LAs for the synthesis of star polymers was reevaluated recently using NMR [42] and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) [43] techniques.

In the case of polyvinylpyridines (PVP) and poly(meth)acrylates, a chlorosilane LA cannot be used because either this agent reacts with the pyridine ring or the produced stars have hydrolyzable C–O–Si groups. In these cases, chloro(bromo)methyl benzenes are the most appropriate LAs.

The synthesis of three-arm poly(2-vinylpyridine) (P2VP) stars using 1,3,5-tri(chloromethyl)benzene have been reported [44]. The samples were characterized by SEC and viscometry. The chloromethylbenzenes suffer halogen–metal exchange leading to LAs with more or fewer chloromethyl groups and consequently to stars with more/fewer than the desired number of arms. The use of bromo instead of chloro derivatives in polar solvents as well as the low temperatures prevents the metal–halogen exchange.

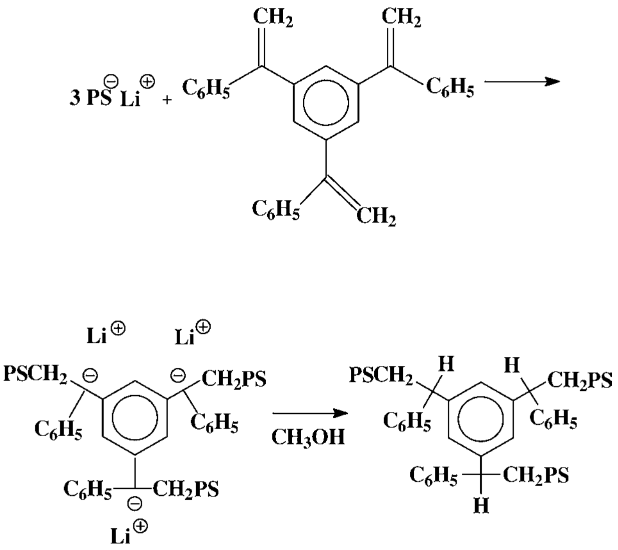


Scheme 7.10

1,2,4,5-Tetra(bromomethyl)benzene was used for the synthesis of four-arm stars bearing poly(*tert*-butyl methacrylate) (P*t*BuMA), PMMA, or P2VP arms [45] (Scheme 7.10). Combined characterization results by SEC and MO revealed the formation of well-defined star polymers.

Diphenylethylene derivatives constitute another class of LAs. 1,3,5-tris(1-phenylethenyl)benzene was used as a living LA for the synthesis of a three-arm PS star [19] (Scheme 7.11). Characterization results from SEC, MO, and LS revealed that a well-defined star was prepared by this procedure. Although the arm MW used was rather low ($M_n = 8.5 \times 10^3$), there was no steric limitation for the synthesis of three-arm PS stars using this coupling agent. Previous efforts to use methyltrichlorosilane (three chlorines on the same Si atom) as a LA for the synthesis of three-arm PS stars were not successful, due to incomplete coupling (steric hindrance effects) [29, 46].

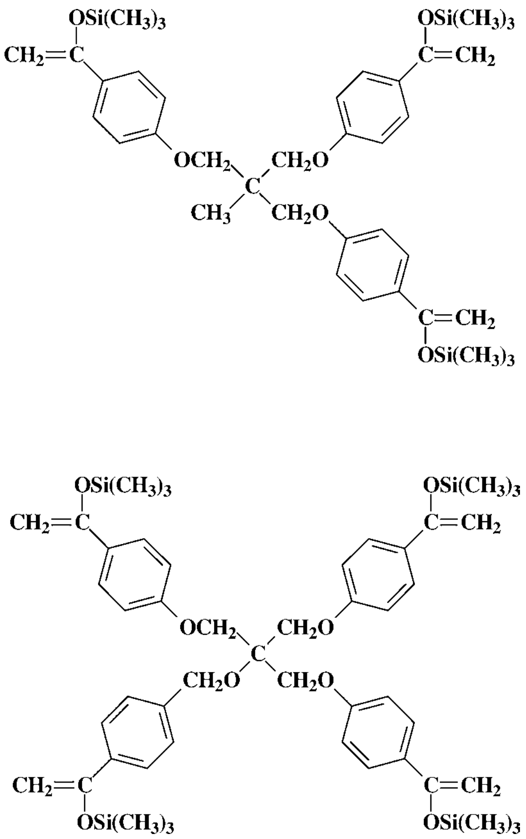
By employing tri- and tetrafunctional silyl enol ethers as coupling agents with living cationic polymerization (Scheme 7.12), three- and four-arm poly(isobutyl vinyl ether) (PIBVE) star homopolymers have been synthesized [47]. The living arms were produced at −15 °C using the $HCl/ZnCl_2$ initiating system in methylene chloride. The coupling of relatively short chains of living PIBVE (DP $\sim$ 10) was shown to occur nearly quantitatively, affording the multiarmed polymers in high yield (>95%). The yield decreased slightly (85–89%) with a longer living chain (DP $\sim$ 50). The MW distribution of the final stars was low.



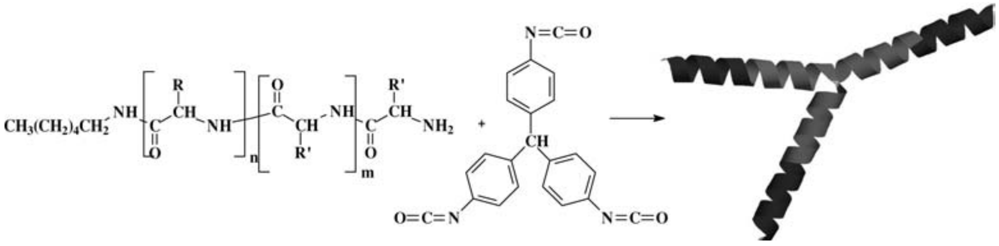
Scheme 7.11

More recently, three-arm star homopolypeptides of poly(γ-benzyl-L-glutamate) (PBLG) and poly(ε-benzyloxycarbonyl-L-lysine) (PZLL), i.e., $(\mathrm{PBLG})_3$ and $(\mathrm{PZLL})_3$, were synthesized [48] by living ROP of the *N*-carboxyanhydride (NCA) of the corresponding α-amino acids and the linking methodology. The synthetic approach involves the preparation of the corresponding living arms, followed by linking with triphenylmethane 4,4′, 4″-triisocyanate at room temperature (Scheme 7.13). The polymerization of the monomers γ-benzyl-L-glutamate NCA and ε-benzyloxycarbonyl-L-lysine NCA was performed using high vacuum techniques, with *n*-hexylamine as the initiator, leading to high MW, well-defined living polypeptides in ~100% yield with low polydispersity. A slight excess of living arms was used for the linking reaction and was subsequently fractionally removed. The polypeptides were extensively characterized by MO, SEC equipped with a LALLS detector, along with NMR spectroscopy. The polydispersity indices were lower than 1.1 and the observed MWs were very close to the theoretically expected ones. The characterization results revealed that the stars exhibited a high degree of molecular and compositional homogeneity.

1,3,5-Tris(bromomethyl)benzene was employed for the coupling of living PMMA chains obtained by group transfer polymerization, leading to three-arm stars [49] (Scheme 7.14). A reexamination of the reaction revealed that the linking efficiency was not quantitative. This behavior can be attributed to the fact that the reaction of the $-\mathrm{CH_2Br}$ groups with the living chain ends occurs in a stepwise manner. Therefore, after each substitution of Br by a chain, the reactivity of the remaining $-\mathrm{CH_2Br}$ groups is reduced as a result of steric hindrance, thus leading to lower conversions.

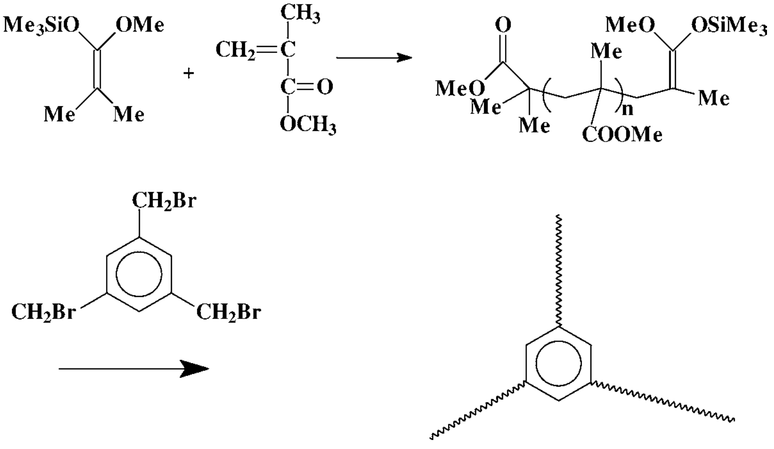


Scheme 7.12



Scheme 7.13

Recently, "click" linking chemistry was applied for the synthesis of star polymers. Gao and Matyjaszewski prepared three- and four-arm PS stars by "clicking" 3- and 4-alkyne LA with azido-terminated PS chains (Scheme 7.15) [50]. The linking reactions were catalyzed by CuBr/*N*, *N*, *N*′, *N*″, *N*″-pentamethyldiethylenetriamine (PMDETA). The procedure was fast and efficient for low MW samples. However, upon



Scheme 7.14

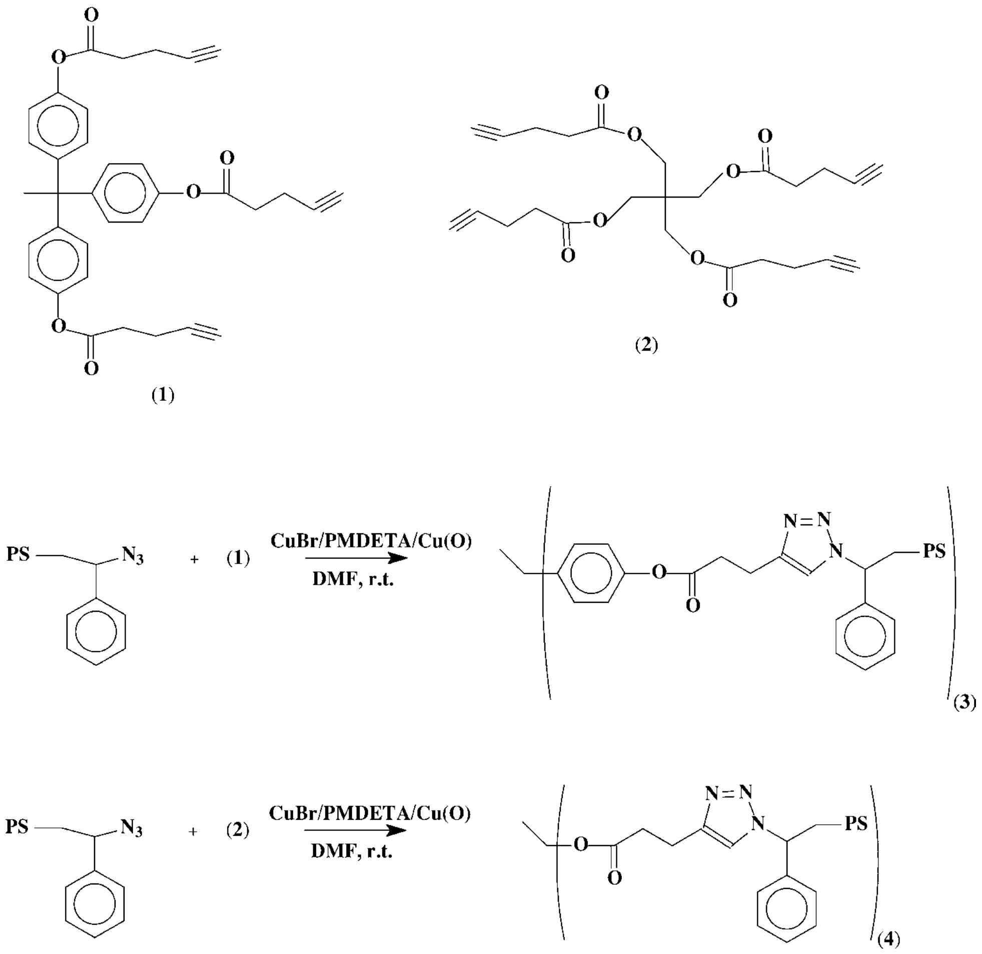
increasing the MW of the PS chains the efficiency was considerably reduced.

Schubert *et al.* [51] reported the synthesis of a seven-arm star PCL by "clicking" an acetylene-functionalized PCL precursor, prepared by ROP of ε-CL at 110 °C, with 5-hexyn-1-ol as initiator, with heptakis-azido-β-cyclodextrin (Scheme 7.16). The "click" reaction was performed under microwave irradiation at 100 °C. To induce complete functionalization of the β-cyclodextrin, 9 equivalents of the acetylene-functionalized PCL was used in the coupling reaction. After the reaction, the excess PCL was removed from the star by preparative SEC.

Tunca *et al.* [52] reported the synthesis of symmetric three-arm star polymers based on the arm-first technique, by "clicking" azide end-functionalized PS, poly(*tert*-butyl acrylate) (P*t*BuA), or poly(ethylene glycol) (PEG) with a trialkyne LA. The coupling efficiencies of PS-N_3, P*t*BuA-N_3, and PEG-N_3 with the trialkyne LA were 87, 85, and 82%, respectively.

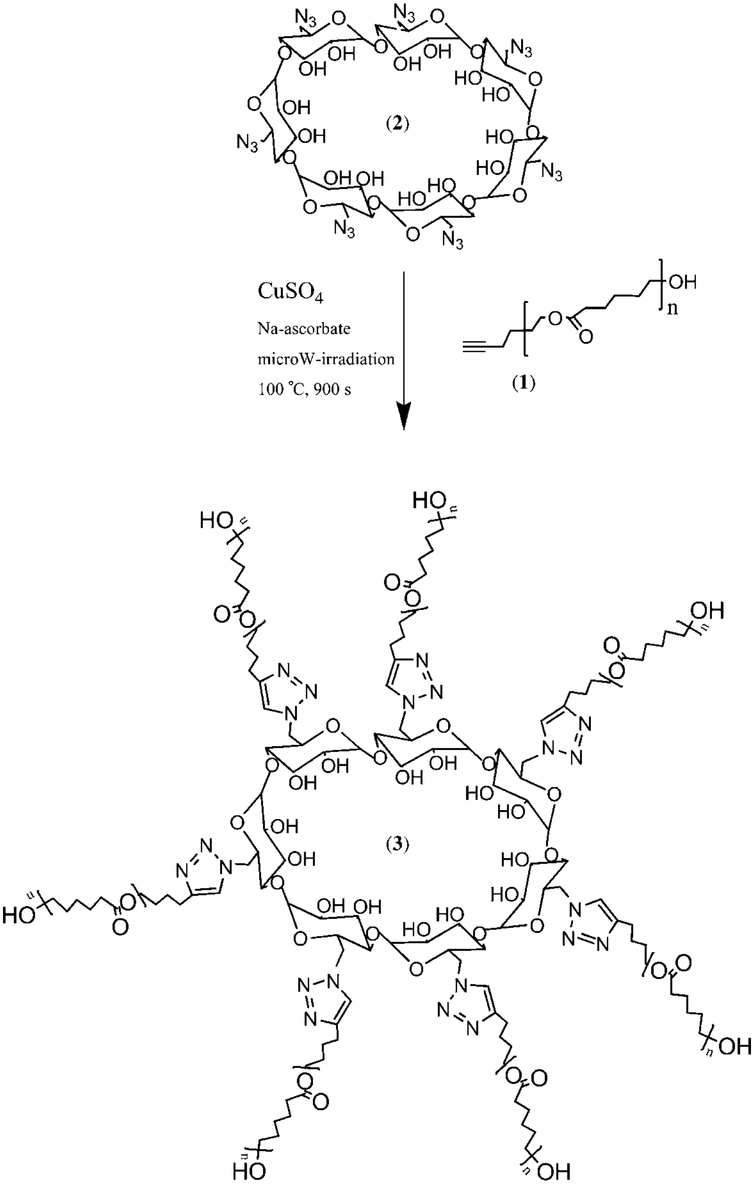
7.2.13 Difunctional Monomers (DFMs)

In this method, an end-reactive polymer precursor is used as initiator for the polymerization of a small amount of a suitable difunctional monomer (DFM). Microgel nodules of tightly cross-linked polymer are formed upon the polymerization. These nodules serve as the junction moiety from which the arms emanate. The functionality of the stars prepared by this method can be determined by MW measurements of the arms and the final star; however, it is very difficult to predict and control the number of arms. The number of arms incorporated in the star structure is influenced by many parameters. The most important is the molar ratio of the DFM over the living polymer. The functionality of the stars increases by increasing this ratio.



Scheme 7.15

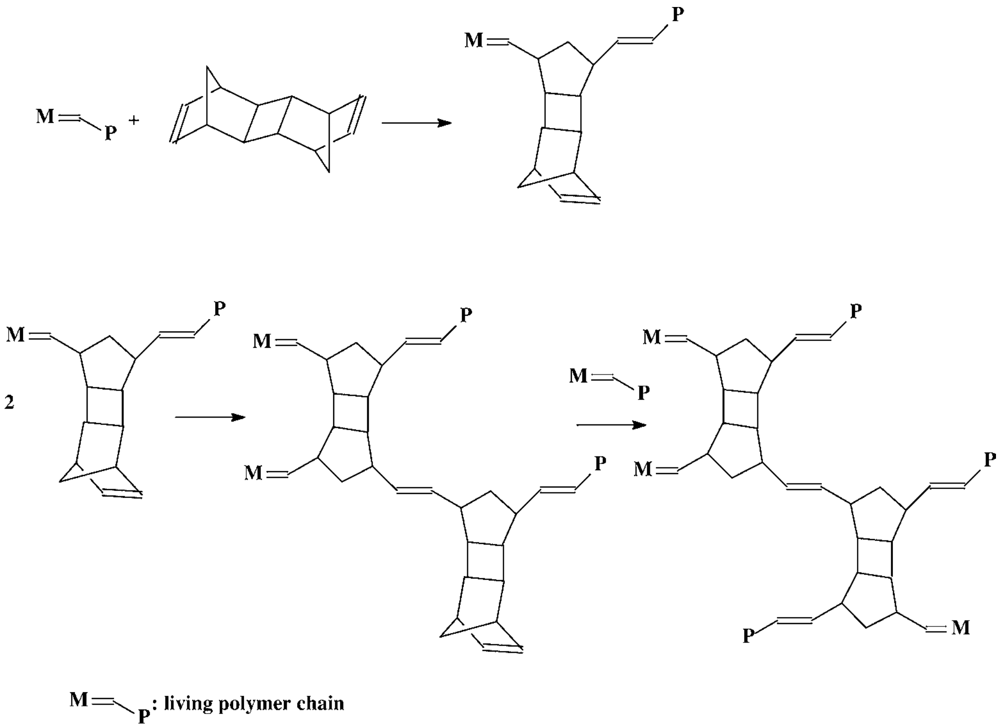
The norbornadiene dimer, *exo-trans-exo*-pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}] tetradeca-5,11-diene was employed as a DFM for the synthesis of star polynorbornene by ring-opening metathesis polymerization (ROMP). Norbornene was polymerized to afford the corresponding living polymer using M(CHR)(NAr)(O-*t*-Bu)$_2$ (M = W or Mo; NAr = *N*-2,6-C_6H_3-*i*Pr_2) as catalyst. The living polymer was then reacted with the DFM to produce the star polymers (Scheme 7.17). The linear living polymer was completely consumed, but the MW distribution of the final product was broader than that of the corresponding arms (mixture of stars with different functionality). The resulted stars are still living and bear active centers at the core of the structure. New arms can grow from these living sites giving rise to the formation of asymmetric stars. However, products with bimodal distributions were obtained, because of the



Scheme 7.16

slower initiation at the core of the star and the faster propagation as the reacting alkylidene centers move away from the sterically crowded core [53].

Several star polymers have been prepared by reacting living polymers synthesized by anionic polymerization with DVB. The method has been applied in the past for the synthesis of PS [54, 55] and polydiene [56] stars.



Scheme 7.17

Rather narrow MW distribution PS stars were obtained when the [DVB]/[PSLi] ratio was varied from 5.5 to 30 and the corresponding functionality ranged from 13 to 39. A similar behavior was obtained for polydiene stars when the [DVB]/[PDLi] ratio was between 5 and 6.5 and the functionality of the star was varied from 9 to 13.

Recently, PMMA stars were prepared by reacting PMMA chains, synthesized by anionic polymerization, with the DFM ethylene glycol dimethacrylate (EGDM) [57]. The polymers were characterized by SEC, LS, and viscometry. It was found that well-defined polymers can be prepared when the arm MW was rather high (e.g., $M_w = 40\,000$). It seems that this high MW is necessary to prevent intercore and gelation reactions from taking place. By reacting EGDM with isotactic living PMMA chains, obtained using *t*-butyl magnesium bromide as initiator in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene [58], a star polymer with 20–30 arms was synthesized. SEC connected with LS and viscometry detectors was used to characterize the sample. A similar reaction using syndiotactic living PMMA chains, obtained with the *tert*-butyllithium (*t*-BuLi)-R_3Al initiator system, failed to give star polymers. However, when EGDM was replaced by the butane-1,4-diol dimethacrylate, a PMMA star was obtained bearing 50–120 arms.

By using the DFM methodology and 2,2,6,6-tetramethyl-1-piperidinyloxy stable radical (TEMPO), star-block copolymers with a great variety of chemically different chains, in terms of MW and composition, were prepared [59]. The synthetic strategy involved the preparation of TEMPO-terminated linear chains and subsequent coupling with the DFMs divinylbenzene or a bis(maleimide) derivative.

The DFM methodology and ATRP were employed for the synthesis of PS [60] and PtBuA star homopolymers [61]. The DFMs used included DVB, 1,4-butanediol diacrylate, as well as EGDM. Several factors were investigated for the formation of nearly monodisperse stars, such as the choice of the exchanging halogen, the solvent, the addition of copper (II) species, the ratio of the coupling agent to the macroinitiator, and the reaction time. The highest efficiency ($\sim$95%) was obtained using a 10–15-fold excess of the DFM over chain ends.

Living PMMA chains, produced by the $RuCl_2(PPh_3)_3$-catalyzed polymerization of MMA were reacted with the DFM bisphenol A dimethacrylate (BPDMA) to afford the corresponding PMMA star polymers [62]. The functionality of the products ranged from 4 to 63. The yield of the linking reaction was found to depend on the concentration and the degree of polymerization of the living arms, as well as the molar ratio of BPDMA over the living chains.

The DFM methodology and RAFT were utilized for the synthesis of PS star homopolymers [63]. The linear macro RAFT PS agent was synthesized in the bulk, at 110 °C, using benzyl dithiobenzoate and AIBN. DVB was used as the DFM. The stars were extensively characterized by NMR and infrared (IR) spectroscopy, as well as by SEC along with dynamic light scattering (DLS). It was found that the molar ratio of DVB/PS and polymerization time influenced the yield, MW, and the polydispersity index of the stars. In most cases, a significant amount of living linear macroagent remained unreacted and was separated from the star by preparative SEC.

7.2.2
Star-Block Copolymers

Star-block copolymers are star polymers in which each arm is a diblock (or a triblock) copolymer and can be prepared by all the methods reported above. The best route involves the linking reaction of a living diblock copolymer, prepared by sequential polymerization of the two monomers, with a suitable LA. Using anionic polymerization and chlorosilane LAs, Fetters *et al.* synthesized star-block copolymers (polystyrene-*b*-polyisoprene)$_n$ [(PS-*b*-PI)$_n$] where $n = 4$, 8, 12, 18 [64, 65]. An example corresponding to four-arm star-block is given in Scheme 7.18. Well-defined structures of low polydispersities were obtained.

C_{60} was also employed for the synthesis of star-block copolymers [66]. Living PS-*b*-P2VP diblocks, having short P2VP chains, were prepared by sequential anionic polymerization in THF. These living diblocks were reacted with a

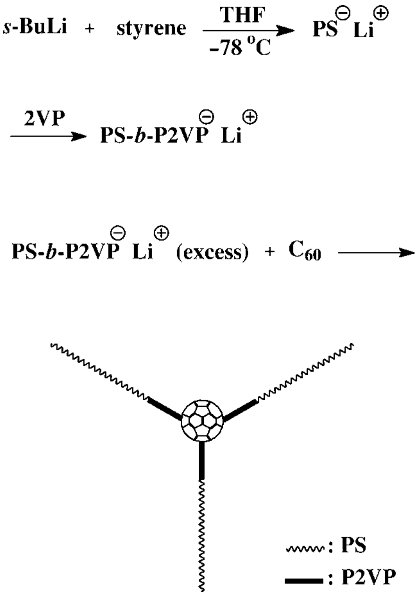
$$s\text{-BuLi} + \text{styrene} \longrightarrow \text{PSLi} \xrightarrow{\text{isoprene}}$$

$$(\text{PS-}b\text{-PI})\text{Li} \xrightarrow{\text{SiCl}_4} (\text{PS-}b\text{-PI})_4$$

Scheme 7.18

suspension of C_{60} in THF leading to the formation of a three-arm star-block copolymer (Scheme 7.19). The corresponding reaction with the living PS homopolymer resulted in the formation of a four-arm star. The lower reactivity of the 2VP anion seems responsible for this behavior. The SEC analysis of the product revealed a broad MW distribution, indicating that a mixture of stars with different functionalities was obtained.

Recently, 12-arm PS-*b*-poly(4-vinylpyridine) (P4VP) star-block copolymers were synthesized using dendritic dodecafunctional macroinitiators [67] and TEMPO-mediated radical polymerization (Scheme 7.20). The polymerizations were conducted in bulk at 120 °C, and the stars synthesized exhibited rather low polydispersity indices (1.06–1.26). In the cases where higher polydispersity indices were obtained, SEC profiles revealed the formation of a small amount of four-arm stars that was subsequently connected to form larger functionality stars. To evaluate the livingness for the TEMPO-mediated radical polymerization of styrene, hydrolysis of the ester central bonds and subsequent SEC measurements were performed. The analysis indicated that the functionality polydispersity was higher than the MW polydispersity (mixture of stars with different functionalities).

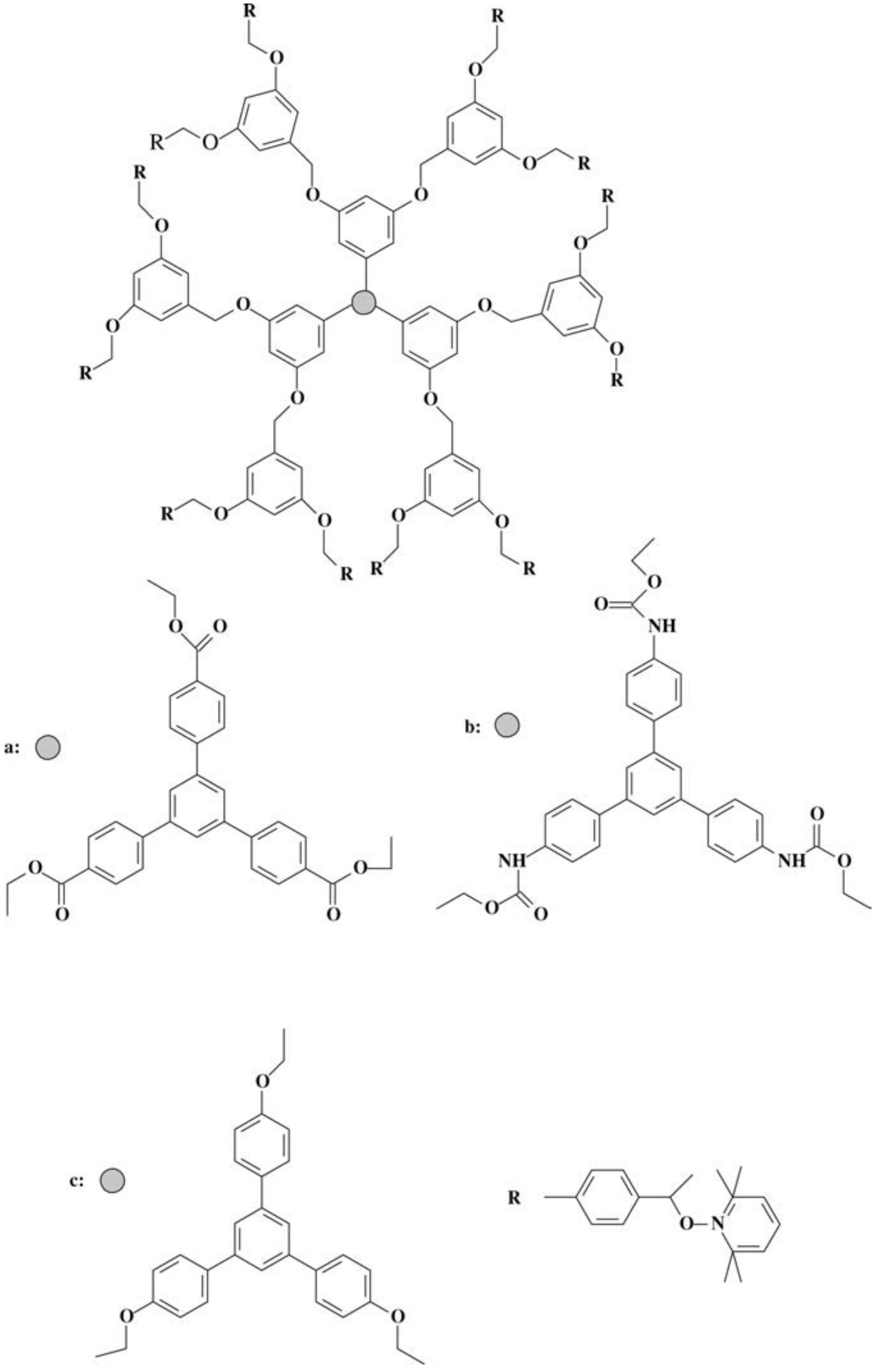


$$s\text{-BuLi} + \text{styrene} \xrightarrow[-78\,^{\circ}\text{C}]{\text{THF}} \text{PS}^{\ominus}\,\text{Li}^{\oplus}$$

$$\xrightarrow{\text{2VP}} \text{PS-}b\text{-P2VP}^{\ominus}\,\text{Li}^{\oplus}$$

$$\text{PS-}b\text{-P2VP}^{\ominus}\,\text{Li}^{\oplus}\ (\text{excess}) + C_{60} \longrightarrow$$

Scheme 7.19



Scheme 7.20

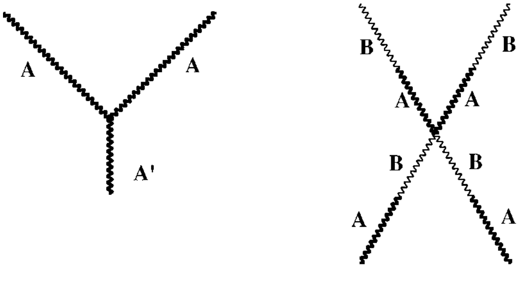
The DFM methodology and RAFT were utilized for the synthesis of PS-*b*-poly(*N*-isopropyl acrylamide) star-block copolymers [63], in a way similar to that already presented for the synthesis of PS star homopolymers. The synthesis of the precursor was performed by sequential polymerization in bulk at 110 °C, using benzyl dithiobenzoate and AIBN. DVB was used as the DFM. The stars were extensively characterized by NMR and IR spectroscopy, SEC along with DLS. It was found that the molar ratio of DVB/PS and the polymerization time influenced the yield, MW, and the polydispersity index of the stars. In most cases a significant amount of living linear macroagent remained unreacted and was consequently separated from the star by preparative SEC.

7.2.3
Asymmetric Stars

Asymmetric stars are a special class of stars characterized by an asymmetry factor compared to the classic symmetric structures described previously. The following parameters have been considered as asymmetry factors:

1. *MW*. All the arms of the star are identical in chemical nature but have different MWs (Scheme 7.21).
2. *Topology*. The arms of the star are block copolymers that may have the same MW and composition but differ with respect to the polymeric block that is covalently attached to the core of the star (Scheme 7.21).

The synthesis of asymmetric stars can be accomplished by the same general methods reported for the symmetric stars but in such way that a controlled incorporation of the arms, differing in MW, or topology is achieved. Efficient methods for the synthesis of asymmetric star polymers were developed only recently.



Molecular weight asymmetry

Topological asymmetry

Scheme 7.21

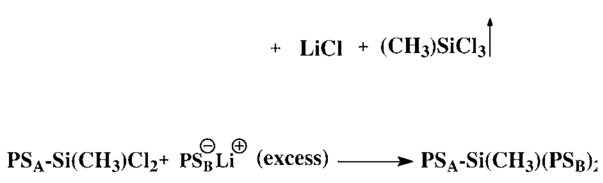
7.2.3.1 Molecular Weight Asymmetry

The chlorosilane method and anionic polymerization techniques for the synthesis of asymmetric stars were initially reported by Fetters and was later developed by Mays, Hadjichristidis, and collaborators [9–12]. Chlorosilanes are used as LAs for the stepwise selective replacement of the chlorine atoms by the polymer chains. This procedure can be achieved taking into account the different reactivity of the living polymer ends toward the Si–Cl bond, as this is determined by the steric hindrance effects, the charge localization on the terminal carbon atom [7], and the excluded volume of the living chain which is affected by the reaction solvent. The reactivity of the living chain end decreases by charge delocalization and by increasing the steric hindrance. The latter can be affected by both structures – that of the living chain end and the chlorosilane LA. The steric hindrance of living end increases (reactivity decreases) in the order BdLi < IsLi < SLi < DPELi. In the case of chlorosilanes, the closer the Si–Cl groups the more sterically hindered (reactivity decreases) is the reaction with the living chains. For example, overall $SiCl_4$ is less reactive than $Cl_2Si{-}CH_2{-}CH_2{-}SiCl_2$. The reactivity is also influenced by other parameters, such as the MW of the living chain, the polarity of the solvent in which the reaction takes place, and the temperature. When all these factors are optimized, well-defined products are produced. However, the disadvantage of this method is that it is time consuming and requires elaborate high vacuum techniques to be performed.

The method was first applied to the synthesis of asymmetric PS stars composed of two arms of equal MWs, PS_B, and a third one, PS_A, with a MW either half or twice that of the identical arms [68] (Scheme 7.22).

Detailed characterization results by SEC, MO, and LS revealed that well-defined structures were obtained. The method was also applied in the synthesis of asymmetric PBd [68] and polyisoprene (PI) [69] stars.

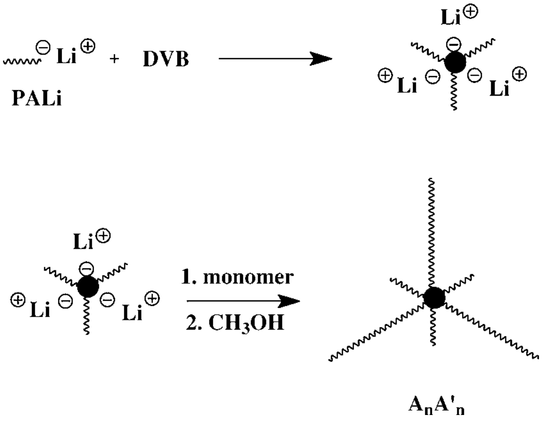
When appropriate living polymer chains react with a small amount of DVB, a star polymer is formed consisting of a highly living cross-linked polydivinylbenzene core from which the arms emanate. The number of the living sites is theoretically equal to the number of the arms of the star. Subsequent addition of a new monomer results in the growth of new arms from the core and therefore in the formation of an asymmetric star of the type



$$PS_A^{\ominus}Li^{\oplus} + (CH_3)SiCl_3\ (\text{excess}) \longrightarrow PS_A\text{-}Si(CH_3)Cl_2 + LiCl + (CH_3)SiCl_3\uparrow$$

$$PS_A\text{-}Si(CH_3)Cl_2 + PS_B^{\ominus}Li^{\oplus}\ (\text{excess}) \longrightarrow PS_A\text{-}Si(CH_3)(PS_B)$$

Scheme 7.22

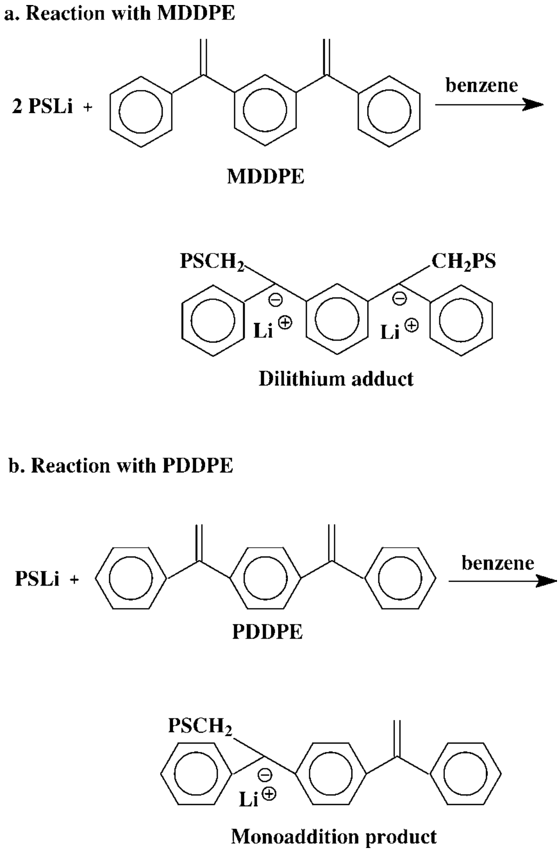


Scheme 7.23

$A_nA'_n$ (A and A′ chains with different MW). This general procedure is depicted in Scheme 7.23.

The main drawback associated with the DVB method is the architectural limitation, i.e., only asymmetric stars of the type $A_nA'_n$ can be prepared. Furthermore, because of steric hindrance, in most cases, a fraction of the living arms A is not incorporated in the star structure, the active sites of the living A_n star are not equally accessible to the newly added A′ monomers, and the initiation rate is not the same for all active sites. Consequently, it is obvious that the final products are structurally ill defined with a rather great dispersity of the *n* values and are characterized by broad MW distributions. Nevertheless, this method is technically important since it can be applied on an industrial scale and also provides the possibility of preparing end-functionalized asymmetric stars after reaction of the growing living branches A′ with suitable electrophilic compounds.

Using this methodology and anionic polymerization, asymmetric stars of the type $(PS_A)_n(PS_B)_n$ were prepared [70]. Living PS chains were obtained by *s*-BuLi initiation and reacted with a small amount of DVB to give a living star polymer. The anionic sites of the star core were subsequently used to initiate the polymerization of a new quantity of styrene. This initiation step was accelerated by the addition of a small quantity of THF. It was revealed by SEC analysis that high MW species were also present, probably due to the formation of linked stars. These structures can be obtained when living anionic branches of one star react with the residual double bonds of the DVB-linked core of another star. In another example, mono-2-bromoisobutyryl PEO ester was used as macroinitiator for the ATRP of DVB, leading to the synthesis of the desired star polymers. Subsequent addition of styrene led to the synthesis of PEO_nPS_m miktoarm stars through the polymerization of styrene from the initiating sites located at the core of the PEO stars [71]. The styrene conversion

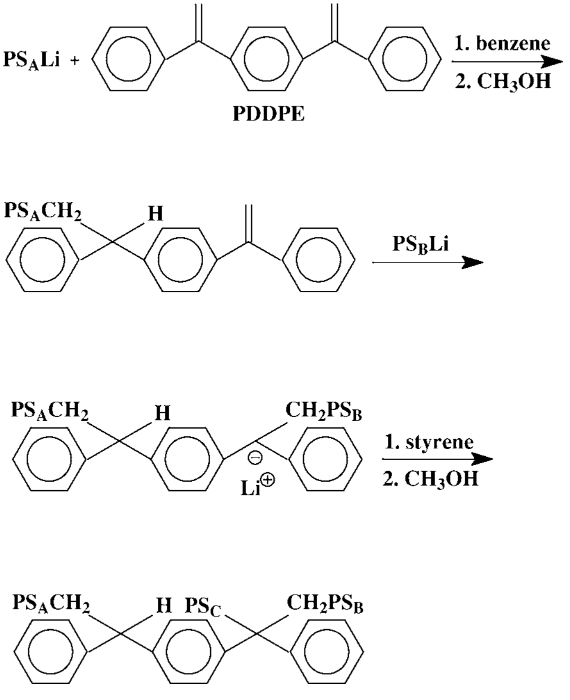


Scheme 7.24

did not exceed 10% to avoid star–star coupling reactions and, therefore, the production of gels.

Rich chemistry was developed by Quirk and collaborators [72] leading to the formation of several types of asymmetric stars by reaction of living PS with either 1,3-bis(1-phenylethenyl)benzene (MDDPE) or 1,4-bis(1-phenylethenyl)benzene (PDDPE) according to Scheme 7.24.

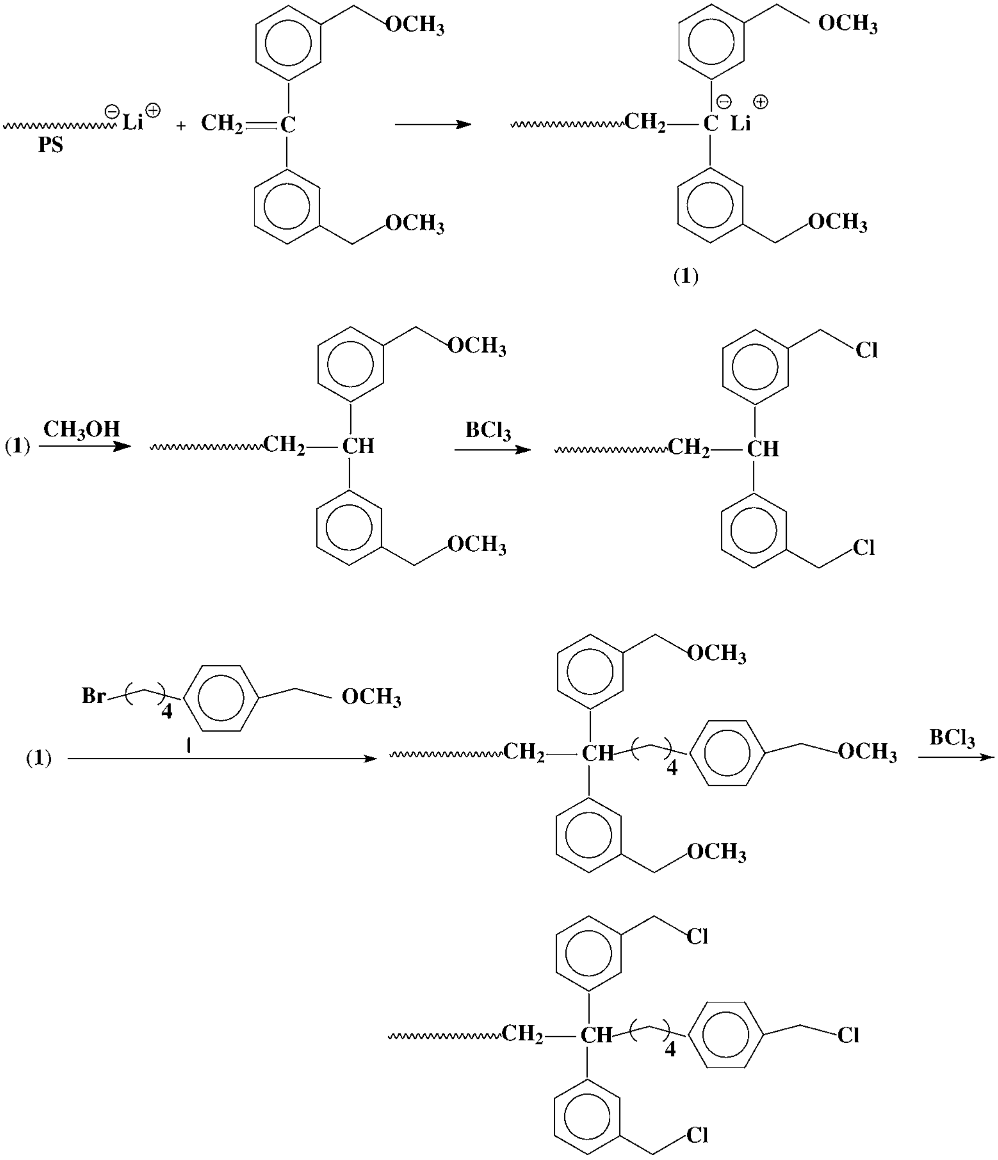
It was shown that 2 mol of the living polymer reacted rapidly with the MDDPE derivatives to form the dilithium adduct in hydrocarbon solvents, whereas in THF monoaddition was reported [73, 74]. This reaction was monitored by UV–visible spectroscopy. The analysis revealed that the stoichiometric addition of PSLi was quantitative. However, PDDPE exhibited a reduced tendency to form the diadduct both in polar and nonpolar solvents. This behavior can be attributed to the delocalization of the negative charge only in the para isomer. Mainly, low MW PSs have been used for these studies.



Scheme 7.25

On the basis of the observation above, a three-arm asymmetric PS star was successfully prepared [75] (Scheme 7.25). The monoadduct product was reacted with a second polystyryllithium chain of a different MW, to form the coupled product. The efficiency of this coupling reaction depends on the control of the stoichiometry between the reactants. Under optimum conditions, the efficiency of the coupling reaction can be higher than 96%. Finally, the addition of styrene led to the formation of the product. The polymerization took place in the presence of THF to accelerate the crossover reaction. SEC analysis revealed the existence of a small quantity of the monoadduct product and the second arm of the PS homopolymer, due to incomplete linking reactions. The weak points of the method include the great care that should be exercised over the stoichiometry of the reactions and the difficulty in isolating and consequently characterizing the third arm. However, the method is valuable since it provides the possibility to functionalize the third arm by reaction with a suitable electrophilic agent.

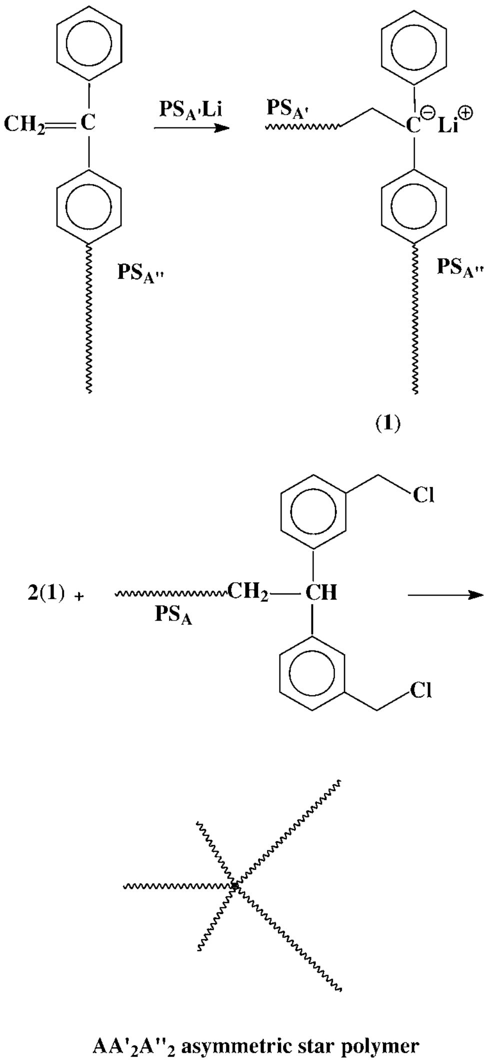
Hirao *et al.* developed a general method employing 1,1-diphenylethylene (DPE) derivatives carrying protected (masked) chloromethyl groups to prepare PS asymmetric stars of the types AA'_2, $AA'_2A''_2$, AA'_3, AA'_4, $AA'A''_2$, and $AA'_4A''_4$ [76, 77]. The procedure is based on the reaction sequence shown in Scheme 7.26. Living PS was reacted with



Scheme 7.26

1,1-bis(3-methoxymethylphenyl)ethylene followed by transformation of the methoxymethyl groups to chloromethyl groups by reaction with BCl_3 in CH_2Cl_2 at 0 °C for 10–30 min. Prior to the reaction with BCl_3, the living end-functionalized PS is able to react with other compounds such as 1-(4′-bromobutyl)-4-methoxymethylbenzene (Scheme 7.26). Despite the difficult multistep procedure, it was shown that PSs with predictable MWs, narrow MW distributions, and almost nearly quantitative degrees of functionalization can be synthesized. Small amounts (<5%) of coupled PS by-products can be produced during the transformation reaction, due to a Friedel–Crafts side reaction among the polymer chains.

DPE-functionalized polymers were also used for linking reactions with living polymeric anions, followed by the coupling with chloromethyl groups. Characteristic examples for the synthesis of AA′$_2$A″$_2$, and AA′$_4$A″$_4$ asymmetric star polymers are given in Schemes 7.27 and 7.28, respectively. Well-defined star polymers with rather low MW arms were obtained with this method.

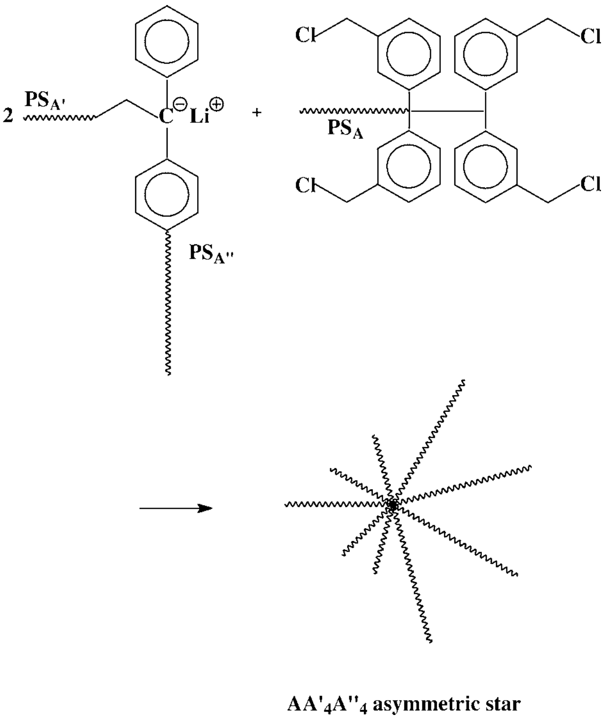


Scheme 7.27

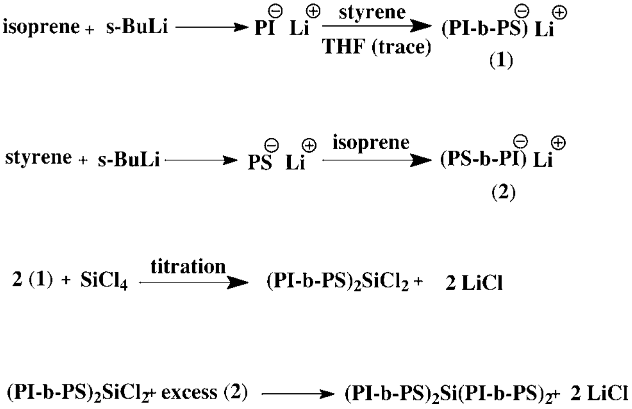
In addition to anionic polymerization, ATRP also led to the preparation of asymmetric stars [78]. ω-Bromopolystyrene was obtained using ethyl 2-bromoisobutyrate as initiator in the presence of the catalyst CuBr and the ligand pentamethyldiethylenetriamine. The end bromine group was reacted with 2-amino-1,3-propanediol leading to PS chains bearing two hydroxyl groups at the same chain end. These hydroxyl groups were subsequently transformed to bromines after reaction with 2-bromoisobutyryl bromide. The new initiating sites were used for the polymerization of styrene, leading to the synthesis of asymmetric PS(PS$'$)$_2$ stars.

7.2.3.2 **Topological Asymmetry**

A novel star-block copolymer architecture, i.e., the inverse star-block copolymer, was reported [79]. These polymers are stars with four poly(styrene-*b*-isoprene) copolymers as arms. Two of these arms are connected to the star center by the PS block, whereas the other two through the PI block. The synthetic procedure is given in Scheme 7.29. Living diblocks(I) were prepared by anionic polymerization and sequential addition of monomers. A small quantity of THF was used to accelerate the initiation of



Scheme 7.28



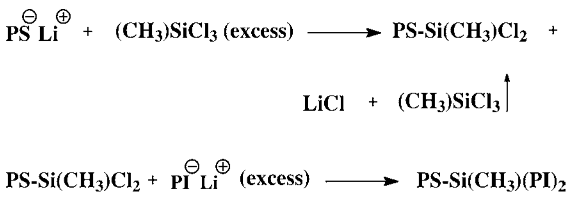
Scheme 7.29

the polymerization of styrene, and the living diblock copolymer(I) was slowly added to a solution of $SiCl_4$. The difunctional LA thus prepared was then reacted with a small excess of the living diblock copolymer(II) to produce the desired product. These living diblocks were end-capped with 3–4 units of butadiene to facilitate the linking reaction. Detailed characterization results by SEC, MO, LS, differential refractometry, and NMR spectroscopy revealed the formation of well-defined products.

7.2.4
Miktoarm Star Polymers

The term miktoarm (from the Greek word μικτός meaning mixed) rather than heteroarm (from the Greek word έτερος meaning the other) star polymers refers to stars consisting of chemically different arms. In the last decade, considerable effort has been made toward the synthesis of miktoarm stars, when it was realized that these structures exhibit very interesting properties [80–82]. The synthesis of the miktoarm star polymers can be accomplished by methods similar to those reported for the synthesis of asymmetric stars. The most common examples of miktoarm stars are the A_2B, A_3B, A_2B_2, A_nB_n ($n > 2$), and ABC types. Other less common structures, like the ABCD, AB_5, AB_2C_2, etc., are now also available.

A near monodisperse miktoarm star copolymer of the A_2B type was first reported by Mays [83], with A being PI and B being PS. The synthetic method adopted was similar to that applied by Fetters [68] for the synthesis of the asymmetric PS and PBd stars. The living PS chains were reacted with an excess of methyltrichlorosilane to produce the monosubstituted macromolecular LA. The steric hindrance of the living polystyryllithium and the excess of the silane led to the absence of any coupled by-product. The excess silane was



$$\overset{\ominus}{PS}\,\overset{\oplus}{Li} + (CH_3)SiCl_3\ (excess) \longrightarrow PS\text{-}Si(CH_3)Cl_2 + LiCl + (CH_3)SiCl_3\uparrow$$

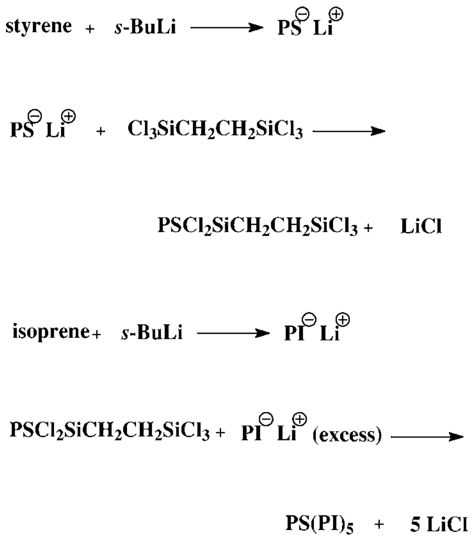
$$PS\text{-}Si(CH_3)Cl_2 + \overset{\ominus}{PI}\,\overset{\oplus}{Li}\ (excess) \longrightarrow PS\text{-}Si(CH_3)(PI)_2$$

Scheme 7.30

removed, and then a slight excess of the living PI chains was added to produce the miktoarm star PS(PI)$_2$. Excess PI was then removed by fractionation. The reaction sequence given in Scheme 7.30 was monitored by SEC and the molecular characterization of the arms and the final product was performed by MO.

This method was later extended by Iatrou and Hadjichristidis [84] to the synthesis of the A$_2$B stars, where A and B were all possible combinations of PS, PI, and PBd. In this case, a more sophisticated high vacuum technique was employed to ensure the formation of products characterized by high degrees of chemical and compositional homogeneity. This was tested using SEC, MO, LS, differential refractometry, and NMR spectroscopy. The method employed for the synthesis of the A$_2$B miktoarm stars can be expanded to the synthesis of A$_3$B structures using silicon tetrachloride (SiCl$_4$) instead of methyltrichlorosilane as the LA. The synthesis of PSPI$_5$ miktoarm stars [85] was accomplished by the reaction sequence outlined in Scheme 7.31.

Amphiphilic multiarm star copolymers of PIB and PEO bearing one PIB arm and two, three, and four PEO arms with identical length were reported



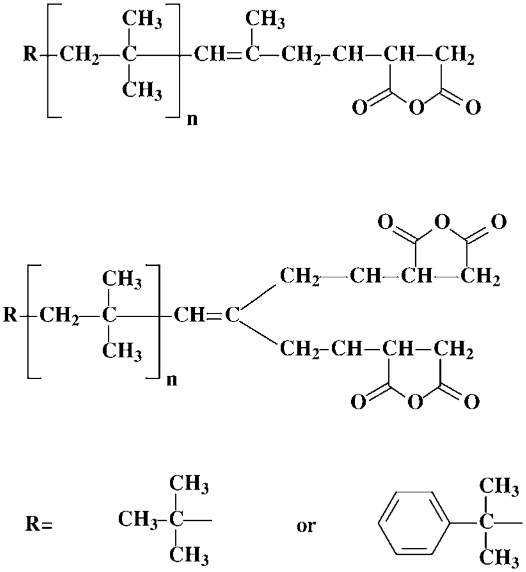
$$styrene + s\text{-}BuLi \longrightarrow \overset{\ominus}{PS}\,\overset{\oplus}{Li}$$

$$\overset{\ominus}{PS}\,\overset{\oplus}{Li} + Cl_3SiCH_2CH_2SiCl_3 \longrightarrow PSCl_2SiCH_2CH_2SiCl_3 + LiCl$$

$$isoprene + s\text{-}BuLi \longrightarrow \overset{\ominus}{PI}\,\overset{\oplus}{Li}$$

$$PSCl_2SiCH_2CH_2SiCl_3 + \overset{\ominus}{PI}\,\overset{\oplus}{Li}\ (excess) \longrightarrow PS(PI)_5 + 5\,LiCl$$

Scheme 7.31



Scheme 7.32

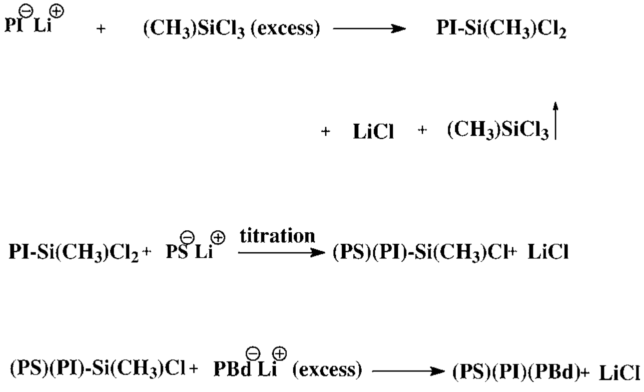
by Lemaire *et al.* [86, 87]. End-chlorinated PIBs with controlled MW and narrow MW polydispersity were prepared by cationic polymerization, and the *tert*-Cl ω-end group was quantitatively converted to anhydride or dianhydride (Scheme 7.32). These species were used as macromolecular coupling agents for α-methoxy-ω-hydroxy PEOs leading to star-shaped polymers. It was found that the best coupling efficiency was obtained with *p*-toluenesulfonic acid as catalyst in mesitylene at 155 °C. The final products, characterized by SEC and MALDI-TOF MS, were mixtures of the stars with unreacted PEO and intermediate products.

Miktoarm star copolymers of the A_2B_2 type, where A is PIB and B is poly(MeVE), were prepared [88] via cationic polymerization. The synthetic strategy involved the reaction of 2,2-bis[4-(1-phenylethenyl)phenyl]propane (BDPEP) and 2,2-bis[4-(1-tolylethenyl)phenyl]propane (BDTEP) with living PIB, resulting in a di-cationic in-chain initiator. This initiator was used for the polymerization of methyl vinyl ether to give the poly(isobutylene)$_2$(poly(methyl vinyl ether))$_2$, (PIB)$_2$(PMVE)$_2$, miktoarm copolymer. Purification of the crude A_2B_2 copolymer was performed on a silica gel column, and the purity of the resulting star was 93%.

The DFM methodology can be applied for the synthesis of miktoarm stars of the type A_nB_n in a manner similar to that of the asymmetric $A_nA'_n$ stars, involving a three-step procedure starting from the synthesis of the living chains A. These living chains initiate the polymerization of a small quantity of the DFM, leading to the formation of a living star polymer carrying a number of active sites within its core equal to the number of arms that have contributed to its formation. During the third step, these active sites are used to polymerize the monomer B, thus producing the miktoarm star A_nB_n. By using anionic polymerization techniques and DVB as the DFM, miktoarm stars was first reported by Funke [17, 18], which were then extended on and improved by Rempp *et al.* [12]. In all cases published in the literature, the A arms are PS chains, whereas a variety of B chains such as P*t*BuMA, P*t*BuA, PEO, P2VP, and poly(ethyl methacrylate) have been used [89–91]. Special care was given to the synthesis of amphiphilic stars bearing hydrophobic and either cationic or anionic branches. The polymerization of the styrene was initiated with *s*-BuLi, except in the case of the PS_nPEO_n stars, where cumyl potassium was used. After the formation of the living PS star, the SEC analysis showed that a considerable part (as high as 15%) of the PS chains was not incorporated in the star structure mainly due to accidental deactivation. When the second monomer was a (meth)acrylate, the active sites were first capped with a unit of DPE to reduce their nucleophilicity. The final stars usually had *n* values between 4 and 20.

The synthesis of the (PS)(PI)(PBd) star terpolymer was accomplished by Hadjichristidis *et al.* [92] using anionic polymerization and controlled chlorosilane chemistry. Living PI chains reacted with a large excess of methyltrichlorosilane to produce the dichlorosilane end-capped PI. After evaporation of the excess silane, the living PS arm was incorporated by a slow stoichiometric addition (titration). Samples were taken during the addition and were analyzed by SEC to monitor the progress of the reaction and determine the endpoint of the titration. When the formation of the intermediate product $(PS)(PI)Si(CH_3)Cl$ was completed, a small excess of the living PBd chains was added to give the final product. The reaction sequence is outlined in Scheme 7.33.

The order of linking of the various arms to the LA is crucial for the success of the synthesis. The less sterically hindered chain end, namely, PBdLi, has to be incorporated last, whereas the most sterically hindered, PSLi, is



$$\mathrm{PI^{\ominus}Li^{\oplus}} + \mathrm{(CH_3)SiCl_3\ (excess)} \longrightarrow \mathrm{PI\text{-}Si(CH_3)Cl_2} + \mathrm{LiCl} + \mathrm{(CH_3)SiCl_3}\uparrow$$

$$\mathrm{PI\text{-}Si(CH_3)Cl_2} + \mathrm{PS^{\ominus}Li^{\oplus}} \xrightarrow{\text{titration}} \mathrm{(PS)(PI)\text{-}Si(CH_3)Cl} + \mathrm{LiCl}$$

$$\mathrm{(PS)(PI)\text{-}Si(CH_3)Cl} + \mathrm{PBd^{\ominus}Li^{\oplus}\ (excess)} \longrightarrow \mathrm{(PS)(PI)(PBd)} + \mathrm{LiCl}$$

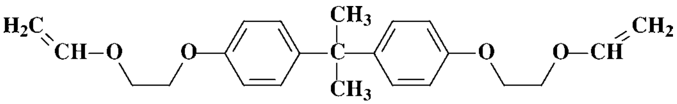
Scheme 7.33

linked in the titration step. Extensive characterization data for the arms as well as for the intermediate and the final product confirmed that the ABC star was characterized by high structural and compositional homogeneity. Two examples of the synthesis of ABCD miktoarm star quaterpolymers were reported in the literature [93, 94].

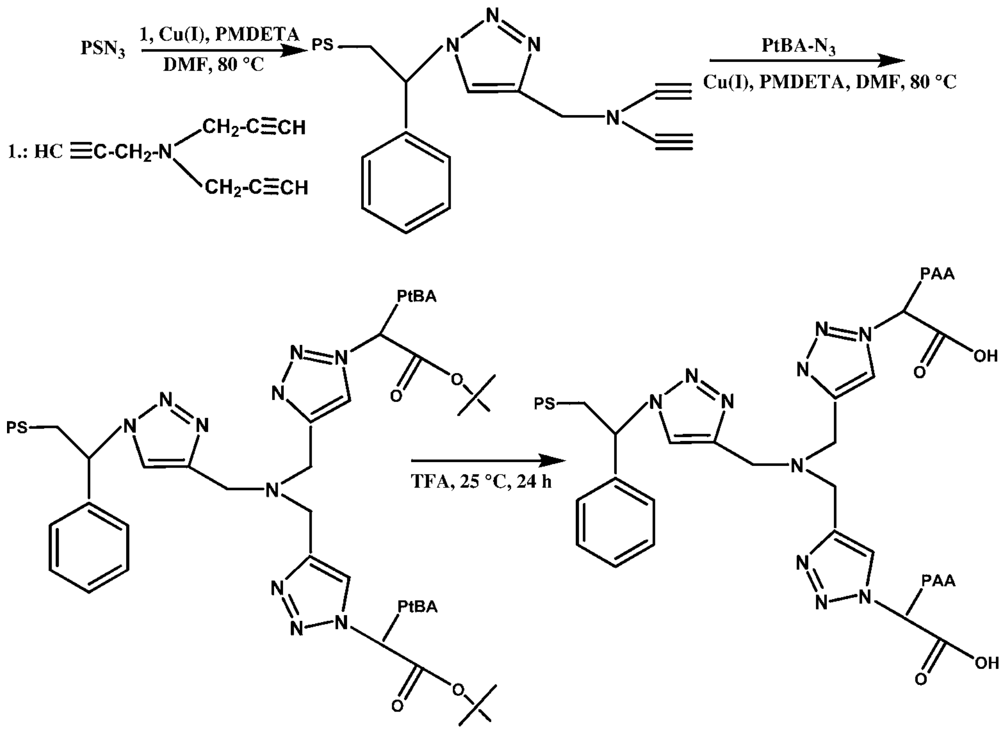
The DPE derivative methods and anionic polymerization were developed by Quirk and Hirao for the synthesis of miktoarm stars with complex architectures. The first procedure relies on the use of either MDDPE or PDDPE, whereas the second on the formation of polymers carrying DPE end groups with methoxymethyl moieties which can be transformed to chloromethyl groups. Other specific methods have also been developed utilizing DPE derivatives for the synthesis of miktoarm stars. The discussion given in the case of the asymmetric stars concerning the advantages and limitations of the methods apply here as well. The recent achievements using this methodology will be presented in the following paragraphs. The synthesis of a wide variety of miktoarm stars with functionalized DPE derivatives and anionic polymerization has been reported recently in a detailed review by Hirao *et al.* [95]. Employment of the iterative methodology already presented for the synthesis of asymmetric stars, miktoarm stars of the type AB_4, AB_8, A_2B_4, A_2B_8, A_2B_{12}, ABC_2, ABC_4, $A_2B_2C_2D$, $A_4B_4C_4D$, ABC, A_3B, A_2B_2, AB_3, A_2BC, AB_2C, ABC_2, and ABCD, where A is PS, B is PI or PαMS, C is PI or poly(4-(4-1,2:5,6-di-*O*-isopropylidene-α-glucofuranose-3-oxy)butoxy)styrene, and D is poly(4-trimethylsilylstyrene), have been prepared.

In addition to anionic polymerization, ATRP has also been used for the synthesis of miktoarm stars of the A_nB_m type. Using DVB, $(\text{P}n\text{BuA})_n(\text{PS})_m$ miktoarm stars were obtained. Bis(2-methacryloyloxyethyl)disulfide was also employed as a DFM for the synthesis of $(\text{PMMA})_n(\text{P}n\text{BuA})_m$ miktoarm stars [96]. In the last case, by using suitable reducing agents it is possible to degrade the core of the star structure. The formation of interstar and intrastar arm–arm coupling was observed. The initiating efficiency of the alkyl bromide sites in the core of the star polymers was determined after cleavage of the degradable stars and the corresponding miktoarm stars. It was found that only 19% of the initiation sites were active for the polymerization of the second monomer.

Cationic polymerization has also been applied in the synthesis of miktoarm stars of the type A_nB_n. Miktoarm stars of isobutyl vinyl ether (IBVE) and hydrolyzed 2-acetoxyethyl vinyl ether (AcOVE) or diethyl 2-(vinyloxy)ethyl malonate (VOEM) [97] were prepared using the divinylether 1 of Scheme 7.34 as the DFM. The living chains of IBVE were used as macroinitiators for the polymerization of the diether, resulting in a star IBVE with a microgel core.



Scheme 7.34

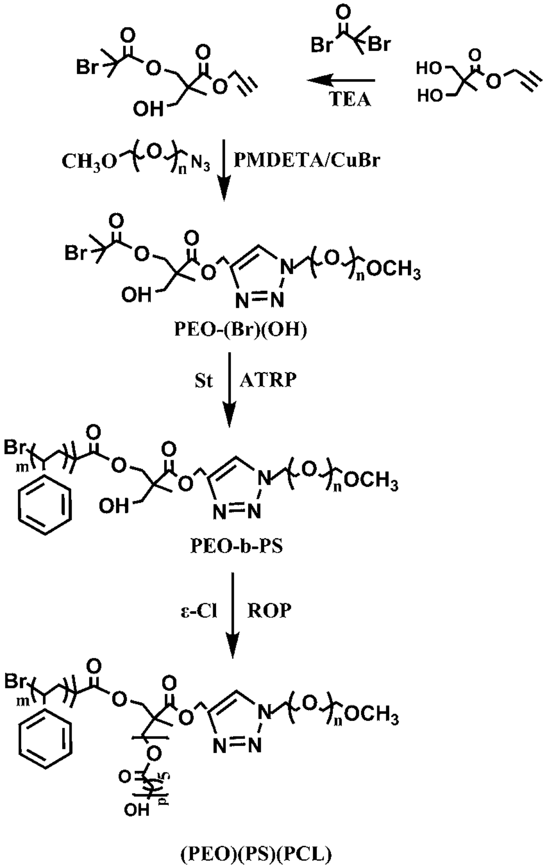


Scheme 7.35

The living sites in the core were used for the sequential polymerization of the other monomers.

Monteiro *et al.* [98] were the first to demonstrate the synthesis of a three-miktoarm star copolymer, $(PS)_2PtBuA$, using ATRP and "click" chemistry. A large excess of tripropargylamine was "clicked" with PS-N_3 to afford $PS-(-\equiv)_2$ (Scheme 7.35). A solution of $PS-(-\equiv)_2$ in dimethylformamide (DMF) was then added to a solution of P*t*BuA-N_3 in DMF at 80 °C to give the three-miktoarm star (yield: 92%). Conversion of the P*t*BuA to poly(acrylic acid) (PAA) with trifluoroacetic acid afforded an amphiphilic three-miktoarm star, $PS(PAA)_2$.

Deng *et al.* [99] reported the synthesis of ABC three-miktoram star terpolymer by "click" chemistry, ATRP, and ROP. An azide-terminated poly(ethylene oxide) (PEO-N_3), was first synthesized and reacted with the trifunctional propargyl 2-hydroxyl-methyl-2-(α-bromoisobutyraloxymethyl)-propionate (PHBP), to generate a PEO macroinitiator (Scheme 7.36). The cycloaddition reaction of PEO-N_3 and PHBP was carried out using the CuBr/PMDETA catalyst at room temperature. It was found that 3.5 h was enough for completion of the reaction. Longer reaction times resulted in radical coupling between the PEO chains. The macroinitiator consisted of two functional groups, a hydroxyl group and an α-bromoisobutyryloxy group. Consecutive ATRP of styrene and

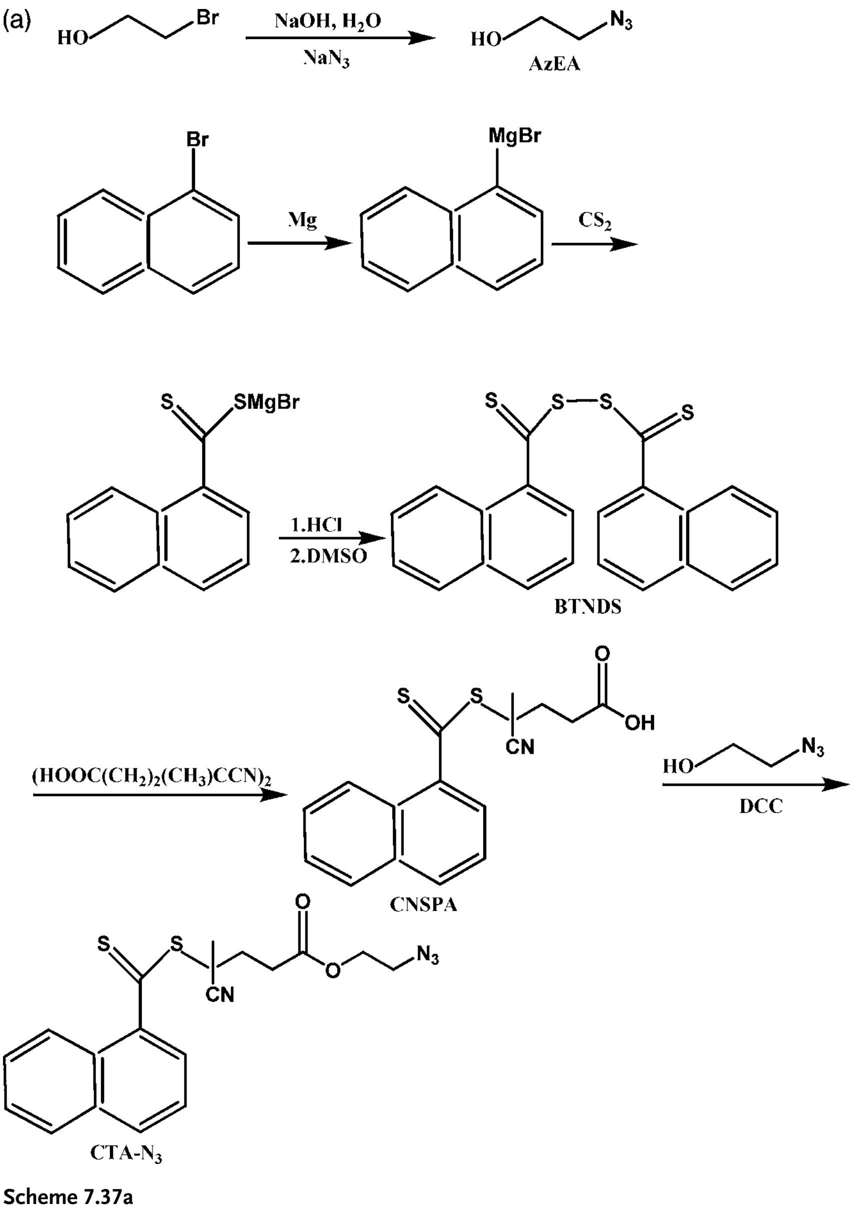


Scheme 7.36

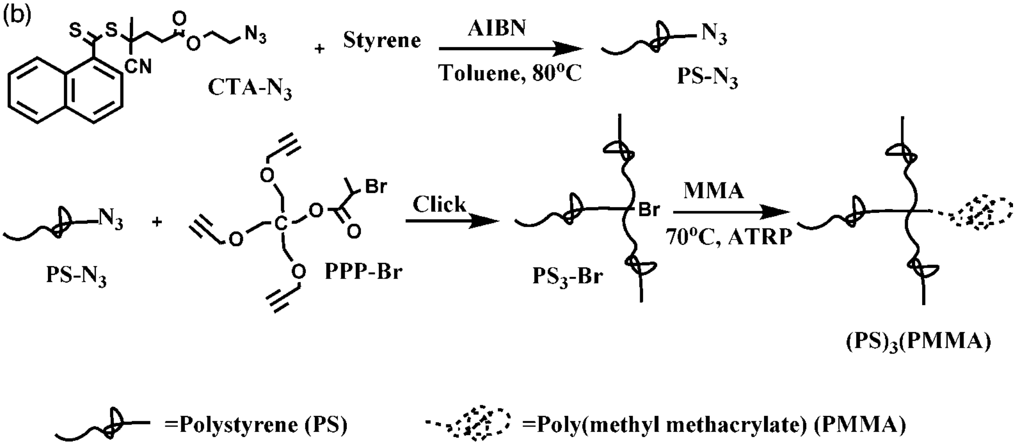
ROP of ε-CL from the PEO macroinitiator produced an ABC three-miktoram star terpolymer with narrow MW distribution.

Kang *et al.* [100] reported an alternative approach for the synthesis of a four-miktoarm star copolymer $(PS)_3PMMA$ by combination of controlled radical polymerizations and "click" chemistry. An azide-functionalized dithioester chain transfer agent ($CTA\text{-}N_3$) was first synthesized, according to Scheme 7.37a. $CTA\text{-}N_3$ was then used to RAFT polymerize styrene to afford $PS\text{-}N_3$. A three-arm star PS was then prepared via "click" reaction with a bromide-containing trialkyne coupling agent, followed by ATRP of MMA to afford the final four-miktoarm star copolymer (Scheme 7.37b).

Tunca *et al.* [101] published a series of papers dealing with the synthesis of three-miktoarm star terpolymers using combination of "click" chemistry and a MFI containing alkyne TEMPO and *tert*-bromide groups (Scheme 7.38). MMA was polymerized first by ATRP (CuCl/PMDETA as catalyst/ligand in toluene, at 60 °C) followed by the nitroxide-mediated polymerization NMP of styrene at 125 °C. Finally, PMMA-*b*-PS with alkyne functionality at the junction point and an azide end-functionalized P*t*BuA (or PEG-N_3) were "clicked" in the presence of CuBr/PMDETA in DMF at room temperature for 24 h to afford the ABC miktoarm star terpolymer.



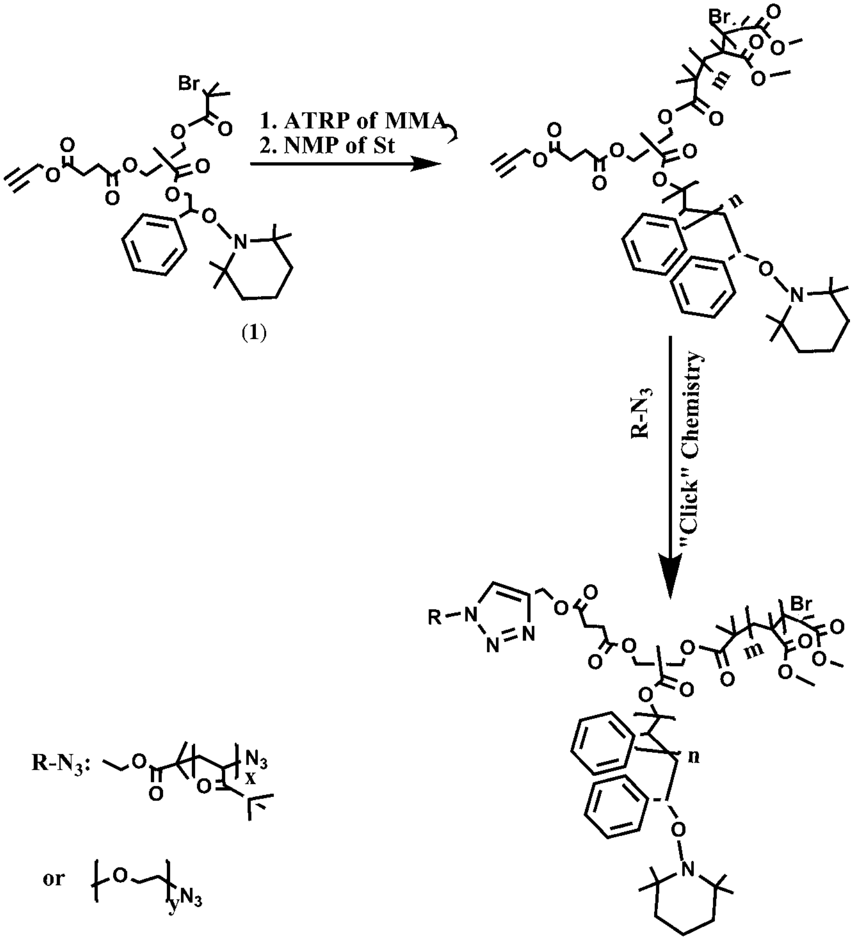
Scheme 7.37a



Scheme 7.37b

The same authors [102] utilized two different one-pot methods for the synthesis of ABC miktoarm star terpolymers. In the first (one-pot/one-step) method (Scheme 7.39), NMP of styrene, ROP of ε-CL, and "click" reaction between PMMA-N_3 or PEG-N_3 and the alkyne group of an MFI (TEMPO, alkyne and hydroxyl groups) were simultaneously carried out for 48 h at 125 °C. In the second (one-pot/two-steps) method, NMP of styrene and ROP of ε-CL were conducted, using the same MFI for 20 h at 125 °C, followed by "clicking" the product with PEG-N_3. In both techniques, the miktoarm star terpolymers were recovered by a simple precipitation in methanol without further purification. The second method resulted in lower polydispersity (~1.1) compared to the first one (~1.3).

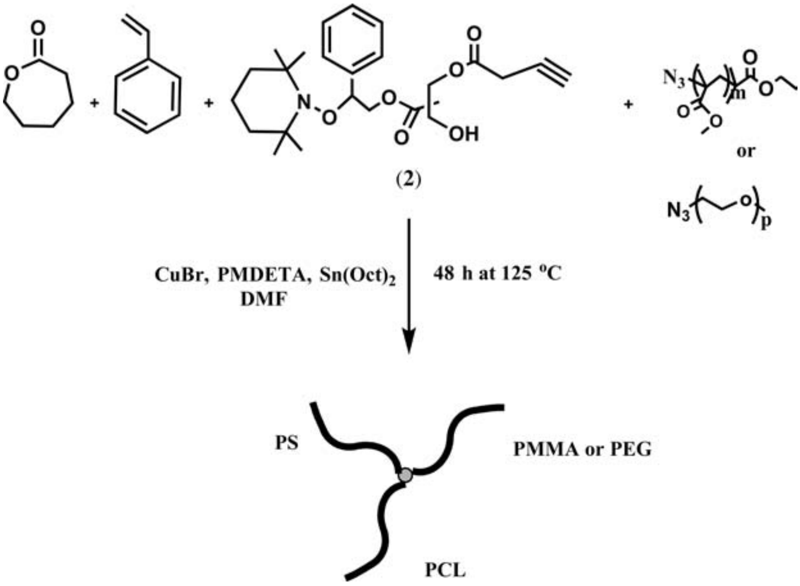
Tunca *et al.* also synthesized a four-miktoarm star quaterpolymer ABCD [103] by "clicking" two diblock copolymers having at the junction point either an alkyne or an azide group (Schemes 7.40a–c). An initiator containing TEMPO and hydroxyl groups **1** was used for the NMP of styrene and ROP of ε-CL at 120 °C (one-pot method) to give PS-*b*-PCL copolymer with bromine functionality at the junction point (Scheme 7.40a). The bromine at the junction point of PS-*b*-PCL was converted quantitatively into azide, using NaN_3 in DMF at room temperature, to afford the N_3 in-chain block copolymer. PEG macroinitiator was prepared via the condensation reaction of PEG-COOH and **2** in the presence of dimethylaminopyridine (DMAP)/dicyclohexylcarbodiimide (DCC) catalysts in CH_2Cl_2 at room temperature, followed by ATRP of MMA to afford the alkyne-in chain PEG-*b*-PMMA (Scheme 7.40b). The separately prepared N_3- and alkyne in-chain PS-*b*-PCL and PEG-*b*-PMMA copolymers were "clicked" (Scheme 7.40c) using CuBr/PMDETA in DMF at room temperature for 48 h to give the four-miktoarm star quaterpolymer (yield: 88%, $M_w/M_n = 1.22$).



Scheme 7.38

7.3
Comb Polymers

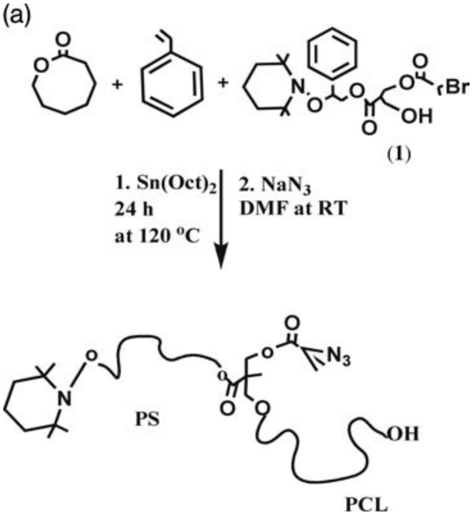
Comb polymers are composed of a main polymer chain, the backbone to which one or more side chains, the branches, are connected through covalent bonds. Comb polymers are homopolymers, i.e., both the backbone and the branches are of the same chemical nature, while graft polymers are composed of chemically different backbone and branches. The branches are usually randomly distributed along the backbone, because of the specific synthetic techniques used. However, more elaborate recent methods have allowed the synthesis of exact comb polymers, where all the molecular and structural parameters can be accurately controlled.



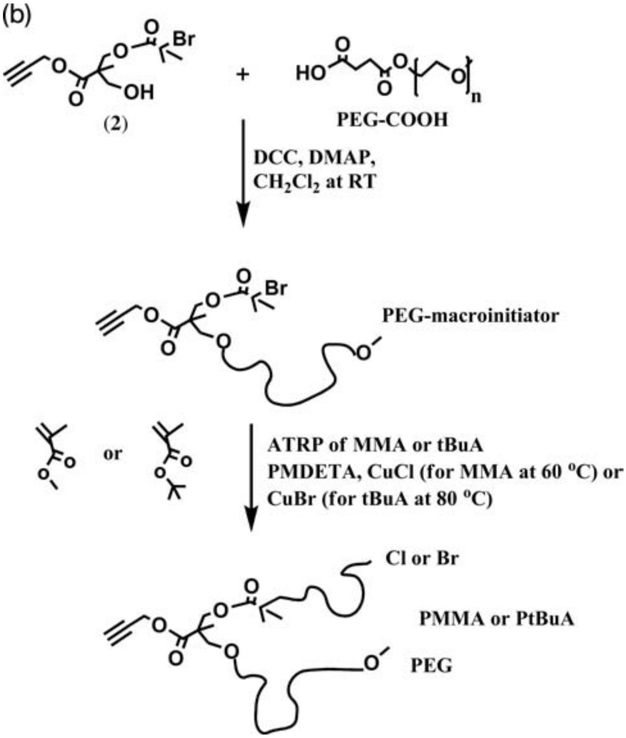
Scheme 7.39

Three general methods have been developed for the synthesis of randomly branched comb polymers: (i) the ''grafting onto,'' (ii) the ''grafting from,'' and (iii) the ''grafting through'' or macromonomer method (Scheme 7.41) [104].

The ''grafting onto'' method involves the use of a backbone chain containing functional groups X randomly distributed along the chain and branches having



Scheme 7.40a



Scheme 7.40b

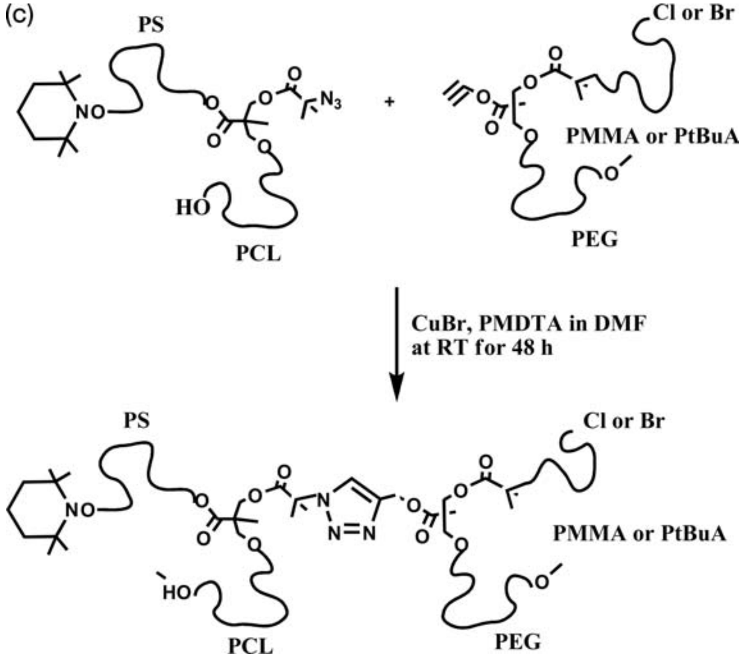
reactive chain ends Y. The coupling reaction between the functional backbone and the end-reactive branches leads to the formation of comb polymers.

In the "grafting from" method active sites are generated randomly along the backbone. These sites are capable of initiating the polymerization of a second monomer, leading to the synthesis of comb polymers.

The most commonly used method for the synthesis of comb polymers is the "grafting through" or macromonomer method [105]. Macromonomer is an oligomeric or polymeric chain bearing a polymerizable end group. Macromonomers having two polymerizable end groups have also been reported [106]. Copolymerization of preformed macromonomers with the same monomer used to construct the macromonomer yields comb polymers.

7.3.1
"Grafting Onto" Methods

One of the methods widely used for the synthesis of comb polymers is the "grafting onto" method, i.e., reaction of preformed polymeric chains having functional groups, with other polymeric chains having active chain



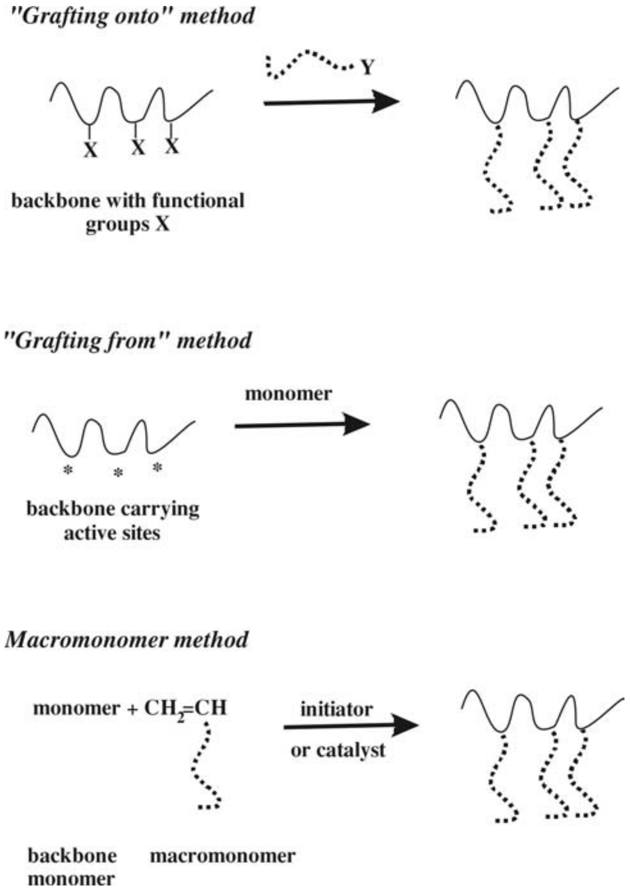
Scheme 7.40c

ends. In most cases, the incorporation of functional groups is performed by chemical modification of the backbone. Characterization of the backbone and the preformed side chains can be performed separately from the comb polymer, thus allowing for the detailed characterization of the final structure.

For example, anionically prepared linear PI was subjected to partial epoxidation, employing a suitable organic peracid, to introduce randomly grafting sites along the polymer chain. The epoxidized polymers were subsequently reacted with living polyisoprenyllithium to afford comb-branched PIs (Scheme 7.42) [107].

7.3.2
"Grafting from" Methods

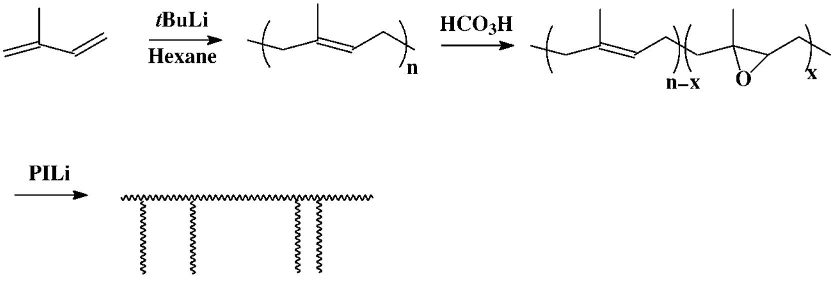
In the "grafting from" method, the backbone is chemically modified to introduce active sites capable of initiating the polymerization of a second monomer. The number of grafted chains can be controlled by the number of active sites generated along the backbone, assuming that each one participates in the formation of one branch. Full structural characterization of the products obtained from a grafting from scheme is very difficult since neither the exact



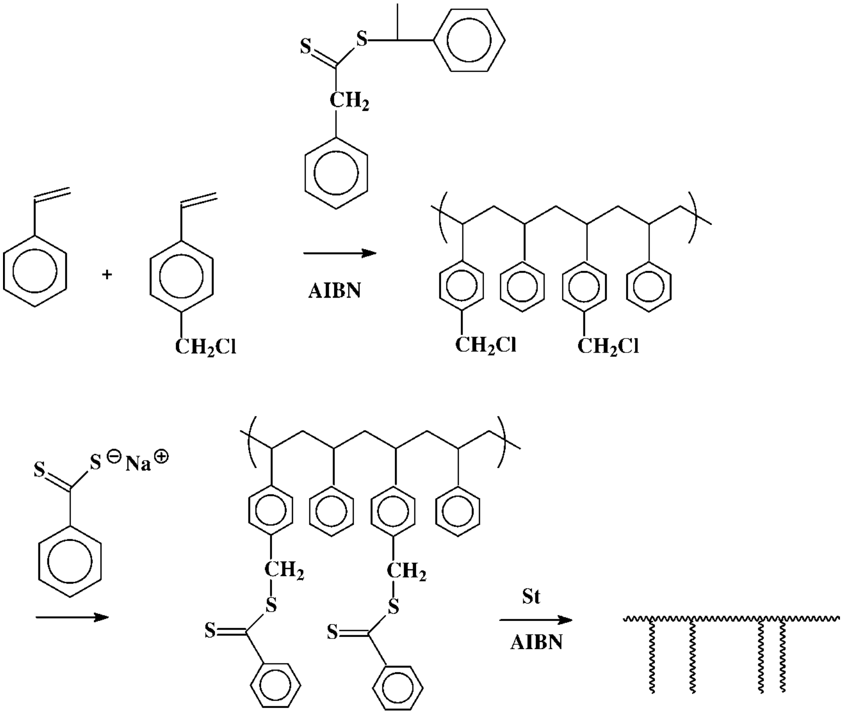
Scheme 7.41

number of side chains added nor their MW can be determined. Additionally, in the case of ionic copolymerization reactions, solubility may be a concern for highly charged macroinitiators, frequently leading to poorly controlled heterogeneous products.

For example, RAFT polymerization was employed for the synthesis of PS combs [108]. The reaction sequence involves the copolymerization of styrene and vinylbenzyl chloride (VBC) in the presence of AIBN and 1-phenylethyl phenyldithioacetate as initiator and chain transfer agent, respectively. The benzylic chloride groups were then reacted with sodium dithiobenzoate to afford PS chains bearing dithiobenzoate pendant groups. Subsequent addition of styrene and AIBN leads to the synthesis of PS combs, since the dithiobenzoate moieties serve as chain transfer agents (Scheme 7.43). The SEC traces were multimodal, indicating the existence of high molecular and structural heterogeneity of the combs.



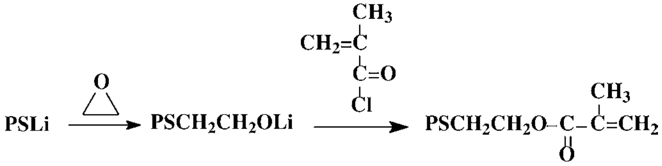
Scheme 7.42



Scheme 7.43

7.3.3
"Grafting Through" or Macromonomer Method

The homopolymerization of macromonomers affords comb-shaped structures, polymacromonomers, or molecular brushes, with an extremely high density of branching, since each monomeric unit bears a polymeric chain as a side group [109]. Depending on graft length and degree of polymerization,



Scheme 7.44

the polymacromonomers may adopt several conformations in solution, such as starlike, comblike, bottlebrush, or flowerlike. The copolymerization of the macromonomers with another conventional monomer results in the formation of comb polymers.

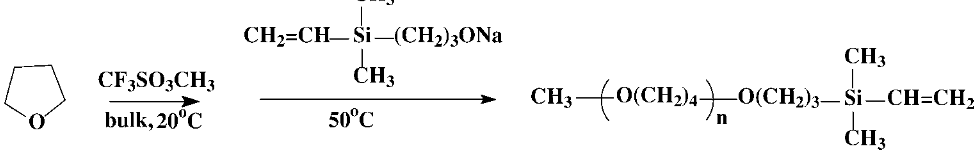
The synthesis of macromonomers can be accomplished by almost all the available polymerization techniques. Among them, living polymerization methods offer unique control over the MW, the MW distribution, and chain-end functionalization.

Anionic polymerization is one of the best methods for the synthesis of well-defined macromonomers. Functional initiation or termination by suitable electrophilic reagent is the best ways for the incorporation of the reactive end groups [110]. According to this methodology, living polystyryllithium was initially reacted with ethylene oxide to form the less reactive alkoxide followed by the reaction with methacryloyl chloride for the synthesis of the macromonomer (Scheme 7.44) [111].

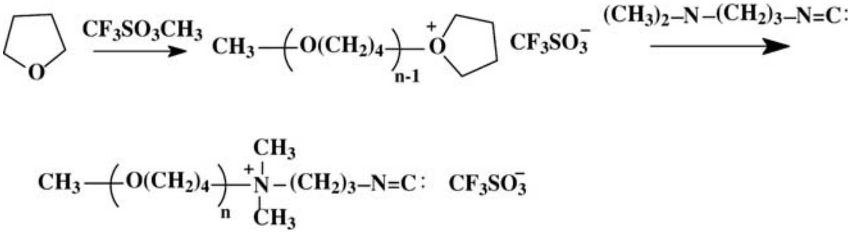
Cationic polymerization has also been used for the synthesis of macromonomers, especially after the development of living cationic polymerization techniques [112]. Macromonomers were prepared by the cationic ROP of THF using methyltrifluoromethane sulfonate followed by termination with 3-sodio-propyloxydimethylvinylsilane to give a macromonomer with vinyl silane end groups (Scheme 7.45) [113].

Termination of living polytetrahydrofuran (PTHF) with 3-(dimethylamino propyl) isocyanide leads to the formation of macromonomers having end isocyanide groups (Scheme 7.46) [114].

Free radical polymerization has been the most common technique for the synthesis of macromonomers, due to the facts that it is not a very demanding experimental method, there is no need for special purification of the reagents, and it is applicable to a wide variety of monomers. However, the method



Scheme 7.45



Scheme 7.46

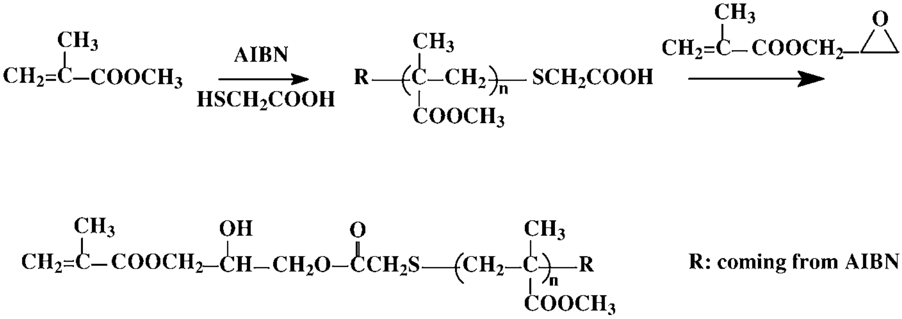
suffers from many disadvantages such as the poor control over the MW, the MW distribution, and the degree of functionalization. The basic method for the incorporation of the functional end groups involves the use of chain transfer agents [115].

PMMA macromonomers have been prepared using thioglycolic acid as a chain transfer agent, followed by reaction with glycidyl methacrylate (Scheme 7.47) [116].

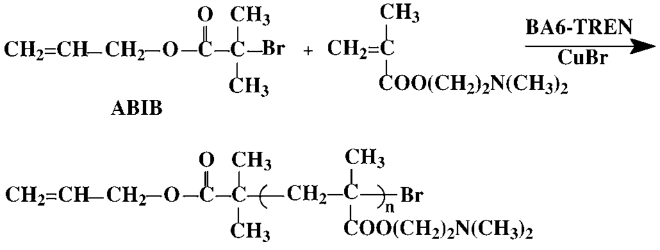
The evolution of the living/controlled radical polymerization techniques (mainly NMP and ATRP methods) very soon led to the synthesis of a wide range of macromonomers. These methods combine the advantages of the free radical polymerization with those of the living polymerization techniques, despite the fact that the control over the functionalization reaction is not always comparable to the anionic polymerization methods [117, 118].

Poly(dimethylaminoethyl methacrylate) macromonomers were prepared by ATRP using allyl 2-bromoisobutyrate (ABIB)/CuBr/tris[2-di(butyl acrylate) aminoethyl] amine (BA6-TREN) or allyltrichloroacetamide/CuBr/BA6-TREN as the initiation systems (Scheme 7.48) [119].

Group transfer polymerization has also been used for the synthesis of macromonomers. The functional end groups are incorporated mainly using the suitable initiation system [120]. Trimethylsilyloxy ethyltrimethylsilyl dimethyl ketene was used as initiator for the synthesis of PMMA macromonomers in the



Scheme 7.47

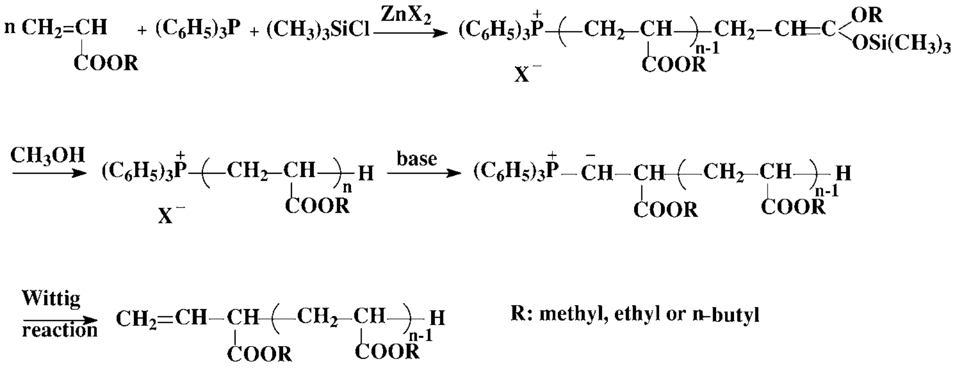


Scheme 7.48

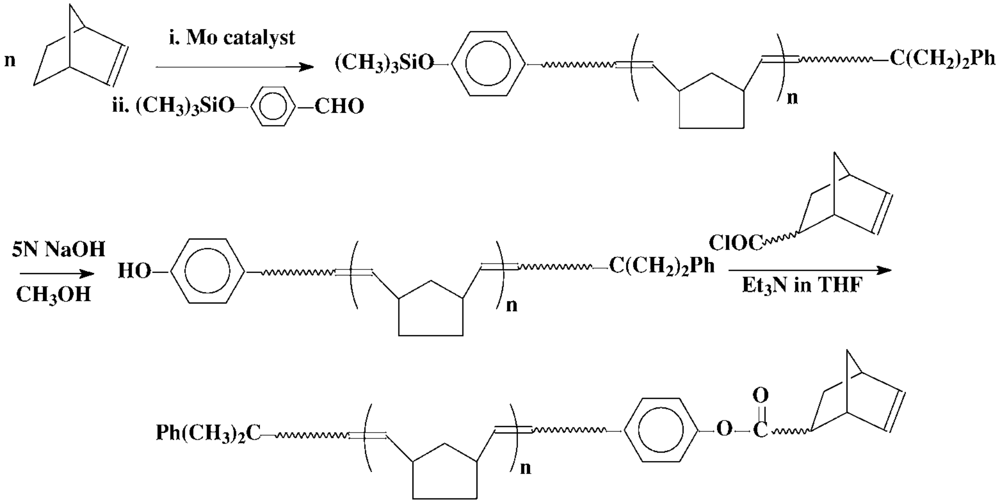
presence of tetrabutylammonium benzoate, which was the catalyst. Treatment with dilute HCl provided the –OH functional macromonomers, which was followed by the reaction with acryloyl chloride to give the final macromonomer structure (Scheme 7.49) [121].

ROMP was employed for the synthesis of polynorbornene macromonomers. A well-defined molybdenum initiator of the type $\mathrm{Mo(CHCMe_2Ph)}$(N-2,6-$^{i}\mathrm{Pr_2C_6H_3}$)$\mathrm{(OR)_2}$, [R=$\mathrm{OCMe_3}$, $\mathrm{OCMe(CF_3)_2}$] was used. The polymers produced were cleaved from the initiator fragment in a Wittig-like reaction using p-$\mathrm{(CH_3)_3SiC_6H_4CHO}$, according to a well-established method. Deprotection under basic conditions gave macromonomers having phenyl end groups. Subsequent reaction with norbornene carboxylic acid chloride yields macromonomers with norbornene end groups (Scheme 7.50) [122].

One of the most widely used methods for the synthesis of comb polymers involves the use of macromonomers, through their copolymerization with the same monomer used to construct the macromonomer [123]. The method offers several advantages for the synthesis of well-defined combs: (i) all the possible polymerization techniques can be employed; (ii) the chain length of the side chains can be controlled by the synthesis of the macromonomers; (iii) the backbone length can be also controlled when a living polymerization method



Scheme 7.49



Scheme 7.50

is used for the copolymerization reaction; and (iv) the number of side chains per backbone can be controlled by the molar ratio of the macromonomer and the comonomer and by the reactivity ratios of the copolymerization system. However, there are several limitations that characterize the macromonomer method for the synthesis of combs. The most important is the lack of control over the spacing of the branches along the backbone. The spacing distribution is determined by the reactivity ratios of the macromonomer and the comonomer. The most important factors affecting the reactivity of the macromonomers are the following: (i) the chemical nature of the polymerizable end group, (ii) the MW of the macromonomer, and (iii) the conversion of the homo- or copolymerization. Among these parameters, the most important is without doubt the nature of the polymerizable end group. According to this statement, the reactivity of the macromonomer is identical to the reactivity of the corresponding low MW monomer. However, this is not always true, because of the increased importance of the above-mentioned parameters. It is well known that interactions between polymer chains are generally repulsive due to excluded volume effects. Consequently, the reactivity of the macromonomer is dramatically reduced during the polymerization upon increasing its MW. In this case, the excluded volume effects prevent the approach of the active center of the growing polymer chain to the polymerizable end group of the macromonomer. Since the above factors reduce the reactivity of the macromonomers, it can be concluded that during the copolymerization with a conventional monomer the comb structure will be very poor in branches at the initial stages of the copolymerization (high reactivity of the comonomer), whereas at the later stages of the copolymerization the structure will be richer in branches (excess of the unreacted macromonomers over the low

MW monomer). Therefore, in most cases, the final product will have a heterogeneous distribution of branches along the backbone.

All the available polymerization techniques can be employed for the synthesis of combs by the macromonomer method. The most common method is the free radical polymerization. The advantages and the drawbacks of the technique also apply in this case. The relative experimental simplicity, the lack of the need to perform exhaustive purifications of the monomers, solvents, etc., the application to an enormous number of macromonomers and monomers, and the possibility to expand the method to an industrial scale production of combs are the major advantages. However, the method suffers several drawbacks, such as the lack of control over the MW of the backbone and the increased polydispersity, as well as the chemical and compositional heterogeneity of the final products.

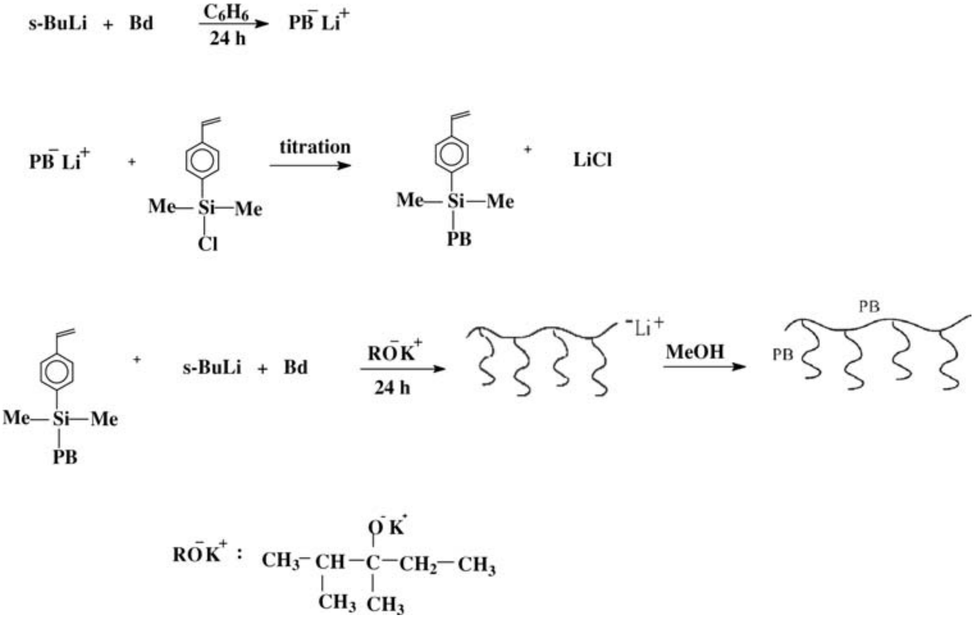
Although free radical polymerization has been the most widely used method for the synthesis of combs by the macromonomer method, the living polymerization techniques offer unique opportunities to control the molecular and structural characteristics of the structures. However, the superior behavior of the living polymerization methods is overbalanced to some extent by the demanding experimental effort needed to perform these kinds of reactions and the relatively small number of monomers that are susceptible to these polymerization reactions.

Among the living polymerization methods, anionic polymerization has been shown to be the most efficient method for the synthesis of complex macromolecular architectures. However, owing to the time-consuming and demanding experimental procedures [124] that are necessary to achieve truly living conditions, the method has not been broadly used for the synthesis of graft copolymers by the macromonomer method.

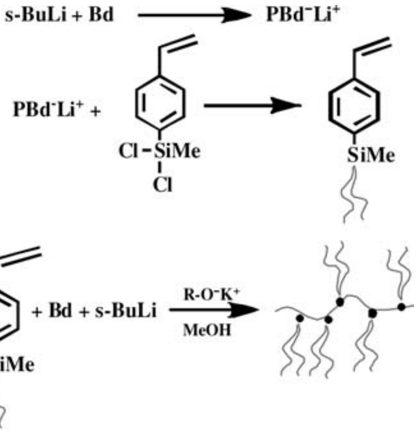
Stereoregular combs were prepared by copolymerization of stereoregular PMMA macromonomers (isotactic or syndiotactic) with MMA using *t*-BuMgBr in toluene at −78 °C or diphenylhexyllithium (DPHLi) in THF at −78 °C [125].

Well-defined PBd combs were prepared by Hadjichristidis *et al.* [126]. Living PBdLi chains were reacted with 4-(chlorodimethylsilyl)styrene (CDMSS) to afford the styrenic macromonomer. The efficiency of this approach relies on the much higher reactivity of the living polymer toward the chlorosilane group rather than the styrenic double bond. Subsequent copolymerization of the macromonomers with butadienes leads to the synthesis of PBd combs. To achieve the random placement of the branches along the backbone, the copolymerization was performed in the presence of potassium alkoxide of 2,3-dimethyl-3-pentanol, which equalizes the reactivity ratios of the styrenic macromonomers and butadiene (Scheme 7.51).

4-(Dichloromethylsilyl)styrene was also employed for the synthesis of double-tailed styrenic-tipped macromonomers (Scheme 7.52). The macromonomers were either copolymerized with Bd in the presence of potassium alkoxide of 2,3-dimethyl-3-pentanol, or homopolymerized to afford double-comb PBds or double macromolecular brushes, respectively [127]. The single or double-tailed



Scheme 7.51



Scheme 7.52

macromonomers were prepared and polymerized *in situ* without isolation and purification, thus avoiding the introduction of impurities and leading to well-defined products.

ATRP has emerged as an important method for the synthesis of a variety of complex architectures with controlled molecular characteristics and much less pronounced chemical and compositional heterogeneity than the conventional free radical polymerization [128]. Therefore, a growing interest exists for the synthesis of combs using this method for the copolymerization of the macromonomers with other comonomers. PMMA macromonomers having methacryloyl end groups were copolymerized with MMA by ATRP to produce the corresponding combs [129]. Comparison with the conventional free radical copolymerization revealed that the reactivity of the PMMA macromonomer in ATRP is much higher, probably due to the different timescale of monomer addition in both processes. The free radicals exist for a few milliseconds, whereas the active radical species in ATRP may exist for several seconds, thus having the opportunity to react with the growing polymer chain.

Coordination polymerization using suitable catalytic systems offers the unique advantage to control polymer chain stereochemistry [130]. Furthermore, it can be applied on an industrial scale for the synthesis of valuable products. However, this method is not a living polymerization, meaning that there is no control over the MWs, and rather broad MW distributions are observed. Recently, with the use of metallocene catalysts it has been possible to achieve a much better control over the polymerization reaction leading to products of better quality [131].

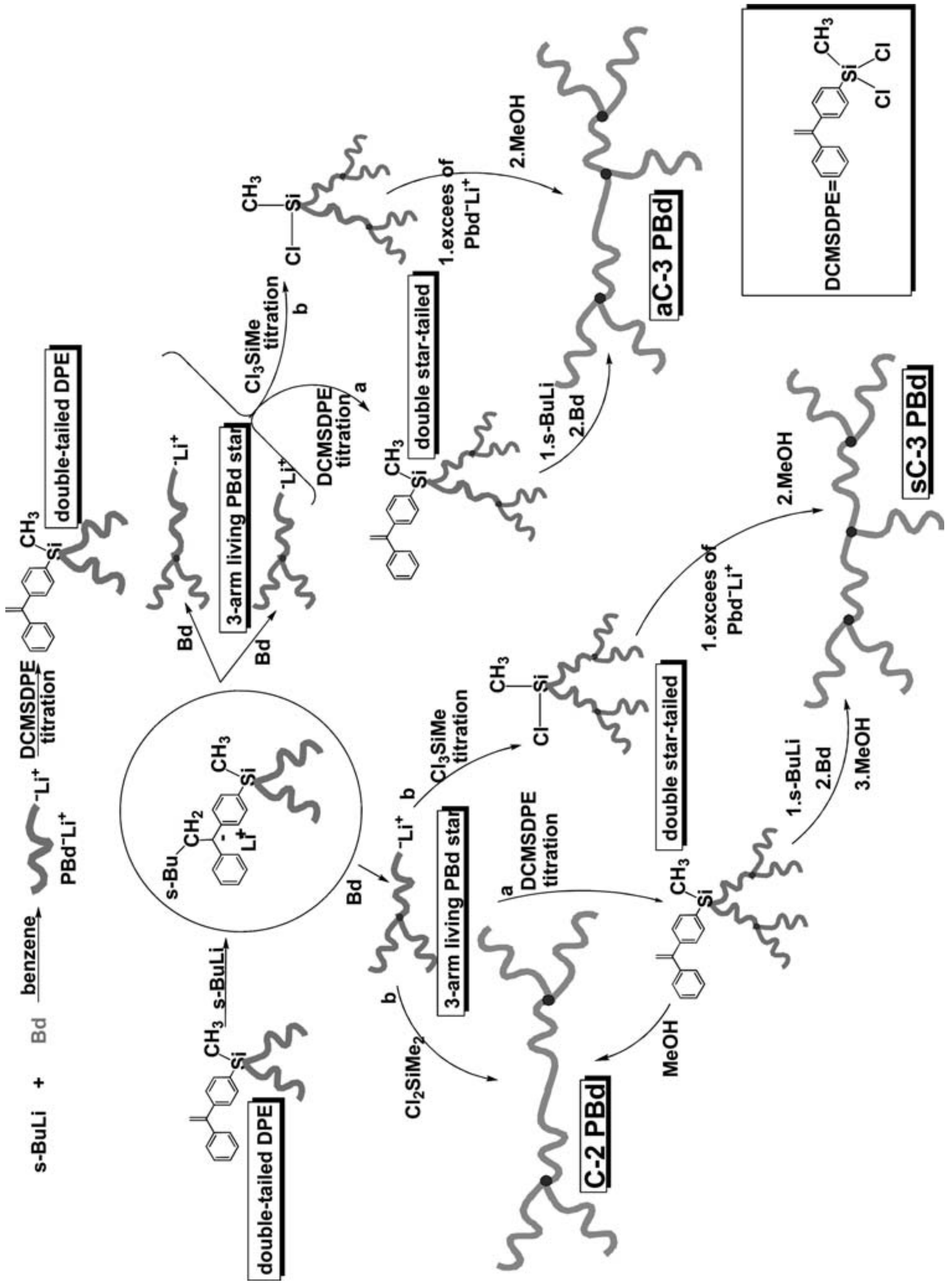
Shiono *et al.* prepared atactic polypropylene (PP) macromonomers through the polymerization of propene with bis(pentamethylcyclopentadienyl) zirconium dichloride/methylaluminoxane (MAO), $Cp_2{}^*\ ZrCl_2$/MAO, and termination by β-hydrogen elimination [132]. The PP macromonomers were copolymerized with propene using *rac*-[Me_2Si(2-Me-Benzind)$_2$]$ZrCl_2$/MAO as the catalytic system to produce atactic PP-*g*-isotactic PP stereo-comb polymers.

The macromonomer method was also employed by Endo *et al.* to prepare syndiotactic PS-*g*-atactic PS stereo-combs [133]. Anionic polymerization was used to prepare vinylbenzyl-terminated PS macromonomers, which were subsequently copolymerized with styrene using $CpTiCl_3$/MAO as the catalyst. Low copolymerization yields (<20%) were obtained in this study.

The term *exact graft copolymers* refers to molecules where all the molecular and structural characteristics, such as the MWs of the backbone and the branches, the MW distributions, the number of branches and the specific grafting points on the backbone, can be controlled and varied at will. The parameters that are most difficult to be controlled are the number and the spacing distribution of branches along the backbone chain.

Exact comb PS polymers of the "H" shape have been prepared by anionic polymerization techniques and controlled chlorosilane chemistry [134].

Two methodologies, based on living star polymers and anionic polymerization high vacuum techniques, were used for the synthesis of exact comb PBds with two (C-2 or H-type) and three identical branches (symmetric, sC-3, H-type with an extra identical branch at the middle of the connector; and asymmetric, aC-3, H-type with the extra identical branch at any other position along the connector) (Scheme 7.53) [135]. The first methodology involves (i) the selective


s-BuLi + Bd
benzene
PBd⁻Li⁺
DCMSDPE titration
double-tailed DPE
CH3
Si
s-BuLi
s-Bu
CH2
Li+
Bd
3-arm living PBd star
⁻Li⁺
Cl3SiMe titration
DCMSDPE titration
a
b
Cl
double star-tailed
1.s-BuLi
2.Bd
3.MeOH
1.exceess of Pbd⁻Li⁺
2.MeOH
aC-3 PBd
sC-3 PBd
Cl2SiMe2
MeOH
C-2 PBd
DCMSDPE=

Scheme 7.53

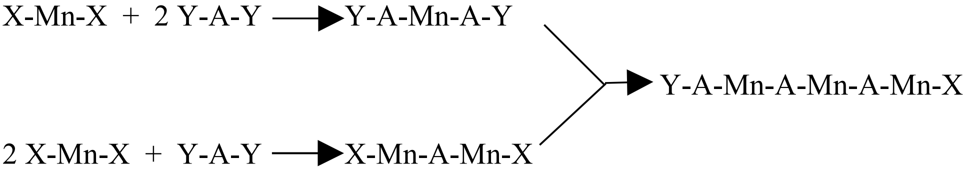
replacement of the two chlorines of 4-(dichloromethylsilyl)diphenylethylene (DCMSDPE, key molecule) with three-arm star PBds, by titration with identical (C-2, sC-3) or different (aC-3) living three-arm star PBds, (ii) the addition of *s*-BuLi to the double bond of DPE, and (iii) the polymerization of butadiene from the newly created anionic site (sC-3, aC-3).The second methodology involves the reaction of living stars with dichlorodimethylsilane (C-2) or the selective replacement of the three chlorines of trichloromethylsilane with star and linear chains (sC-3, aC-3). Intermediate and final products were characterized via SEC, LALLS, and ^{1}H NMR. The first methodology does not require fractionation, but in contrast to the second methodology cannot afford polymers with branches of identical MW. Both methods are general and can be extended to combs with two or three different branches at controllable positions along the backbone.

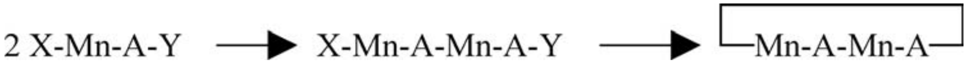
7.4
Cyclic Polymers

The first attempts to synthesize cyclic polymers involved ring–open chain equilibrium based on backbiting reactions of poly(dimethylsiloxanes) [136]. However, this method was limited to low MW and polydisperse cyclic polymers and is characterized by the inability to isolate the corresponding linear precursor to prove the cyclic structure by comparing the properties. Now, living polymerization processes leading to narrow MW distribution polymers are generally preferred. The linear precursor of the cyclic polymer had either two identical or two different functional groups capable of reacting with each other. In the first case, an α,ω-homodifunctional macromolecule was synthesized first, followed by the reaction with an appropriate difunctional LA. In the second case, an α,ω-heterodifunctional macromolecule was prepared using a functional protected initiator and by neutralizing the living site with the appropriate LA containing another protected group. The cyclic structure is formed by the coupling reaction of the two reactive groups.

The first case is shown below schematically:

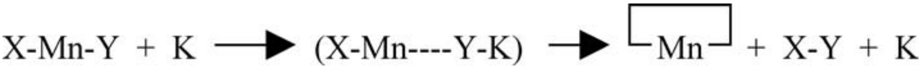
In addition to the intramolecular reaction, several intermolecular reactions can occur:





These reactions lead to undesirable high MW polycondensates, either linear or cyclic, and which should be removed from the low MW desirable cyclic product.

In the second case the cyclization requires an activation step:



This synthetic approach presents several advantages, e.g., an exact stoichiometry of addition of the two reagents is not required, since the two reactive groups are in the same molecule and only a catalytic amount of the activator K is necessary. In both cases, the possibility of intramolecular versus intermolecular reaction depends on their effective concentration. The probability of intramolecular reaction, i.e., of finding the ω-end of a chain within a small reaction volume v_e close to the α-end is given by

$$P_\mathrm{i} = (3/2\pi)^{3/2} v_\mathrm{e} / \langle r^2 \rangle^{3/2}$$

where $< r^2 >^{3/2}$ is the mean square end-to-end distance of the chain in the reaction medium. The probability of the intermolecular reaction, i.e., of finding the chain end of another molecule is given by

$$P_\mathrm{e} = (N_\mathrm{A} c/M) v_\mathrm{e}$$

where N_A is Avogadro's number, c the concentration of the polymer, and M the molecular weight. The concentration at which the intra- and intermolecular reaction are equally like is given by

$$c_{\mathrm{equal}} = \left[(3/2\pi)\langle r^2\rangle\right]^{3/2} M/N_{\mathrm{A}}$$

This equation shows that (i) the more dilute the polymer solution, the more probable is the cyclization over the polycondensation and (ii) at the same MW, the doubled concentration (higher yield) can be used for heterodifunctional compared to homodifunctional polymers. The practical strategies used for the preparation of cyclic copolymers will be presented below.

7.4.1
Cyclic Polymers from Precursors with Homodifunctional Groups

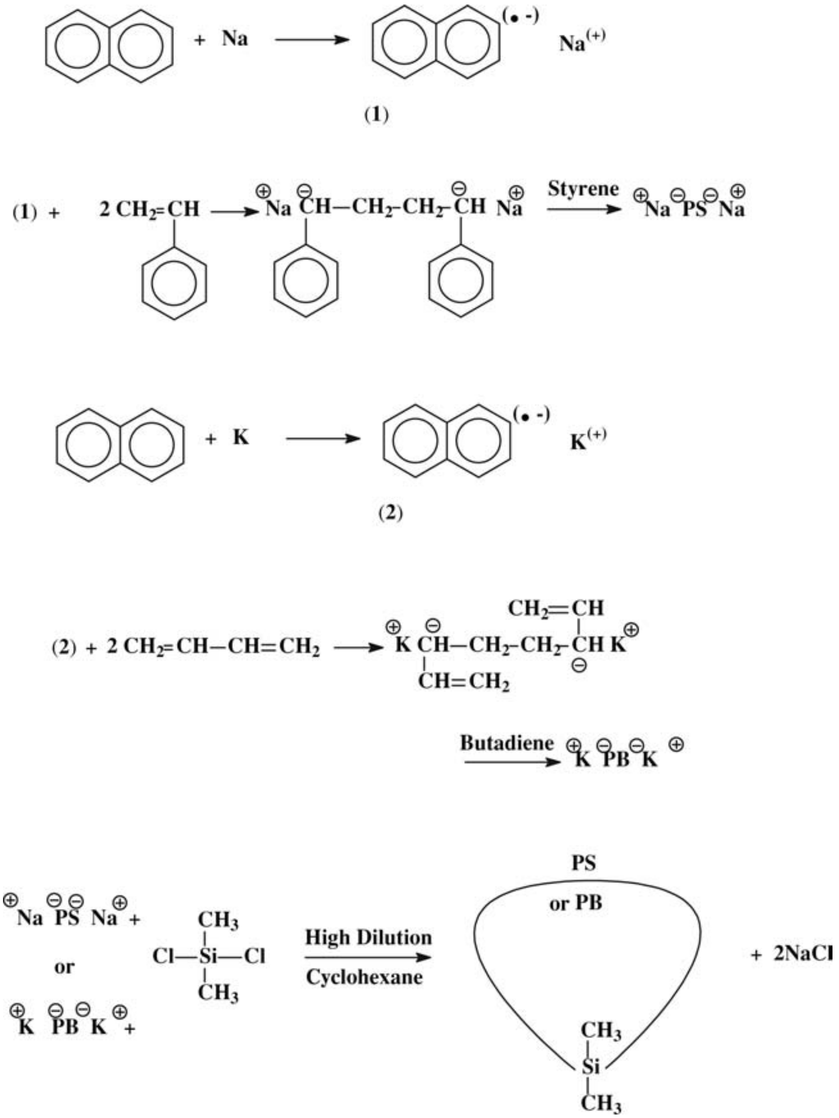
Many different LAs and functional groups have been proposed for the synthesis of cyclic polymers when using homodifunctional groups. However, the general strategy followed by most authors is similar and can be outlined as follows:

1. preparation of a monodisperse α-ω homodifunctional living polymer;
2. reaction of the living polymer with a homodifunctional LA;
3. fractionation for purification of the cyclic polymer.

In all cases, a high dilution of the linking reaction was used to increase the yield of cyclization.

7.4.2
Cyclic Homopolymers

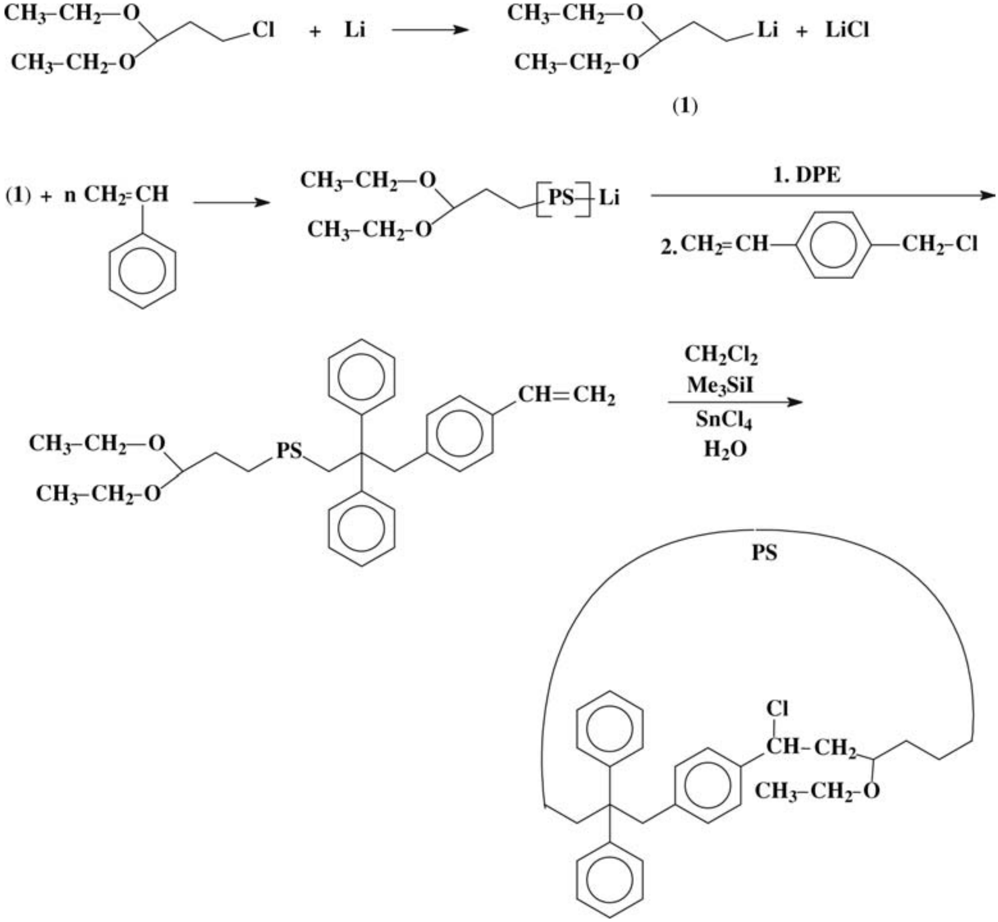
Roovers *et al.* [137] synthesized cyclic PS under high vacuum conditions using naphthalene sodium as a difunctional initiator. The polymerization solvent was a mixture of THF and benzene in a ratio of 1 : 1 (v/v). The LA was dichlorodimethylsilane, and the linking reaction was performed in cyclohexane at room temperature, close to theta conditions for PS. Roovers synthesized a series of cyclic PSs with MWs from 2.0 to 55×10^4 g mol^{-1}. The separation of the cyclic from the linear precursor was achieved by ultracentrifugation. The $g' = [\eta]_{\mathrm{r}}/[\eta]_{\mathrm{l}}$ values, where $[\eta]_{\mathrm{r}}$ and $[\eta]_{\mathrm{l}}$ are the intrinsic viscosities of the cyclic and the corresponding linear polymer respectively, varied from 0.58 to 0.68, in good agreement with the theoretically and experimentally reported values. A few years later and using the same experimental procedures, the same group prepared cyclic PBds [138] (Scheme 7.54). THF was the polymerization solvent, resulting in a 60% of 1,2 content. From the g' values, it was concluded



Scheme 7.54

that some of the cyclic PBds were contaminated by their linear precursors [139].

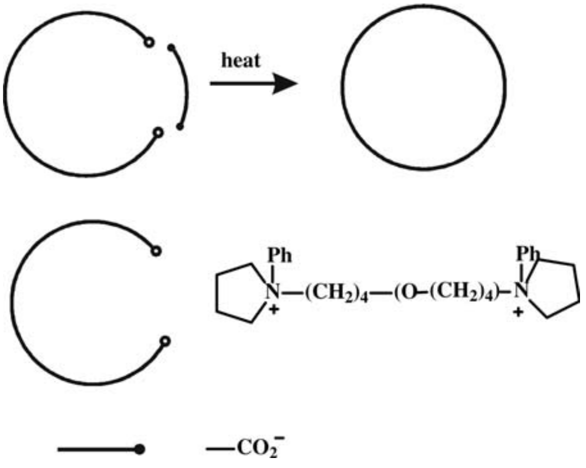
Deffieux was one of the first to use precursors with α,ω-heterodifunctional reactive groups. With his collaborators [140] he synthesized α-acetal-functionalized linear PS by using 3-lithiopropionaldehyde diethylacetal as initiator. After polymerization, the living anion was reacted first with DPE



Scheme 7.55

and then with *p*-chloromethylstyrene. The acetal group of the initiator was converted into the α-iodo ether group with trimethylsilyliodide. The cyclization was performed as shown in Scheme 7.55. The yield was between 80 and 85%. The MW range of the cyclics prepared was between 2000 and 6700. The presence of 10% linear precursor in the final product was detected by NMR spectroscopy.

A novel methodology has been utilized by Tezuka [141] for the synthesis of various nonlinear polymer topologies with high efficiency, by exploiting the self-assembly principle to preorganize linear polymer precursors and subsequently convert them into covalently linked structures. Tezuka used self-assembly through coulombic interactions of hydrophobic macromolecules, bearing moderately strained cyclic onium salt end groups, with multifunctional low MW molecules bearing carboxylate groups as counterions.

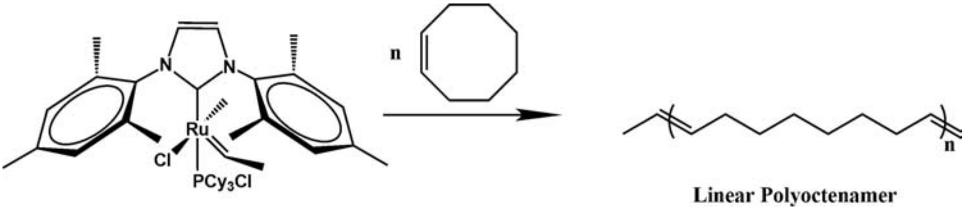


Scheme 7.56

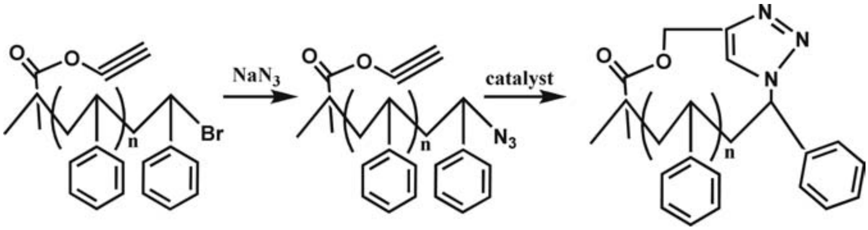
Under high dilution conditions, the aggregates were subjected to heat to convert the ionic interactions into covalent linkages by a ring opening reaction (Scheme 7.56). Using this strategy, poly(THF), PS, and poly(dimethylsiloxane) cyclic homopolymers were synthesized.

A new synthetic route to cyclic polymers was developed by Grubbs [142], in which the ends of growing polymer chains remain attached to a metal complex throughout the entire polymerization process (Scheme 7.57). The approach eliminates the need for linear polymeric precursors and high dilution, which are the drawbacks of traditional macrocyclization strategies, and also removes the barrier to producing large quantities of pure cyclic material. The potential of this strategy was demonstrated by the synthesis of cyclic polyethylenes (PEs), whose physical properties were found to be distinguishable from their linear analogs.

More recently, a novel approach for the synthesis of cyclic copolymers was reported by Matyjaszewski using ‘‘click’’ chemistry [143]. α-Alkyne-ω-azido-terminated PS chains were self-coupled in the presence of CuBr in dimethyl formamide solution at room temperature. Alternatively, α,ω-diazido-terminated PS was ‘‘clicked’’ with dipropargyl ether at room temperature. SEC



Scheme 7.57



Scheme 7.58

analysis revealed the presence of high MW polycondensation products. In addition, low MW materials with smaller hydrodynamic volumes than those of the corresponding linear functionalized precursors were also traced, providing direct evidence for the preparation of cyclic polymers by this procedure.

Grayson *et al.* [144] reported the synthesis of cyclic PS using "click" cyclization coupling (Scheme 7.58). Styrene was polymerized in bulk with the heterofunctional initiator propargyl 2-bromoisobutyrate in the presence of CuBr/PMDETA to produce Br-PS-alkyne. The Br end group was transformed to azide with sodium azide in DMF. For polymer concentrations above 0.1 mM in the presence of Cu(I) as catalyst in THF/water, condensation was favored. Dilution below that concentration favored intramolecular cyclization. The cyclization reaction was successfully carried out on two linear N_3-PS-alkyne with M_n of 2200 and 4200.

7.4.3
Cyclic Block Copolymers

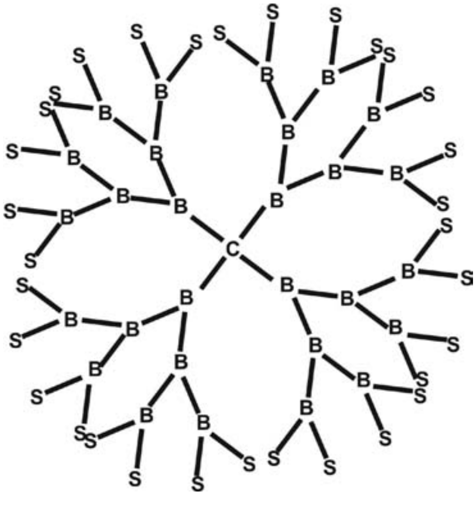
Cyclic block copolymers with blocks that microphase separate in bulk are expected to form only loops at both sides of the interface, while their linear triblock analogs are able to form loops and bridges. This significant difference is expected to give very interesting morphological properties to the cyclic copolymers.

Employing anionic polymerization and high vacuum techniques, Hadjichristidis *et al.* [145] synthesized cyclic block copolymers of PS-d8 and PBd. The synthetic approach involved the reaction of (1,3-phenylene)-bis(3-methyl-1-phenylpentylidene) dilithium initiator with butadiene in the presence of sec-BuOLi, followed by polymerization of St (or St-d_8). The cyclization of the resulting α,ω-difunctional triblock copolymer was performed using bis(dimethylchlorosilyl) ethane under high dilution conditions. The copolymers were characterized by SEC, MO, NMR and UV spectrometry, and viscometry. The micelles formed in the selective solvents *n*-decane (for PBd) and dimethylformamide (for PS-d_8) were characterized by small-angle neutron scattering (SANS) and DLS. It was found that the aggregation number of the cyclic copolymers was the smallest among the different macromolecular architectures. Moreover, the SANS data for the triblocks in *n*-decane indicated the presence of 37% dangling chains, which did not appear in the data for the corresponding cyclic copolymers. Considering that 5% of dangling chains can be detected, the data prove that the cyclic copolymers are at least 87% pure. A scaling model was used to justify the difference in the aggregation numbers between the four different copolymers.

7.5
Dendritic Polymers

The term *dendrimer* was originally coined by Tomalia *et al.* [146] to describe a family of regularly branched poly(amidoamines) (PAMAM) in which all bonds converge to a single point, each repeat unit contains a branch junction, and a large number of identical functional groups are present at the chain ends. The graphical representation of a dendrimer is shown in Scheme 7.59. A central core, or focal point, is connected to a number of layers, or generations of internal building blocks, which are in turn connected to numerous chain ends. The dendritic or dendrimer-like polymers are structurally analogous to regular dendrimers, but contain polymer chains of variable length between each branching unit rather than short spacers. Owing to their unique physical and chemical properties, dendrimers and dendritic polymers have found use in many industrial and academical areas.

For the synthesis of dendrimers and dendritic polymers, two fundamentally different strategies have been employed: the divergent approach (from inside out), and the convergent approach (from the outside in). In either route, dendrimers can be prepared with high regularity and controlled molecular weighs. The main drawback of the divergent approach is that by increasing



Scheme 7.59

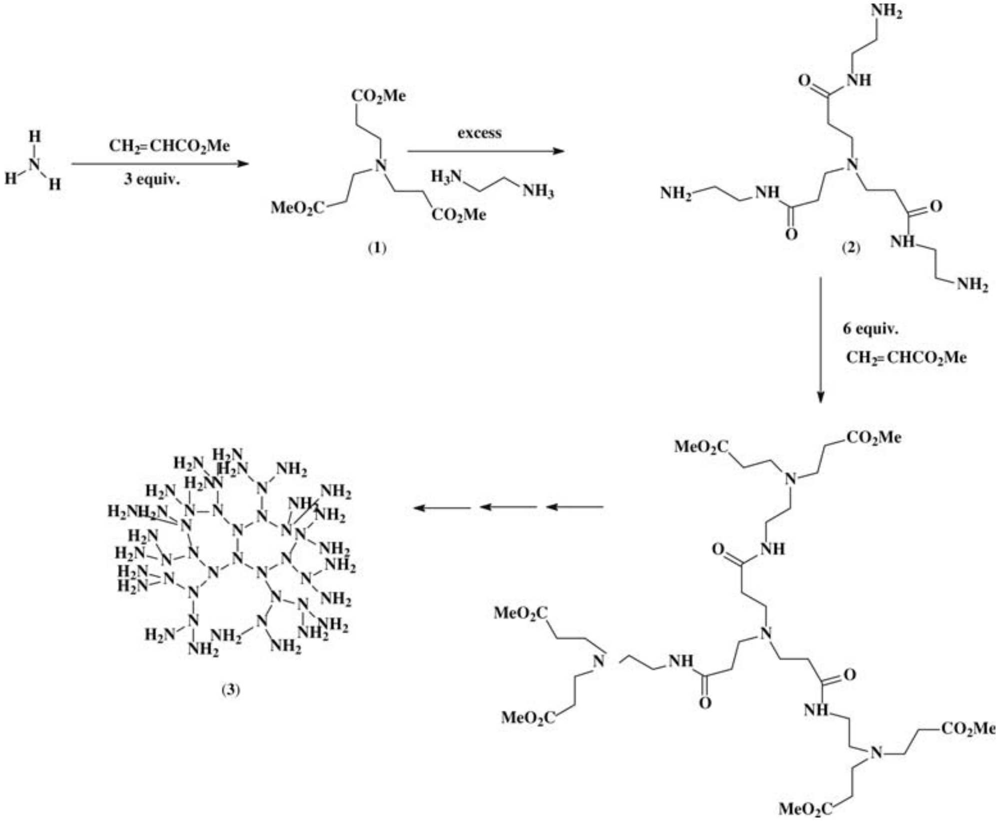
the number of reactions required to fully functionalize the chain ends during the growth of the dendrimers, maintaining and tracing perfect growth and removing the large excesses of reagents needed to force these reactions are difficult. The convergent growth method is the opposite of the divergent strategy; in this case, growth begins in the periphery of the dendrimer and proceeds inwards, with the final reaction being the attachment to a polyfunctional core. In this methodology, large parts of the dendrimer are synthesized separately, and are finally interconnected to form the dendrimer. The advantage of this approach over the divergent methodology is that if incomplete attachment of a large part occurs, it can be easily traced and corrected.

7.5.1
Dendrimers

A wide variety of dendrimers have been presented in the literature: PAMAM, poly(propyl imine) (diaminobutane-dendr-NH_2), polyethers, polyesters, poly(ester amides), poly(ether amides), polyalkanes, poly(phenylacetylenes), polysilanes, phosphorous dendrimers, and others [147–151]. The pioneering synthetic strategy developed by Tomalia *et al.* [146] for starburst dendrimers and of Newcome *et al.* [147] for cascade molecules is now recognized as the divergent growth approach. Perhaps, the most well-known divergent synthesis of dendritic macromolecules is the preparation of PAMAM by Tomalia *et al.* [146] (Scheme 7.60).

The synthesis starts with a polyfunctional core, in this case ammonia, and reaction with methyl acrylate results in the formation of the triester **1**. The second step of this two-step repetitive process is regeneration of the reactive amino groups at the chain ends accomplished by exhaustive amidation with a large excess of 1,2-diaminoethane to give the first-generation dendrimer, **2**, in which the number of reactive amino groups has doubled from three for ammonia to six for **2**. Repetition of the two-step process then leads to larger dendritic macromolecules, the structure of which follows a strict geometrical progression.

The convergent methodology was demonstrated by Fréchet *et al.* in 1989 [152]. The advantages of the convergent methodology were later demonstrated by Hawker and Fréchet [153] in the synthesis of a series of dendritic polyether macromolecules based on 3,5-dihydroxybenzyl alcohol as the monomer unit (Scheme 7.61). The starting material is the benzylic ether (**1**), which after reaction with carbon tetrabromide and triphenylphosphine regenerates the reactive bromomethyl group (**2**). Alkylation of **2** with the monomer unit under typical Williamson conditions leads to the next-generation dendron (**3**) in which the number of surface groups has doubled but there is still a single functional group at the focal point. The procedure has been repeated to the

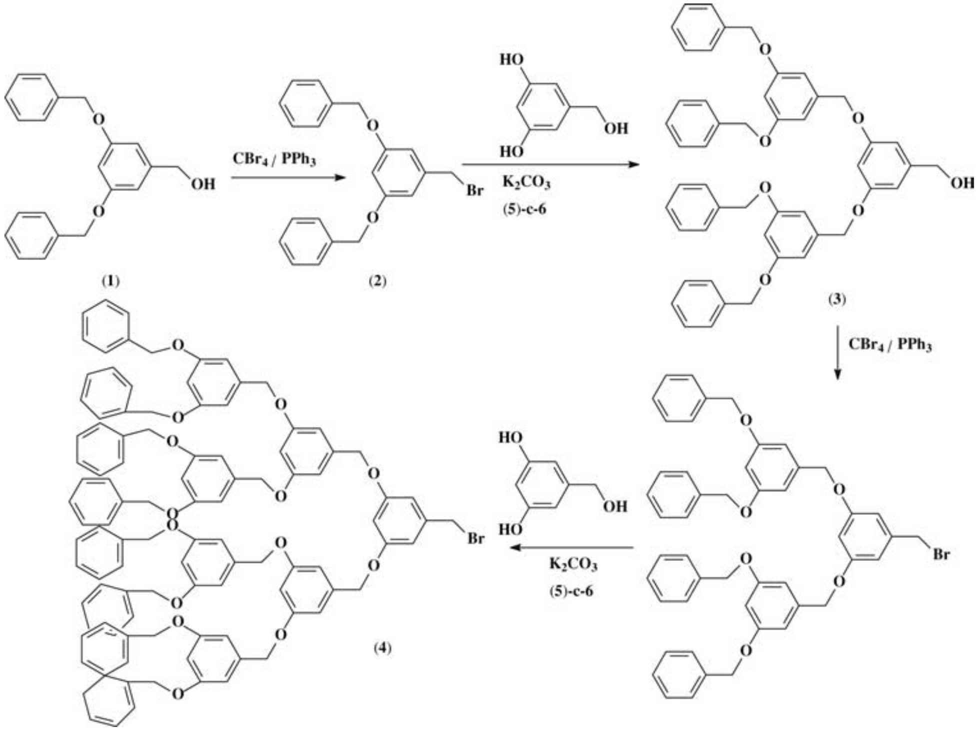


Scheme 7.60

sixth generation dendron which has 64 (2^6) surface benzyl groups, with a molecular formula of $C_{889}H_{763}BrO_{126}$ and a MW of 13 581.

"Click" chemistry has also been applied for the functionalization or even the synthesis of dendrimers. The traditional convergent approach was used for the synthesis of 3,5-dioxybenzyl ether dendrimers. Dendrons of different generations were synthesized and subsequently coupled to a central trifunctional core, affording dendrimers with 3, 6, 12, 24, and 48 chain-end acetylene groups [154] (Scheme 7.62a). A variety of azides incorporating reactive functional groups, such as nucleoside, carbohydrate, dye, or large dendrons (Scheme 7.62b), were subjected to "click" reactions with the acetylene-functionalized dendrimers, in the presence of $Cu(PPh_3)_3Br$ or $(EtO)_3PCuI$, to afford the corresponding functionalized structures (overall yield: 85–90%) (Scheme 7.62c).

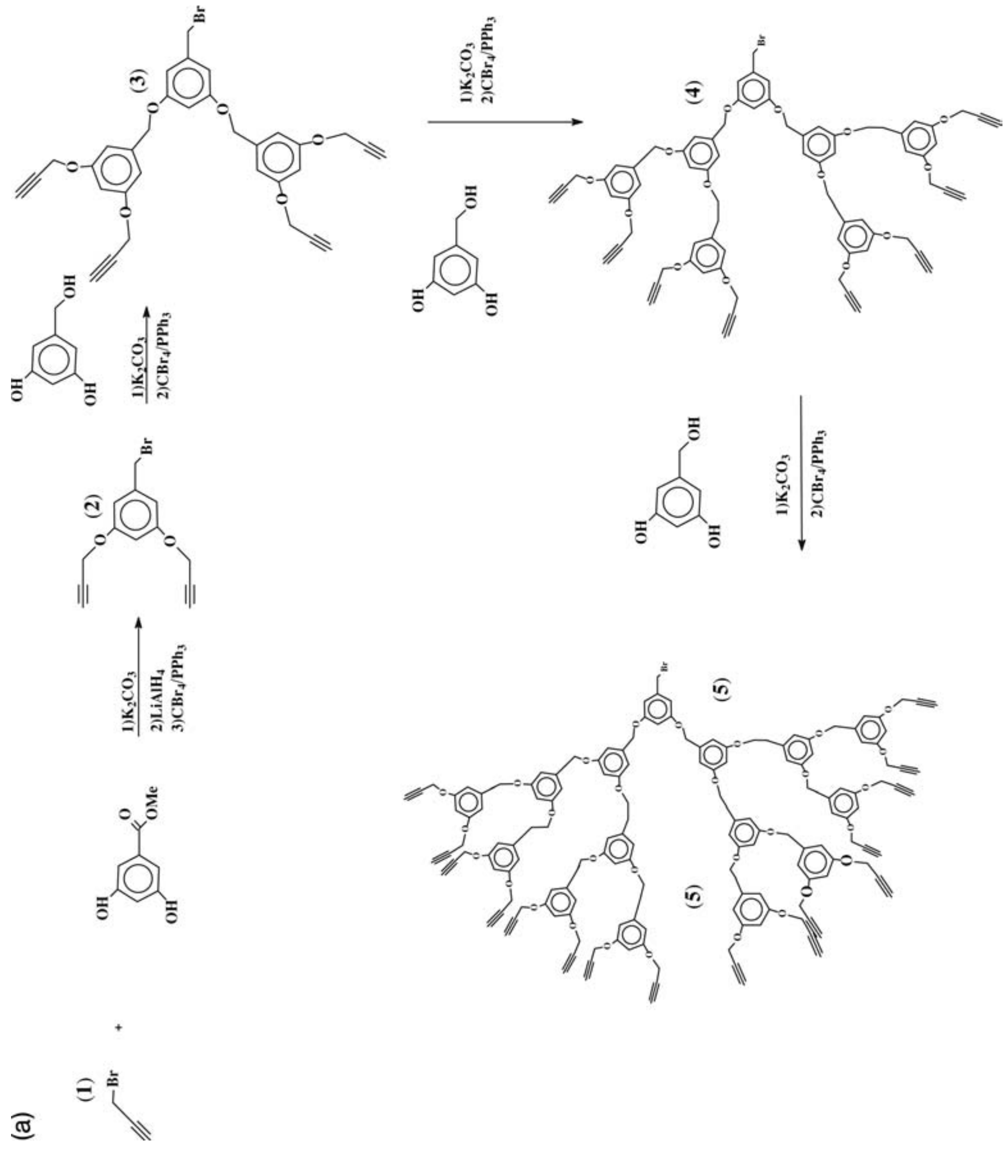
The convergent approach was employed for the synthesis of dendrimers using AB_2 monomers based on terminal alkynes and alkyl halide functionalities. Separate dendrons were synthesized employing "click" reactions and



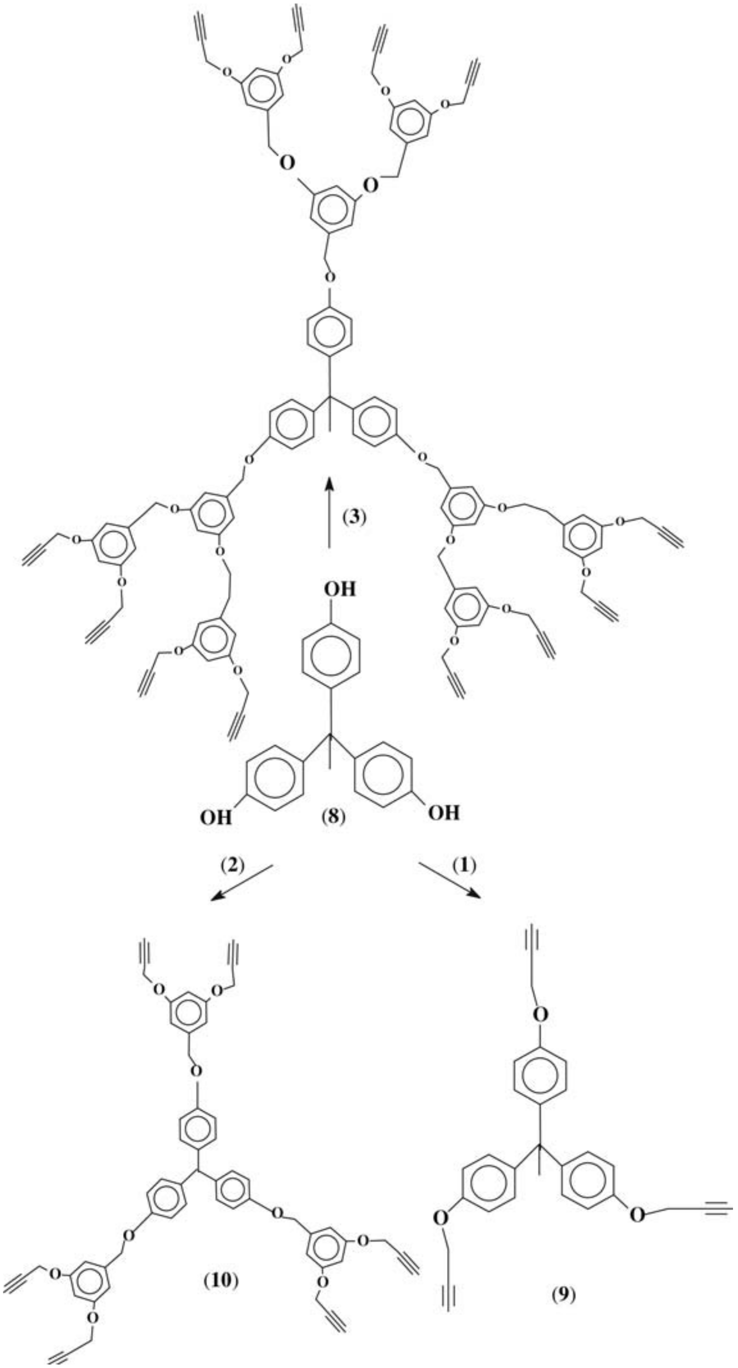
Scheme 7.61

were then coupled to a central core to provide the final dendritic structure [155] (Scheme 7.63). The alkyne groups of the AB_2 monomer were reacted with a suitable azide in the presence of $CuSO_4$ and sodium ascorbate in a mixture of water and *tert*-butyl alcohol to afford the desired bistriazoles in near quantitative yields. The chloride groups were then transformed to azides by reaction with sodium azide. Subsequent reaction with the AB_2 monomer generated the second-generation dendron. These steps were repeated for the synthesis of higher generation materials. Owing to the insolubility of the higher MW products in water, the ''click'' reaction was performed with $Cu(PPh_3)_3Br$. The triazole dendrons of the third and fourth generation, having an azide focal point, were finally coupled to a variety of trifunctional cores carrying alkyne functions, leading to the synthesis of the desired dendrimers.

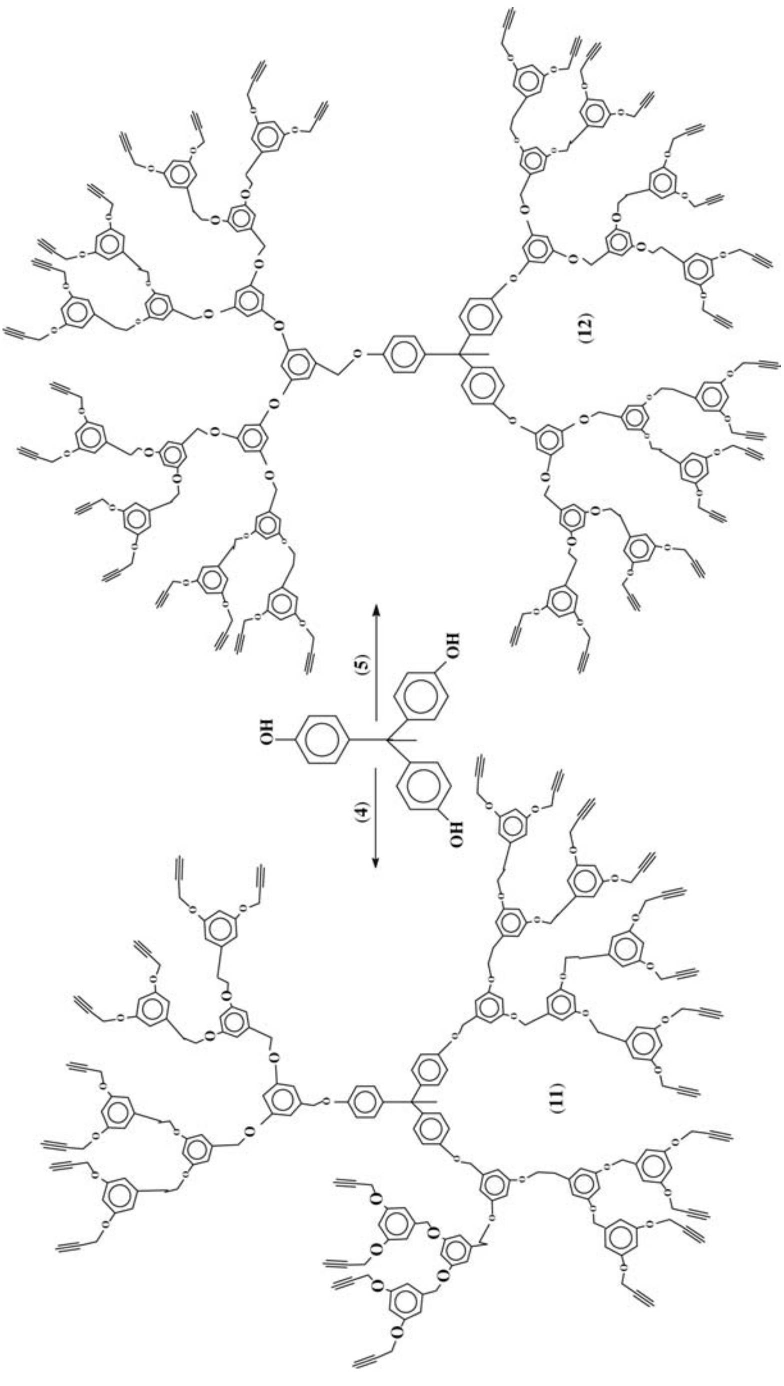
The divergent methodology and ''click'' reactions were also applied for the synthesis of dendrimers. 4-Carboxy-4′-[bis(2-chloroethyl)amino]azobenzene was synthesized and was subsequently either esterified with propynol to afford the corresponding molecule with an available triple bond, or reacted with NaN_3 to substitute the chloride groups with azides (Scheme 7.64) [156]. These products were used as building blocks for the construction of dendrimers


(a)
(1)
Br
+
OH
OH
O
OMe
1)K2CO3
2)LiAlH4
3)CBr4/PPh3
(2)
Br
OH
OH
OH
1)K2CO3
2)CBr4/PPh3
(3)
Br
1)K2CO3
2)CBr4/PPh3
OH
OH
OH
(4)
Br
OH
OH
OH
1)K2CO3
2)CBr4/PPh3
(5)
Br
(5)

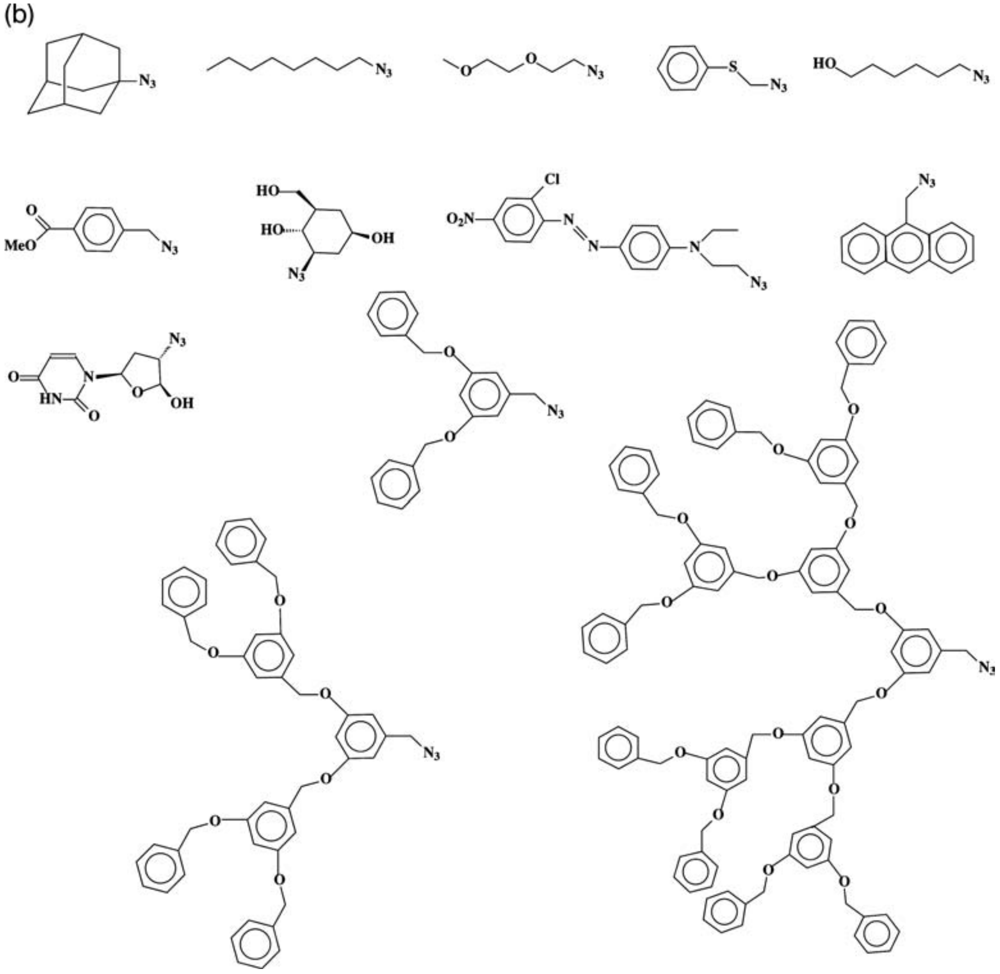
Scheme 7.62a



Scheme 7.62a (*continued*).



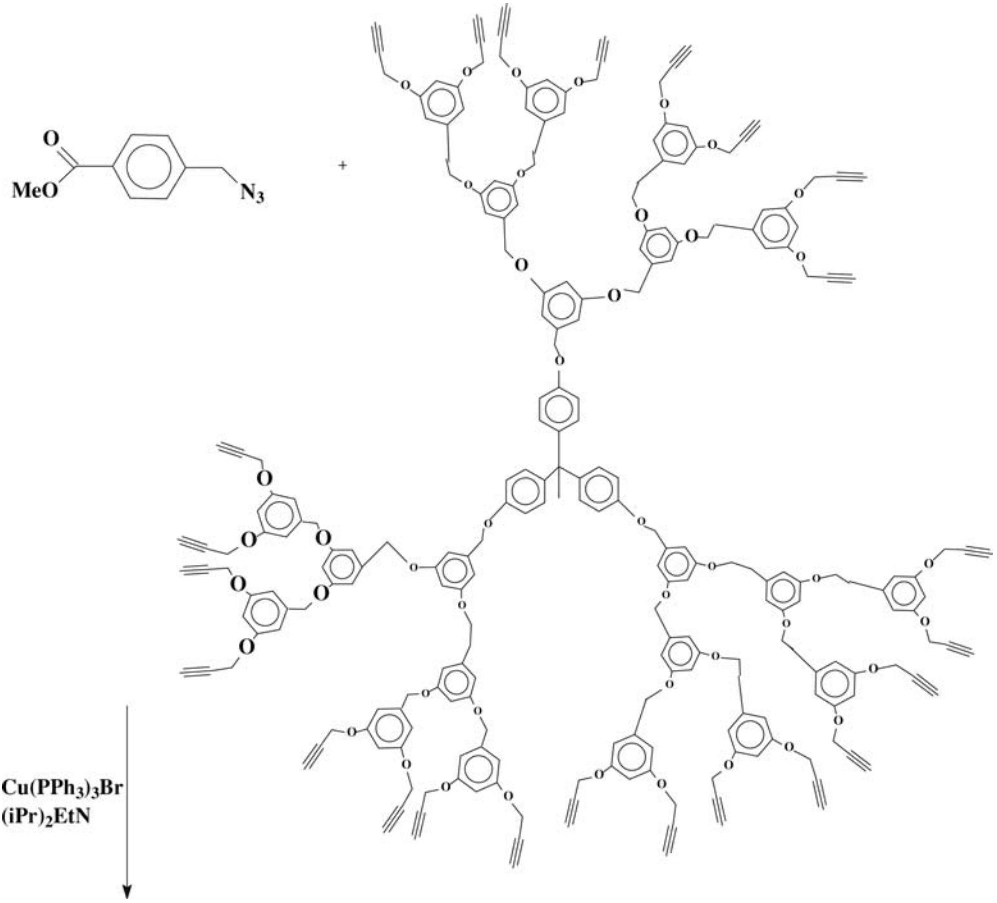
Scheme 7.62a *(continued).*



Scheme 7.62b

through an iterative sequence involving "click" reactions between the azide-terminated dendrons with the alkyne-functionalized compounds.

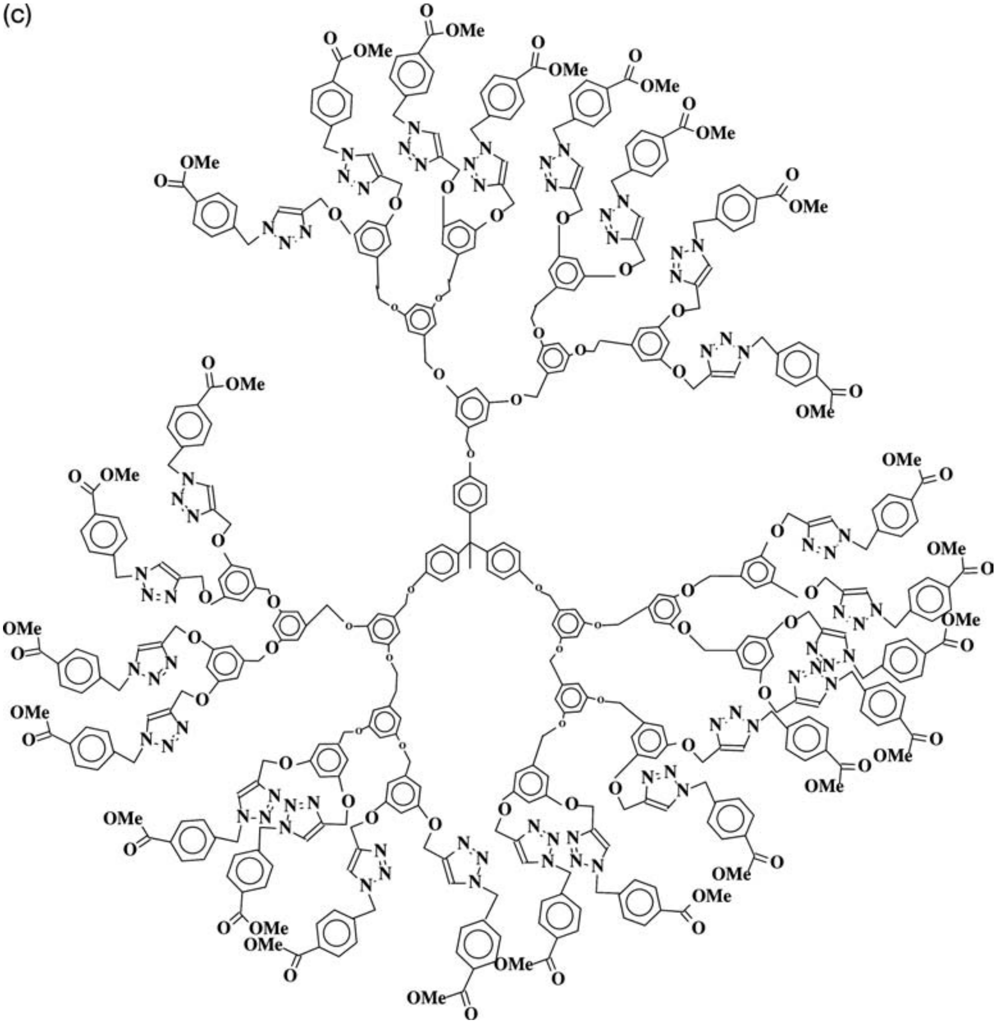
1,2-Bis(2-azidoethoxy)ethane and 1-propargyl-3,5-dihydroxymethylene benzene were reacted under typical "click" chemistry conditions to give the first-generation dendrimer [157] (Scheme 7.65). The hydroxymethylene groups were then converted to chlorides by treatment with $SOCl_2$ and finally to azides after reaction with NaN_3. Dendrimer growth then proceeded through a reaction sequence involving "click" reactions between the azido end groups of the growing dendrimer and the alkynyl group of the monomer followed by the reactivation and transformation of the hydroxyl groups to azides. Using this divergent approach, dendrimers of up to the third generation were prepared.



Scheme 7.62b (*continued*).

7.5.2
Dendritic Polymers

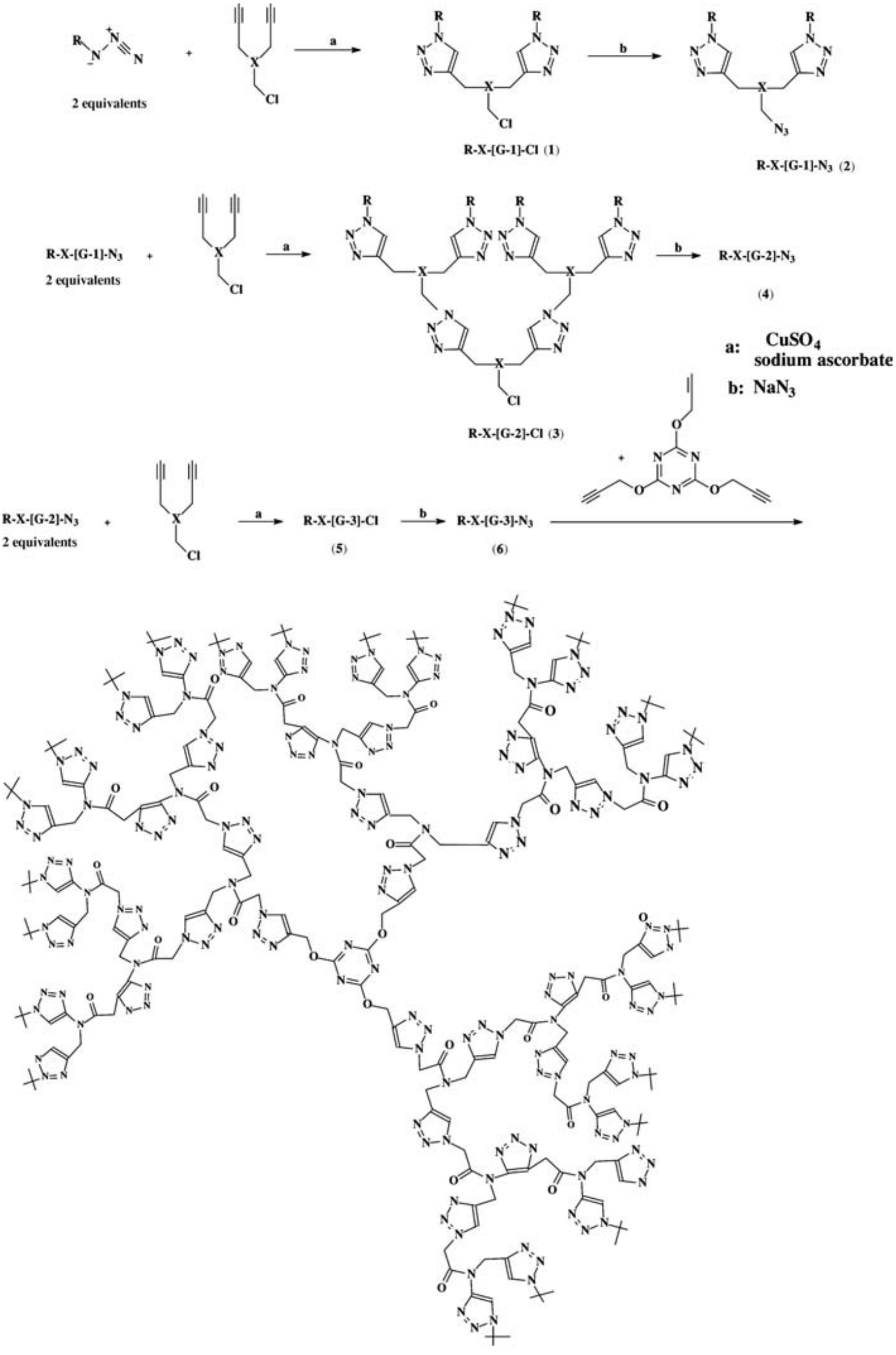
The preparation of well-defined G-2 dendritic homo- and copolymers of isoprene and styrene was reported by Chalari and Hadjichristidis [158] via stepwise convergent anionic polymerization. The synthesis of second-generation (G-2) dendritic polymers of isoprene (I) and styrene (S) was achieved with anionic polymerization high vacuum techniques and the following steps: (i) selective reaction of a living chain with the chlorosilane group of CDMSS (a dual-functionality compound) to produce a macromonomer; (ii) addition of a second living chain (same or different) to the double bond of the macromonomer; (iii) polymerization of I with the anionic sites; and (iv) reaction of the produced off-center living species with



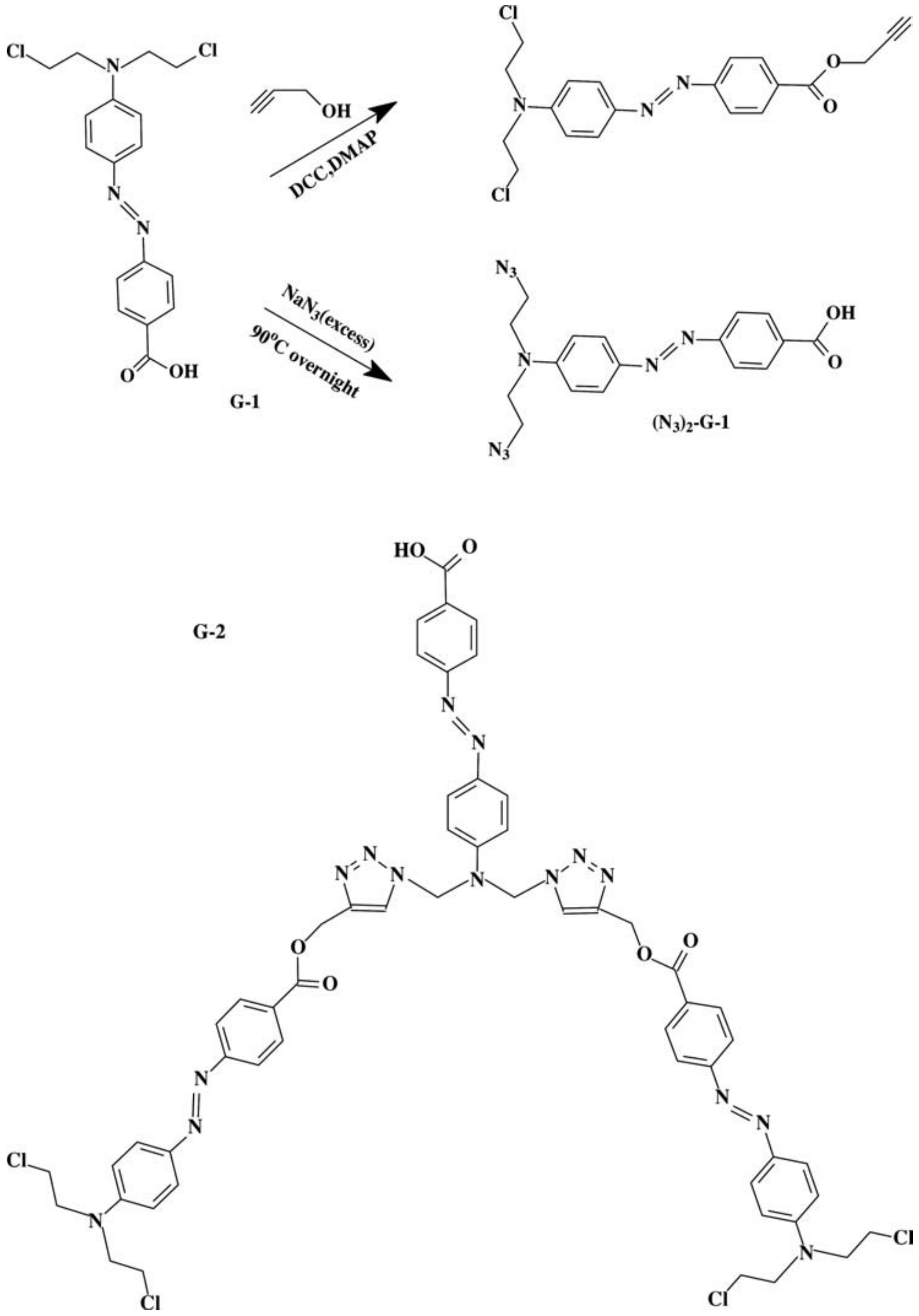
Scheme 7.62c

trichloromethyl silane or tetrachlorosilane (CH_3SiCl_3 or $SiCl_4$). The combined characterization results indicated that the G-2 dendritic macromolecules synthesized, i.e., $(S_2I)_3$, $(SI'I)_3$, $(I''I'I)_3$, $(I'_2I)_4$, had high molecular and compositional homogeneity. The success of the synthesis relied on the selective reaction between living chains and the dual-functionality compound CDMSS. This stepwise synthesis provides good control over the reaction, leading to dendritic polymers with structural and compositional homogeneity.

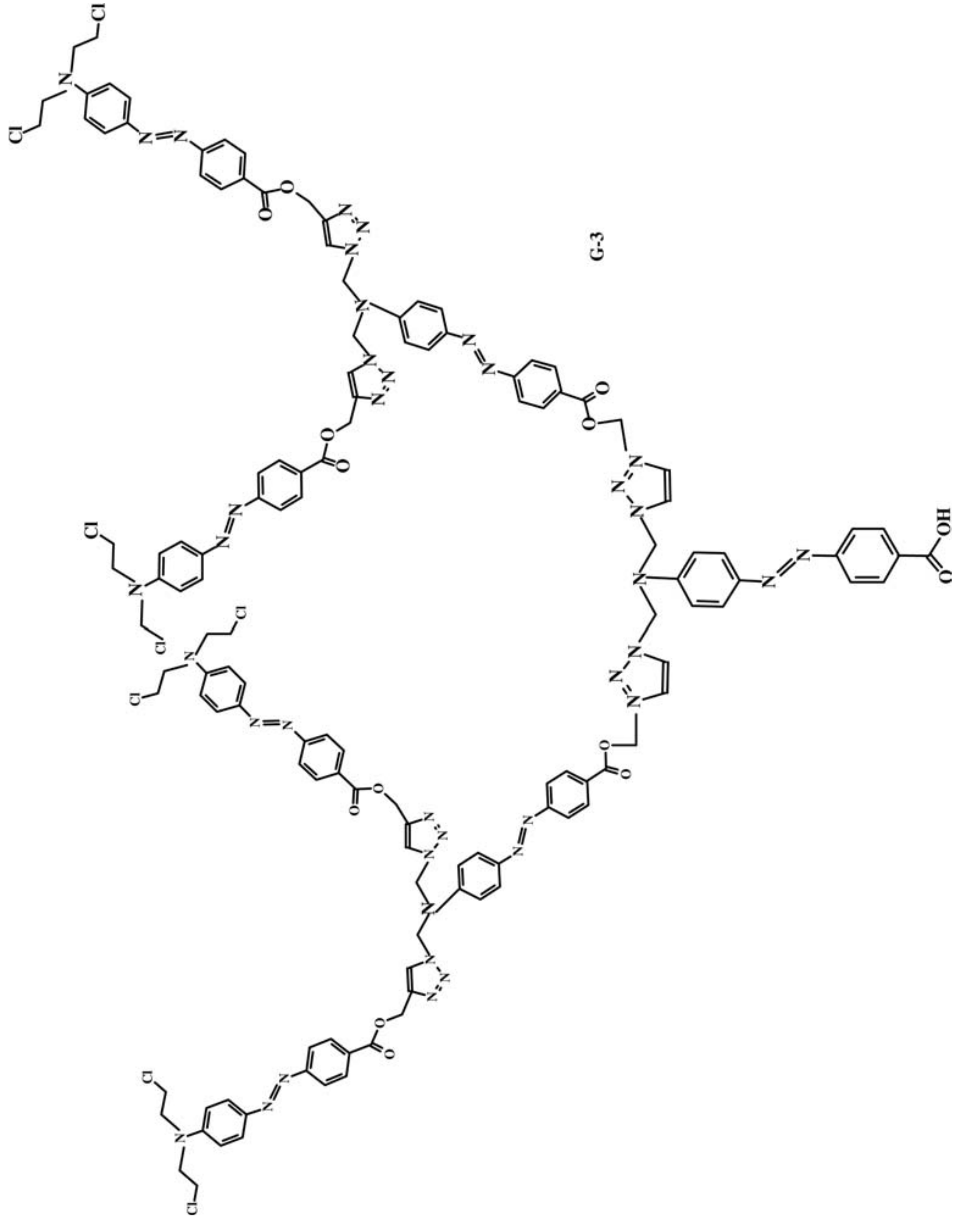
A better control for the synthesis of dendritic PBd polymers was adopted using the nonhomopolymerizable dual-functional LA, DCMSDPE. Living


2 equivalents
a
R-X-[G-1]-Cl (1)
b
R-X-[G-1]-N$_3$ (2)
R-X-[G-1]-N$_3$
2 equivalents
a
b
R-X-[G-2]-N$_3$
(4)
R-X-[G-2]-Cl (3)
a: CuSO$_4$ sodium ascorbate
b: NaN$_3$
R-X-[G-2]-N$_3$
2 equivalents
a
R-X-[G-3]-Cl
(5)
b
R-X-[G-3]-N$_3$
(6)

Scheme 7.63

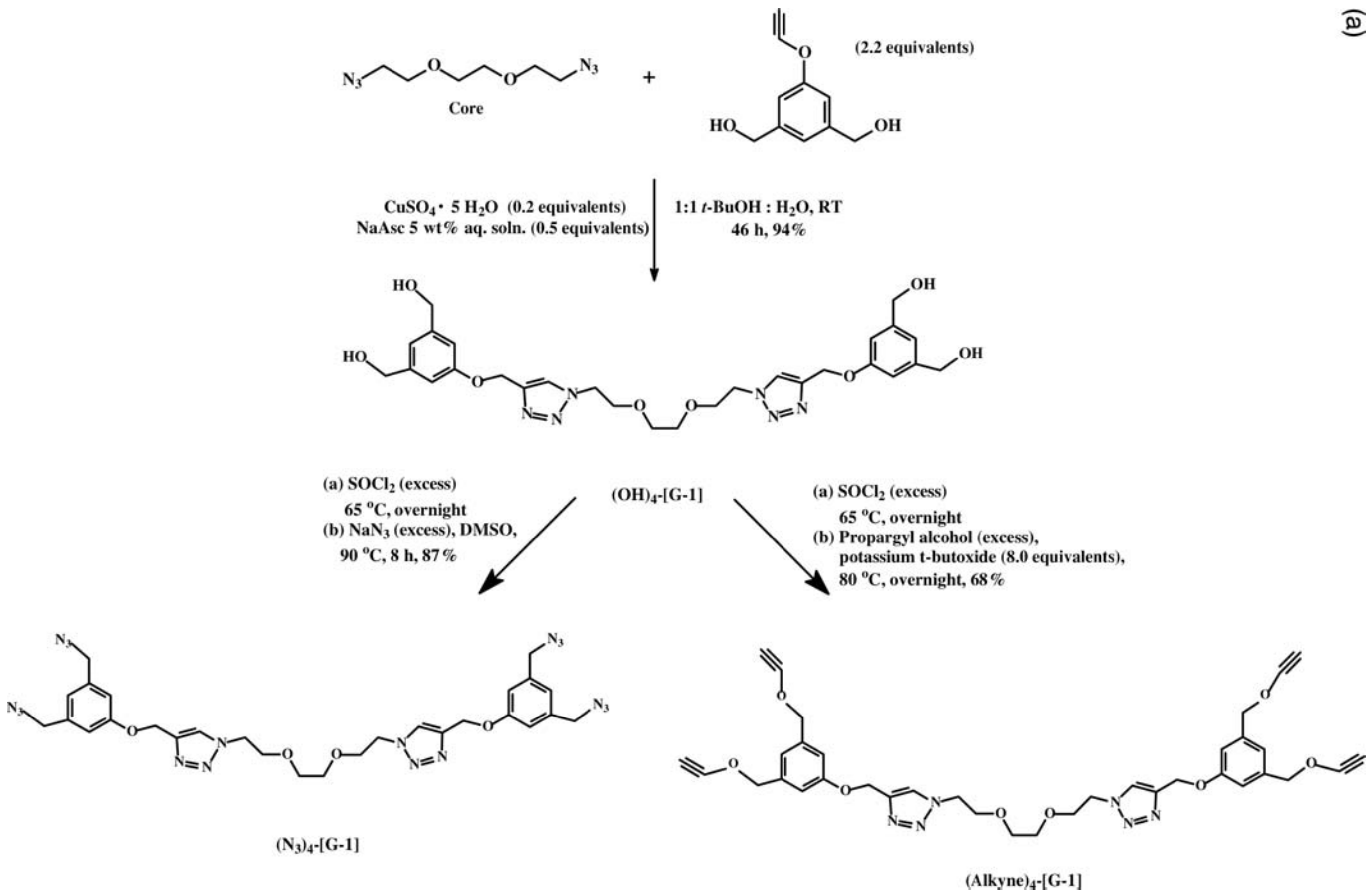


Scheme 7.63 (*continued*).

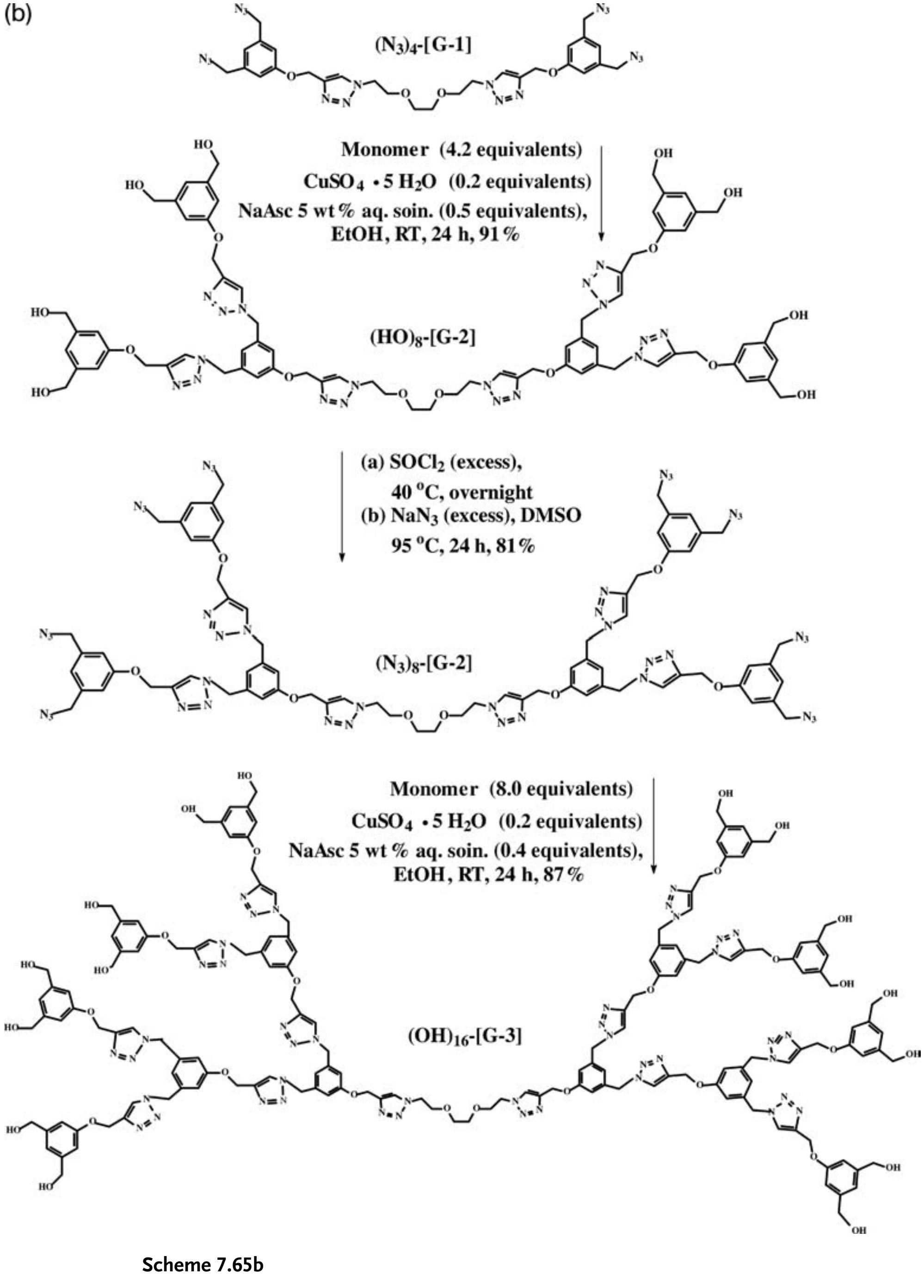


G-3

Scheme 7.64

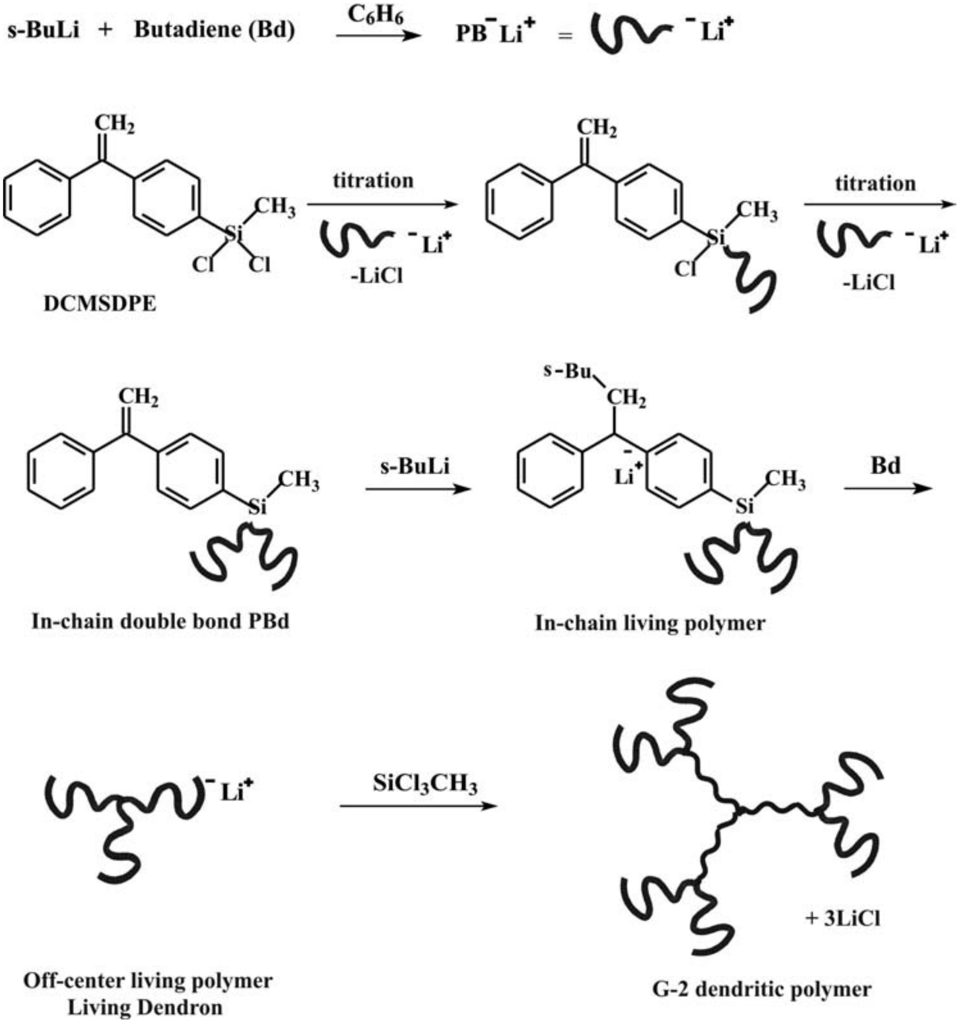

(a)
Core
(2.2 equivalents)
CuSO4 • 5 H2O (0.2 equivalents)
NaAsc 5 wt% aq. soln. (0.5 equivalents)
1:1 t-BuOH : H2O, RT
46 h, 94%
(OH)4-[G-1]
(a) SOCl2 (excess)
65 °C, overnight
(b) NaN3 (excess), DMSO,
90 °C, 8 h, 87%
(a) SOCl2 (excess)
65 °C, overnight
(b) Propargyl alcohol (excess),
potassium t-butoxide (8.0 equivalents),
80 °C, overnight, 68%
(N3)4-[G-1]
(Alkyne)4-[G-1]

Scheme 7.65a


(b)
(N3)4-[G-1]
Monomer (4.2 equivalents)
CuSO4 • 5 H2O (0.2 equivalents)
NaAsc 5 wt % aq. soln. (0.5 equivalents),
EtOH, RT, 24 h, 91%
(HO)8-[G-2]
(a) SOCl2 (excess),
40 °C, overnight
(b) NaN3 (excess), DMSO
95 °C, 24 h, 81%
(N3)8-[G-2]
Monomer (8.0 equivalents)
CuSO4 • 5 H2O (0.2 equivalents)
NaAsc 5 wt % aq. soln. (0.4 equivalents),
EtOH, RT, 24 h, 87%
(OH)16-[G-3]

Scheme 7.65b

PBdLi chains were linked selectively with the two chlorosilyl groups, leading to the synthesis of PBds bearing in-chain double bonds. The steric hindrance of the two phenyl groups of DCMSDPE prevented the reaction of the double bond with the living polymers. The remaining double bond was subsequently activated by *s*-BuLi to afford the in-chain living polymer. Addition of a new quantity of Bd resulted in the formation of a living three-arm star polymer, which was then linked to trichloromethylsilane to give the second-generation dendritic polymer (Scheme 7.66) [159]. Using the same methodology, the third-generation dendritic PBd was also prepared.



Scheme 7.66

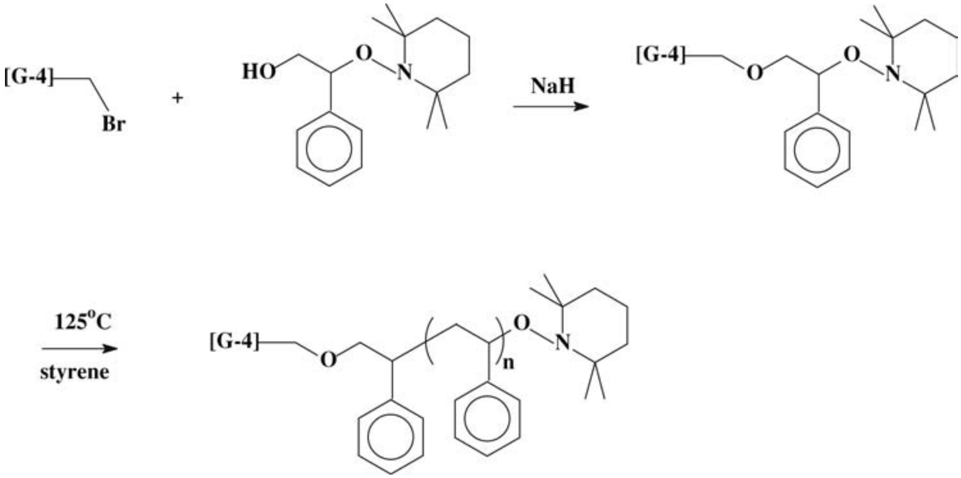
7.6
Complex Macromolecular Architectures

Recent developments in synthetic methodologies have allowed the synthesis of novel macromolecular structures with excellent control over the topology, microstructure, and composition [1, 8, 160]. The application of organic chemistry reactions for the transformation of the macromolecular chains as well as the synthesis of new initiators and LAs along with the combination of different polymerization methods are the main tools for the synthesis of complex macromolecular architectures.

7.6.1
ω-Branched Polymers

These polymers can be considered linear chains having a number of covalently attached chains at one of their ends. Such products are called *palm-tree* or even *umbrella* polymers and their synthesis can be achieved either by a divergent or a convergent method. According to the divergent method, the linear polymer has a number of initiating sites located at the chain end. Through these sites, new polymer chains can grow, leading to the formation of a ω-branched structure. Alternatively, the branched structure may act as initiator for the synthesis of the linear chain. An example is given in Scheme 7.67 [161].

The convergent method involves the linking of preformed chains to suitable linking sites located at the main chain end. This approach was applied for the synthesis of the umbrella copolymers. PS-*b*-PBd block copolymers with a short PBd block of the 1,2 microstructure were prepared by anionic polymerization.

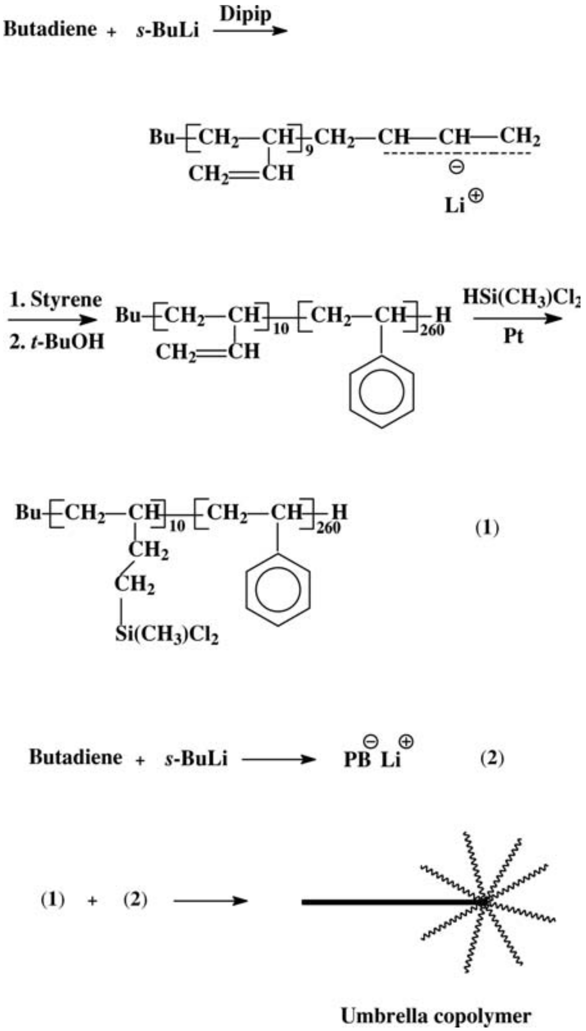


Scheme 7.67

The polydiene block was hydrosilylated for the introduction of Si–Cl groups. Subsequent linking of these groups with living P2VP chains afforded the desired PS(P2VP)$_x$ structures [162] (Scheme 7.68).

7.6.2
α,ω-Branched Polymers

These polymers can be considered linear macromolecules having a number of covalently attached chains at both chain ends. Their synthesis can be achieved



Scheme 7.68

employing methods similar to those used for ω-branched polymers, except that the reactions are performed at both chain ends. Copolymers of the type B_3AB_3 are termed *super-H shaped copolymers* and, more generally, copolymers of the type B_nAB_n are characterized in the literature as ''pom–pom'' or ''dumbbell'' copolymers.

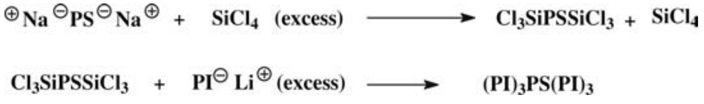
Using a convergent approach and anionic polymerization techniques associated with suitable chlorosilane chemistry, $(PI)_3PS(PI)_3$ super-H shaped copolymers were prepared [163]. A difunctional PS chain, derived from the polymerization of styrene in THF using sodium naphthalene as initiator, was reacted with a large excess of $SiCl_4$, leading to the synthesis of PS chain end functionalized at both ends with $-SiCl_3$ groups. After elimination of the excess $SiCl_4$ and addition of living PI arms, the desired super-H structure was achieved (Scheme 7.69).

Employing a similar method, $(PI)_5PS(PI)_5$ copolymers (pom–pom shaped) were synthesized [85]. Living PI chains were reacted with a hexafunctional chlorosilane in a SiCl : Li ratio = 6 : 5, giving the five-arm star with a remaining SiCl group at the central point. Subsequent reaction with a difunctional PS led to the synthesis of the pom–pom copolymer (Scheme 7.70).

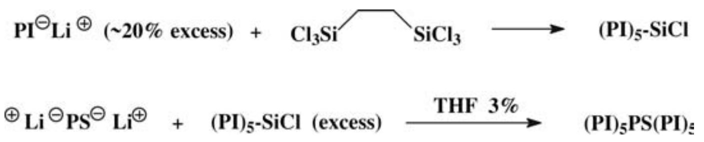
The divergent methodology was applied for the synthesis of pom–pom or dumbbell copolymers with higher functionalities. Triblock copolymers PBd-*b*-PS-*b*-PBd containing short PBd blocks with 1,2 microstructure were prepared by anionic polymerization techniques [164]. The vinyl side groups of the PBd blocks were subjected to the hydroboration–oxidation reaction for the incorporation of hydroxyl groups. These groups were subsequently transformed to alkoxides to initiate the polymerization of ethylene oxide, leading to the synthesis of $(PEO)_nPS(PEO)_n$ dumbbell copolymers (Scheme 7.71).

Structures resembling dumbbell copolymers have also been prepared. In this case, a living anionic difunctional PS connector was linked with polyether dendritic groups [165] (Scheme 7.72).

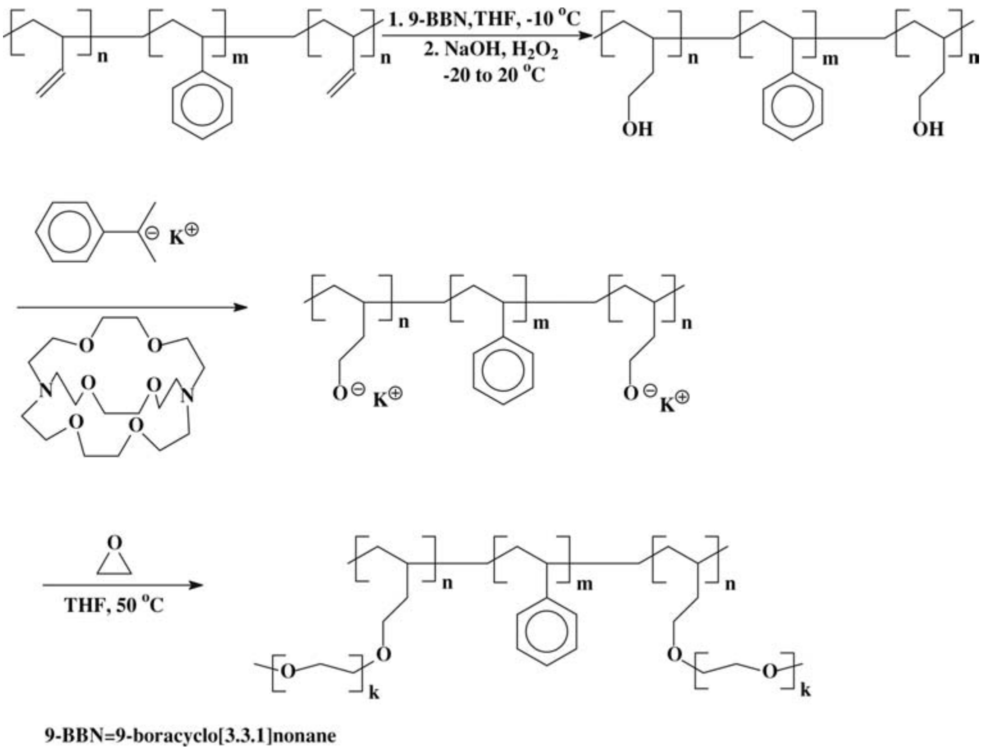
A barbell-like ABA-type triblock copolymer, comprised of poly(L-lysine) (PLL) dendrimers (A) and PEG connector (B) was reported [166]. The synthetic



Scheme 7.69



Scheme 7.70

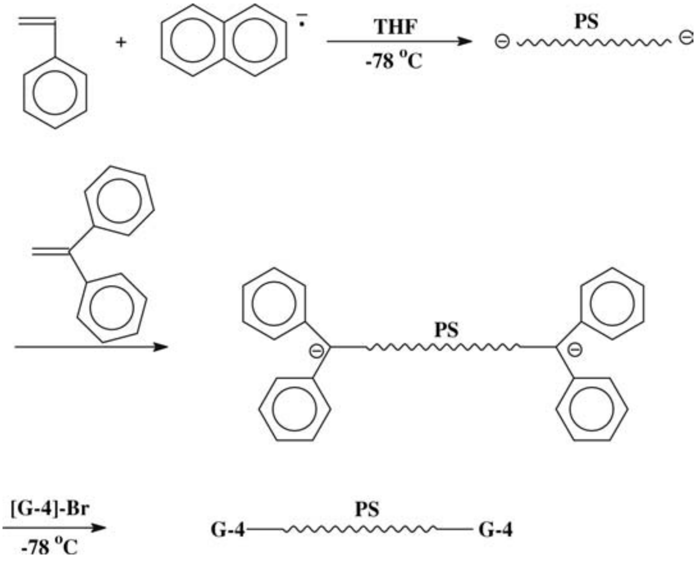


Scheme 7.71

route involved the use of an α,ω-diamino-functionalized PEG as the polymeric support for the attachment of $-NH_2$-protected lysine via an amidation reaction. The PLL dendrimer was generated at both ends of B by repeated liquid-phase peptide synthesis, as shown in Scheme 7.73. The intermediate products along with the final copolymers were characterized by MALDI-TOF MS. The results revealed that narrow MW dispersity copolymers were synthesized having low MWs.

The convergent approaches offer a better structural control provided that the linking reactions are efficient and free of steric hindrance effects. On the other hand, the divergent methods usually lack the precise control over the structure, since they require the generation of initiation centers at both ends of a polymer chain. The growth of polymer chains through these initiation sites may not be uniform, because of steric hindrance, association phenomena, kinetic differentiations, etc., leading to products with structural defects and chemical inhomogeneities.

Macromonomers can also be used for the synthesis of α,ω-branched polymers. A difunctional living polymer chain can be used as a macroinitiator to polymerize macromonomers to produce a pom–pom (or dumbbell) copolymer,



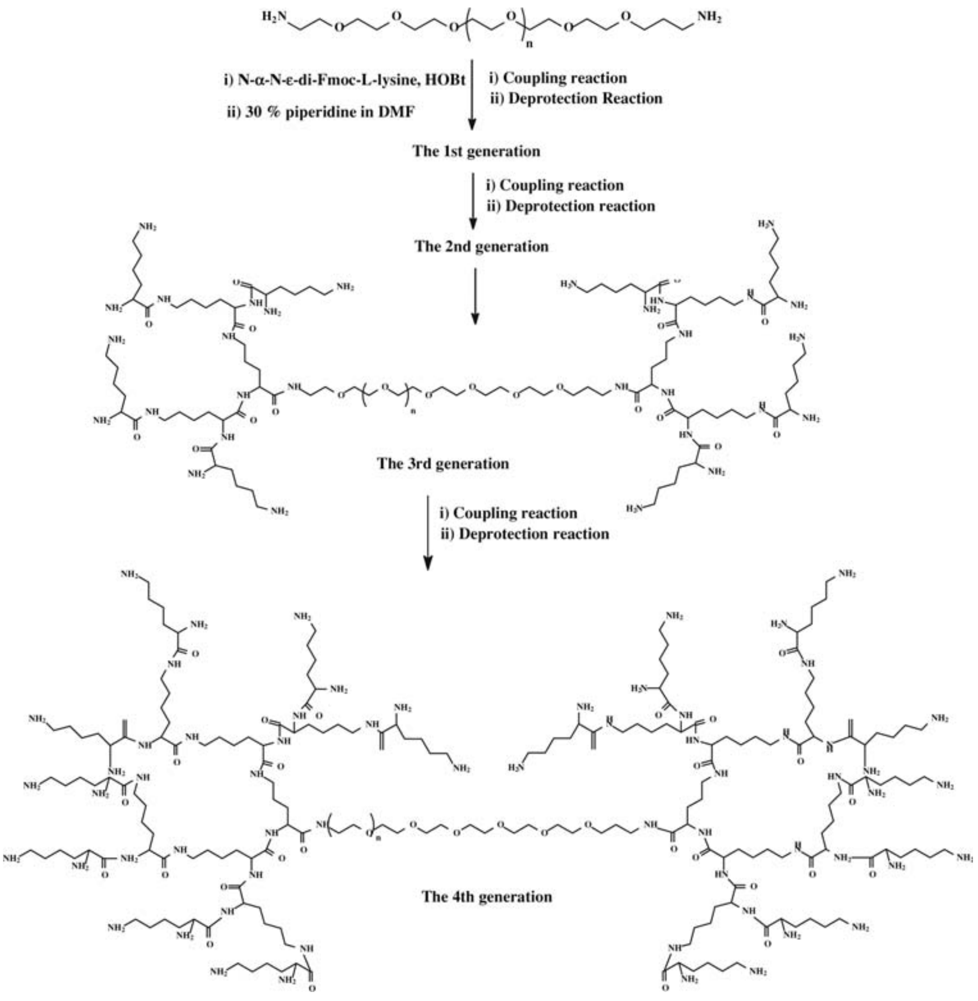
Scheme 7.72

if a small number of macromonomers is added at the end of the living polymer chain (Scheme 7.74) [105].

In an extension of the methodology involving DPEs, the preparation of chain-end functionalized polymers with a definite number of bromomethylphenyl (BnBr) end groups and their utilization in the synthesis of dumbbell polymers has been reported [167]. The synthesis of linear PS chain capped at each end with 2, 4, 8, or 16 BnBr groups is illustrated in Scheme 7.75. A living difunctional PS chain was reacted with DPE, a derivative bearing one *tert*-butyldimethylsilyloxymethylene group. Subsequent reaction with LiBr/$(CH_3)_3SiCl$ transformed the end groups to BnBr moieties. DPE carrying two *tert*-butyldimethylsilyloxymethylene groups was activated with *s*-BuLi and reacted with the bromomethyl units of the telechelic PS chains. Subsequent transformation to BnBr functions affords a linear PS macromolecule with two end groups at each chain end. The procedure can be repeated for the incorporation of up to 16 BnBr groups at each chain end. Linking of living PS polymers end-capped with a DPE unit resulted in the formation of well-defined dumbbell polymers with a predetermined number of branches.

7.6.3
Hyperbranched and Dendrigraft Polymers

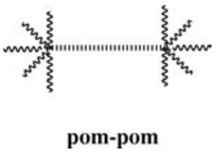
Hyperbranched and dendrigraft polymers belong to the family of dendritic polymers [168]. However, they are not characterized by the strict structural and



Scheme 7.73

molecular control attained from dendrimers [169]. Hyperbranched polymers are obtained using two different approaches. The first involves the use of single monomers (single monomer methodology, SMM) of the general type AB_n and can be subdivided to one of the following procedures: (i) polycondensation of AB_n monomers, (ii) self-condensing vinyl polymerization (SCVP), and (iii) self-condensing ring opening (SCROP) and proton transfer polymerization (PTP). The second approach involves the use of two types of monomers (double monomer methodology, DMM).

The one-pot polycondensation reaction of AB_n monomers, according to the SMM, led to the synthesis of a wide variety of hyperbranched structures, such as



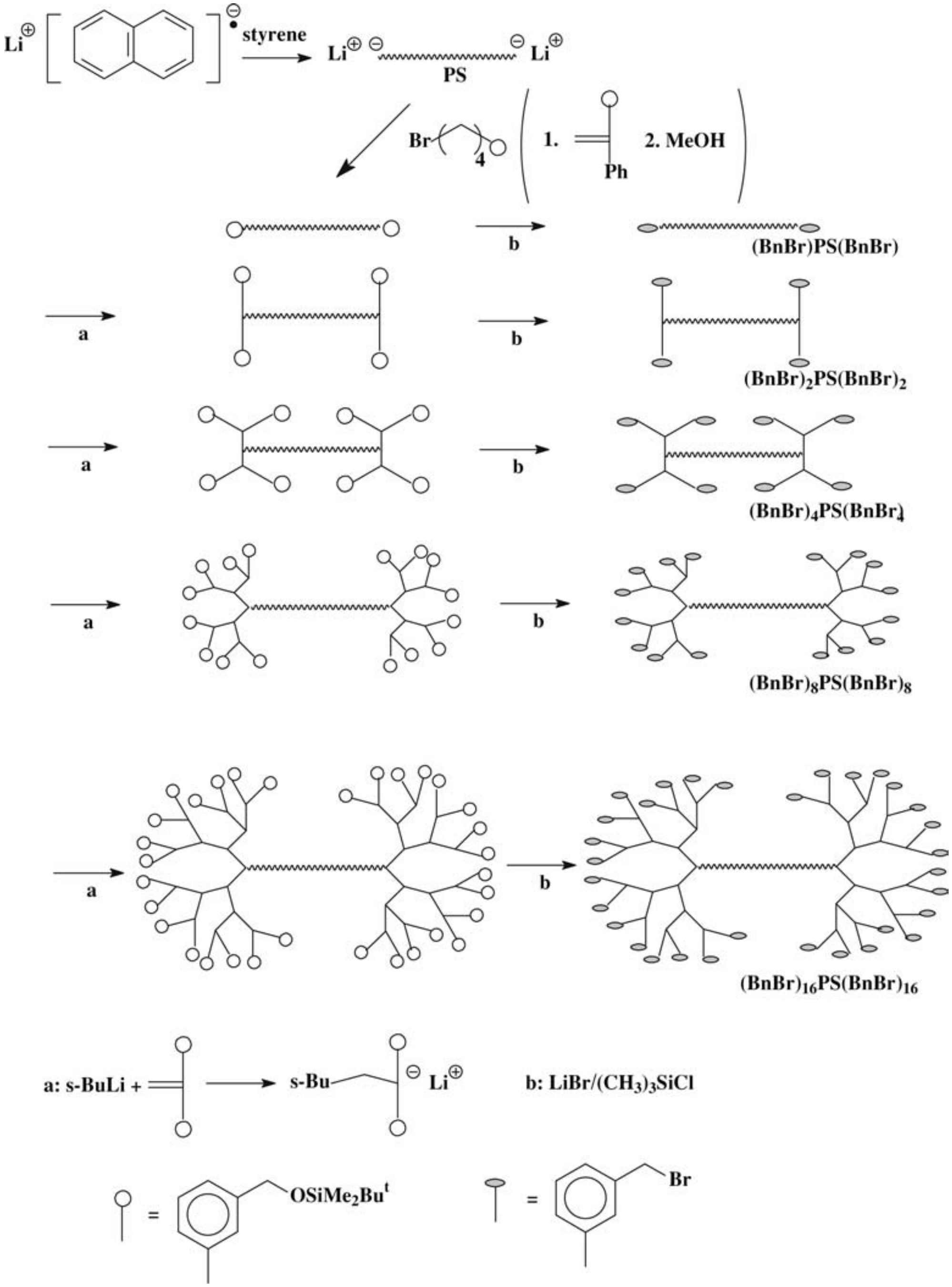
Scheme 7.74

poly(phenylenes) [170], polyesters [171], polyethers [172], poly(ether ketones) [173], and polycarbonates [174]. The products are characterized by limited control over the structure and broad MW distributions ($M_w/M_n \approx 2$) [175].

SCVP was initially proposed by Fréchet [176], and involves the use of vinyl monomers of the AB type. A stands for the vinyl group and B is a group that can be activated to form an initiating site B*, capable of initiating the polymerization of the vinyl A groups. Therefore, the AB molecules can act simultaneously as monomers and initiators and therefore are usually called *inimers*. Several living or controlled polymerization techniques have been employed leading to a variety of hyperbranched structures [177]. ATRP techniques have been employed as well for the synthesis of hyperbranched polymers. A one-pot polymerization procedure using *p*-(chloromethyl)styrene in the presence of Cu(I) and 2,2-bipyridyl was reported [178]. In this case, *p*-(chloromethyl)styrene acts both as the monomer and the initiator, since the chlorine atom can be abstracted homolytically to form benzyl radicals. 2-[(2-Bromopropionyl)oxy]ethyl acrylate was also homopolymerized using CuBr and di-*tert*-butyl-2,2′-bipyridine or 4,4′-di-5-nonyl-2,2′-bipyridine [179]. Hyperbranched polymers of rather broad MW distributions were obtained in both cases.

SCROP has been applied for the synthesis of polyethers, polyesters, and polyamines [180], whereas PTP led to the synthesis of hyperbranched polysiloxanes and polyesters bearing hydroxyl and epoxy end groups [181].

The DMM involves the polycondensation of A_2 and B_3 (or generally B_n, $n > 2$) monomers. The disadvantage of this procedure is that it usually leads to gelation. To obtain soluble products, the polymerization should be conducted in dilute solutions and terminated before reaching the critical gelation point. In addition, the monomer feed ratio and the monomer addition manner dramatically affect the properties of the final products. Examples of hyperbranched polymers prepared by this methodology include the products of the reactions between *p*-phenylene diamine and trimesic acid [182], 1,2,7,8-diepoxyoctane and 1,1,1-tris(hydroxymethyl)ethane [183], 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and tri-(*p*-aminophenyl)amine [184], etc. It is generally considered that the reactivity of the A and B groups is identical. However, in several monomer pairs, nonequal reactivity of the functional groups was observed [185]. In this case, the monomers can be described as AA′ and $B'B_2$, where the reactivity of the A′ and B′ groups is higher than that of the A and B groups. Owing to this inherent difference in reactivity, AB_2 intermediate monomers are formed

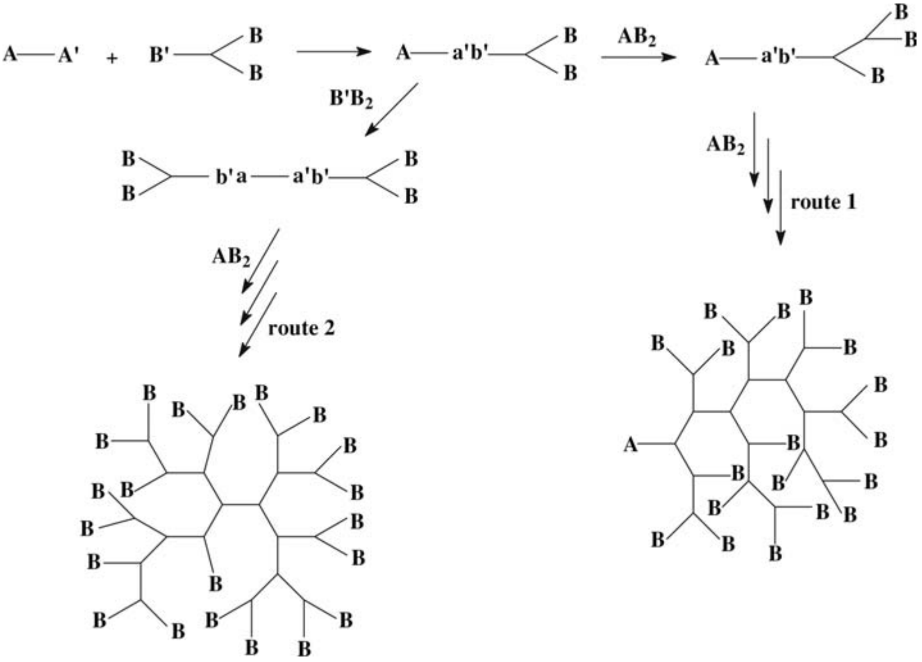

Li⊕
styrene
Li⊕ ⊖ PS ⊖ Li⊕
Br 4
1.
Ph
2. MeOH
b
(BnBr)PS(BnBr)
a
(BnBr)2PS(BnBr)2
(BnBr)4PS(BnBr)4
(BnBr)8PS(BnBr)8
(BnBr)16PS(BnBr)16
a: s-BuLi +
s-Bu
⊖ Li⊕
b: LiBr/(CH3)3SiCl
=
OSiMe2But
Br

Scheme 7.75

in situ. Further reaction of these AB_2 species results in the formation of hyperbranched polymers (Scheme 7.76).

Dendrigraft polymers are produced following the generation-based growth system but are constructed from polymeric building blocks [186]. Therefore, high MWs can be obtained after only a few generations. Each grafting step can be considered as a new generation. The grafting reaction is a random process and, consequently, dendrigraft polymers are not strictly defined as dendrimers. However, much narrower MW distributions ($1.1 \leq M_w/M_n \leq 1.5$) are obtained compared to the hyperbranched polymers. These structures are also referred to in the literature as *comb-burst* [187] or *arborescent* [188] polymers.

The dendrigraft polymers can be prepared by all the reported methods available for the synthesis of comb polymers and graft copolymers, i.e., "grafting onto," "grafting from," and "grafting through" procedures. The "grafting onto" scheme relies on the generation of grafting sites along a polymer backbone followed by coupling with living polymer chains. The "grafting from" methodology involves the formation of active polymerization sites onto the polymeric backbone and the growth of side chains from these sites. Both procedures can be considered as divergent approaches for the synthesis of dendrigraft polymers. However, the "grafting through" procedure is envisioned as a convergent approach and involves the reaction of living

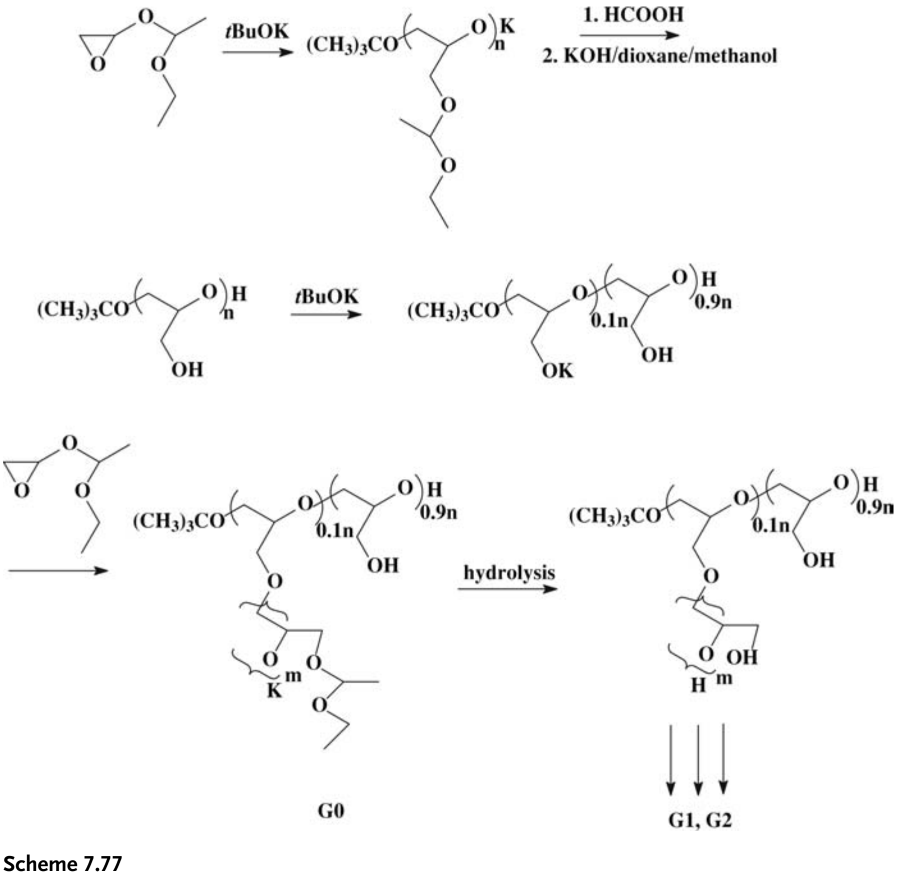


Scheme 7.76

preformed polymeric chains with a DFM bearing a vinyl group and another functionality capable of growing new side chains or terminating living chains through coupling.

Arborescent PS homo- and PS-*g*-P2VP copolymers have been synthesized [189] via an approach that combines the repetitive anionic polymerization of styrene, the attachment of acetyl groups by partial acetylation of the benzene rings of styrene, and reaction of living anionic polymeric chains with the acetyl groups. For the synthesis of the arborescent copolymers, P2VPLi chains were used in the final linking reaction. It was found that quantitative grafting occurred when the active sites were transformed to −2VPLi instead of −SLi. The polymerizations along with the coupling reactions were conducted in a mixture of THF/toluene at −78 °C to afford arborescent polymers with two generations and low polydispersity indices.

''Grafting from'' procedures were performed for the synthesis of highly branched poly(2,3-epoxypropan-1-ol) by anionic ROP [190] (Scheme 7.77).



Scheme 7.77

Linear poly(2,3-epoxypropan-1-ol) was initially prepared by polymerizing glycidol acetal using potassium *tert*-butoxide as initiator followed by deprotection of the acetal groups with formic acid and KOH/methanol/1,4-dioxane mixtures. Partial titration of the pendent hydroxyl groups with potassium *tert*-butoxide formed new initiating sites capable of initiating the anionic polymerization of a new portion of glycidol acetal. Additional cycles afforded highly branched polyglycidols.

Macromonomers have also been used as intermediate structures for the synthesis of highly branched or dentritic macromolecules by means of the convergent approach. When a bifunctional compound carrying a polymerizable vinyl group and a group capable of linking a living polymer chain is slowly added into a living polymer solution, consecutive macromonomer formation and macromonomer addition reactions can take place. Bifunctional compounds that have been used are CDMSS, and VBC [191]. Depending on the degree of branching and the MW of the living polymers, the final product may be a dendrigraft structure. Possible reactions involving the reaction of polystyryllithium with VBC are given in Scheme 7.78.

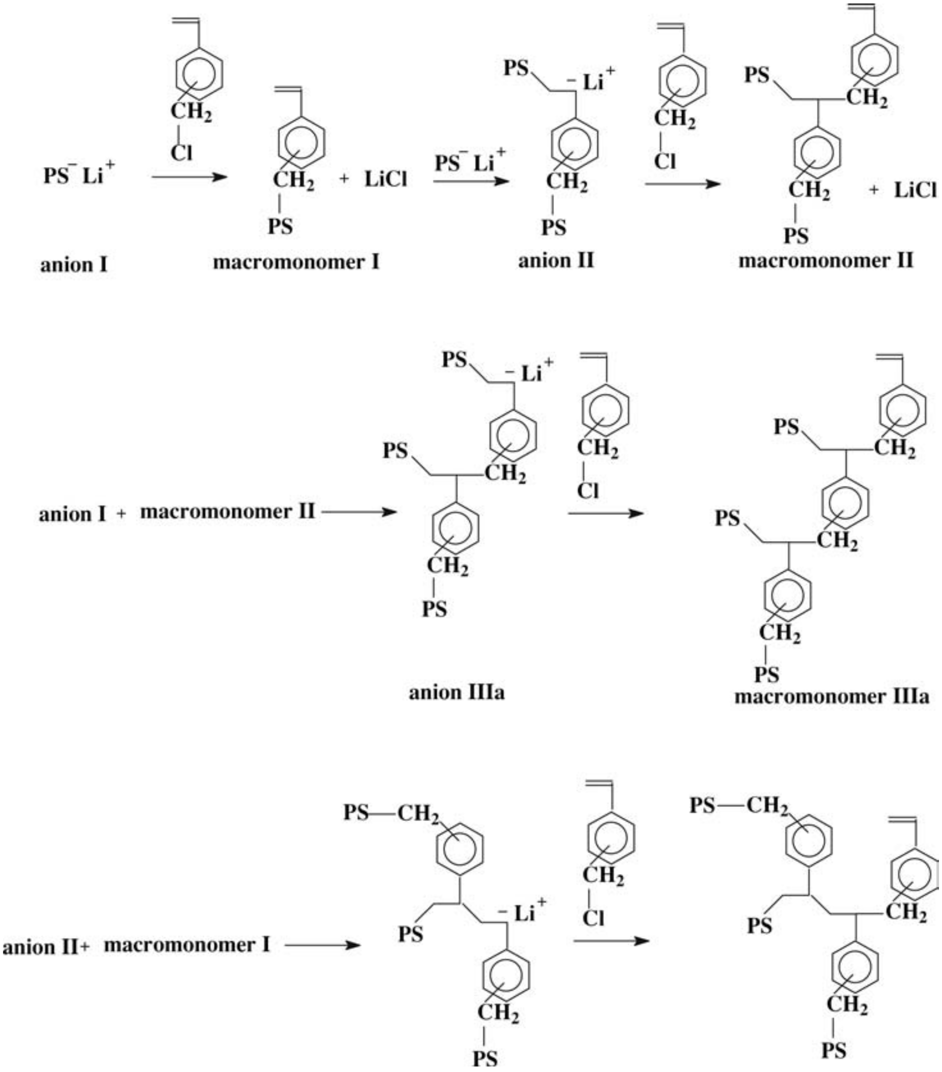
The characteristic of this procedure is that the complex architectures are formed in a one-pot reaction. However, there is no absolute control during the progress of the synthesis, and the products are rather polydisperse with high MW heterogeneity. Especially in the case of VBC, several side reactions may take place, imposing extra difficulties in obtaining well-defined polymers. Monomeric or dimeric terminations of the living PS chains, α-proton abstraction from VBC, and lithium–halogen exchange are possible side reactions. By choosing the suitable reaction conditions (solvent, temperature, reaction time, etc.), these side reactions can be minimized but not eliminated. The dendritic structures prepared were characterized from the existence of a functional styryl group at the focal point or the core, respectively. It was therefore possible to copolymerize these complex macromonomers with styrene or MMA for the synthesis of graft copolymers, imposing star polymers or dendrimers as side chains [192]. The products, shown in Scheme 7.79, had very broad MW distributions and were characterized by increased compositional and molecular heterogeneity.

7.6.4

Other Complex Architectures

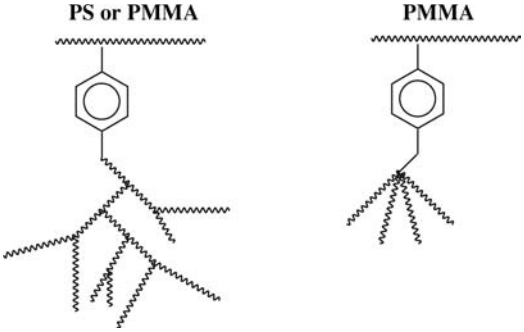
The DPE methodology and anionic polymerization techniques were adopted for the synthesis of linear-star-linear PSs of the types PS-(PS)$_n$-PS ($n = 2$, 4, 8, 16) and PS-(PS)$_n$-PS-(PS)$_n$-PS ($n = 2$, 4, 8) [167]. The synthesis involved the preparation of the corresponding in-chain functionalized polymers with a definite number of BnBr groups, as shown in Schemes 7.80 and 7.81.

Living PS macroanion was reacted with a PS chain end functionalized with a DPE unit, resulting in the synthesis of a linear PS macromolecule with an



Scheme 7.78

in-chain anionic center, which was deactivated *in situ* with 1-(4-bromobutyl)-4-(*tert*-butyldimethylsilyloxymethyl)benzene. The silyl ether groups were further transformed to BnBr moieties by treatment with LiBr/$(CH_3)_3SiCl$. Using the PS-(BnBr)-PS intermediate, the coupling and transformation reactions in the iterative reaction sequence were repeated four more times to synthesize the PS-$(BnBr)_n$-PS ($n = 2, 4, 8, 16$) in-chain functionalized polymers. Subsequent coupling with living PS chains end-capped with a DPE unit produced the desired PS-$(PS)_n$-PS ($n = 2, 4, 8, 16$) structures.



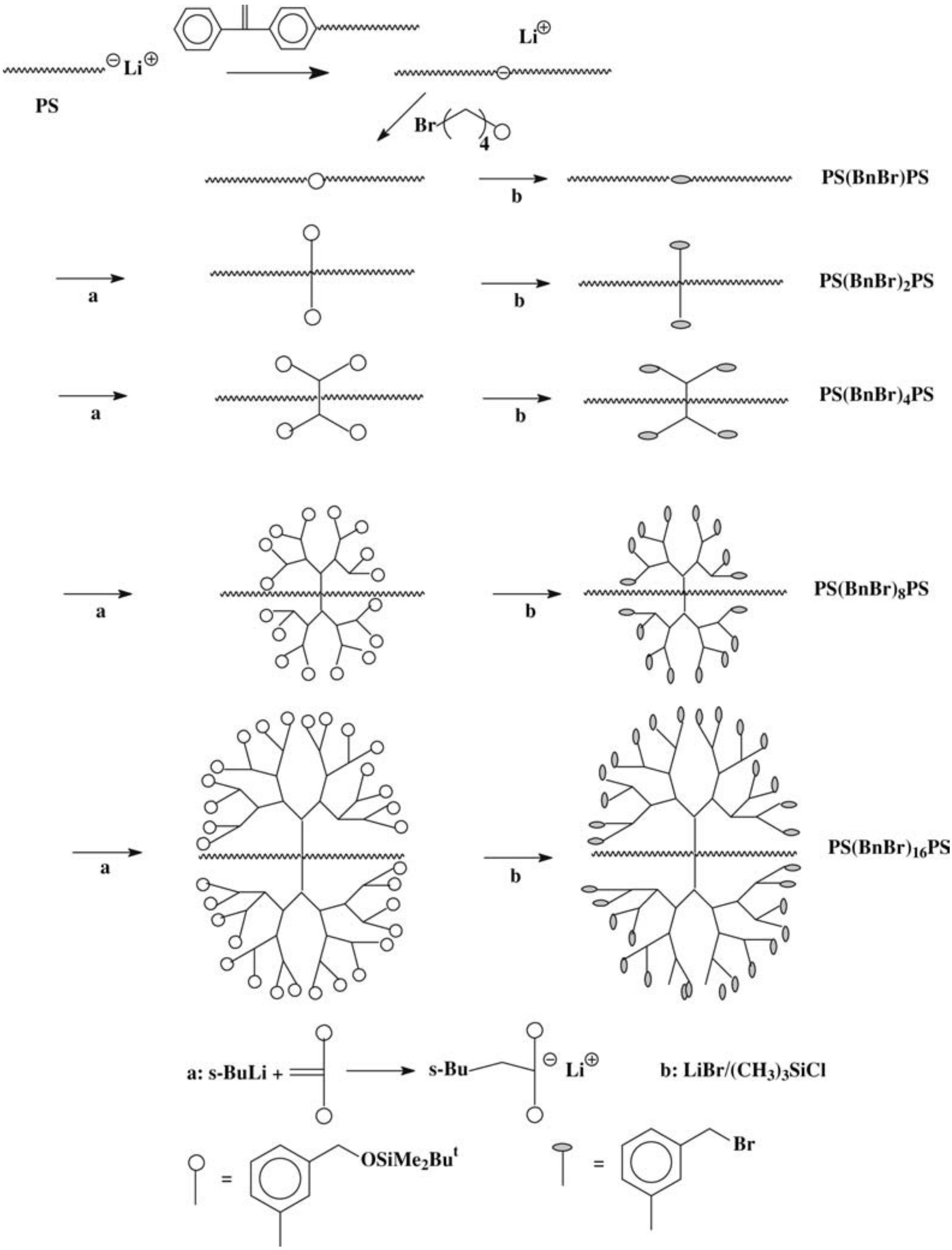
Scheme 7.79

A similar method was adopted for the synthesis of the PS-(PS)$_n$-PS-(PS)$_n$-PS ($n = 2, 4, 8$) polymers. Living PSLi was reacted with an α,ω-chain end-functionalized PS with DPE moieties followed by reaction with 1-(4-bromobutyl)-4-(*tert*-butyldimethylsilyloxymethyl)benzene to deactivate the generated two anionic sites. The same procedure as previously reported was employed for the introduction of BnBr functions, and by employing the iterative reaction sequence, the synthesis of the PS-(BnBr)$_n$-PS-(BnBr)$_n$-PS ($n = 2, 4, 8$) functionalized polymers was achieved. Coupling with PSLi end-capped with DPE afforded the PS-(PS)$_n$-PS-(PS)$_n$-PS ($n = 2, 4, 8$) structures.

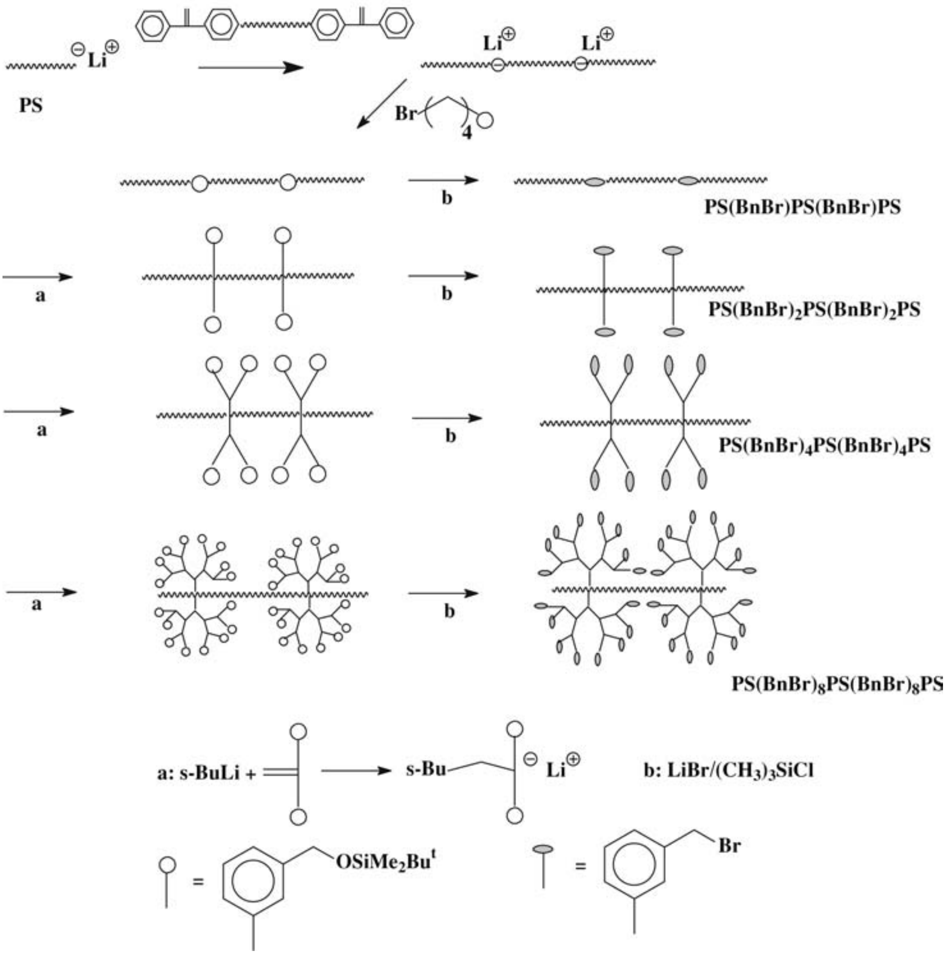
The electrostatic self-assembly and covalent fixation method has been utilized for the synthesis of complex macromolecular architectures, as shown in Scheme 7.82. Telechelic PTHF bearing *N*-phenylpyrrolidinium groups was aggregated with the suitable tetra- and hexacarboxylate counterions in dilute solutions and were subsequently heated to promote the ring opening of the end groups, leading to the covalent fixation of the polymer chains to the carboxylate moiety core and the formation of the desired polycyclic polymers [141, 193].

Θ-shaped PTHF was also obtained by the same method. A trifunctional three-arm PTHF star polymer with *N*-phenylpyrrolidinium end groups was subjected to the covalent conversion process in the presence of a tricarboxylate to afford the Θ-shaped structure [193].

A five-step strategy was reported by Jérôme *et al.* [194] for the synthesis of a two-tail tadpole-shaped copolyester, whose tails were grafted with PEO chains (Scheme 7.83). ε-CL was initially polymerized using the cyclic tin dialkoxide 2,2-dibutyl-2-stanna-1,3-dioxepane. A small amount of α-(1-acryloxyethyl)-ε-caprolactone (αAεCL) was subsequently added to incorporate a few monomer units. The pendant acrylic unsaturated units were then subjected to cross-linking reaction by UV irradiation, leading to a macrocyclic polyester free of any endocyclic tin alkoxide. This structure was further employed as a macroinitiator for the copolymerization of ε-CL and α-chloro-ε-caprolactone (αClεCL). The side chloride groups were quantitatively transformed into azides


PS
Li⊕
Br
4
PS(BnBr)PS
PS(BnBr)₂PS
PS(BnBr)₄PS
PS(BnBr)₈PS
PS(BnBr)₁₆PS
a
b
a: s-BuLi +
s-Bu
Li⊕
b: LiBr/(CH₃)₃SiCl
=
OSiMe₂Buᵗ
Br

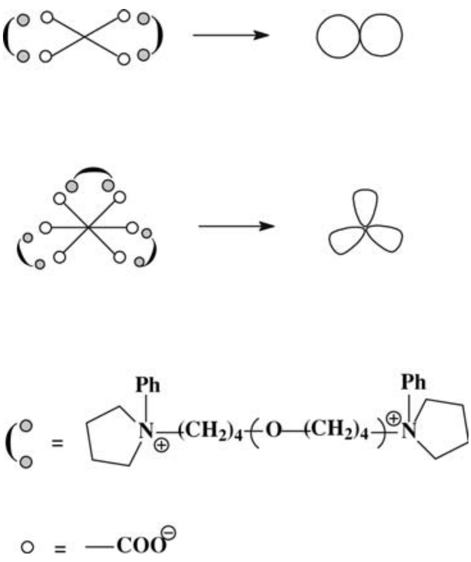
Scheme 7.80



Scheme 7.81

through reaction with sodium azide, without degrading the polyester chains. Alkynyl end-capped PEO was prepared by esterification of the end hydroxyl group of PEO monomethyl ether with 4-pentynoic acid in the presence of DCC and DMAP. The azide groups of the tadpole-shaped copolyester were finally subjected to ''click'' reaction with the alkynyl end-capped PEOs in the presence of CuI and triethylamine. It was found that each arm of the copolyester was grafted with 53 PEO chains. SEC analysis revealed that rather broad MW distributions were obtained.

This work was further expanded to the synthesis of eight-shaped tadpole copolyesters with each arm being grafted with PEO chains [195] (Scheme 7.84).



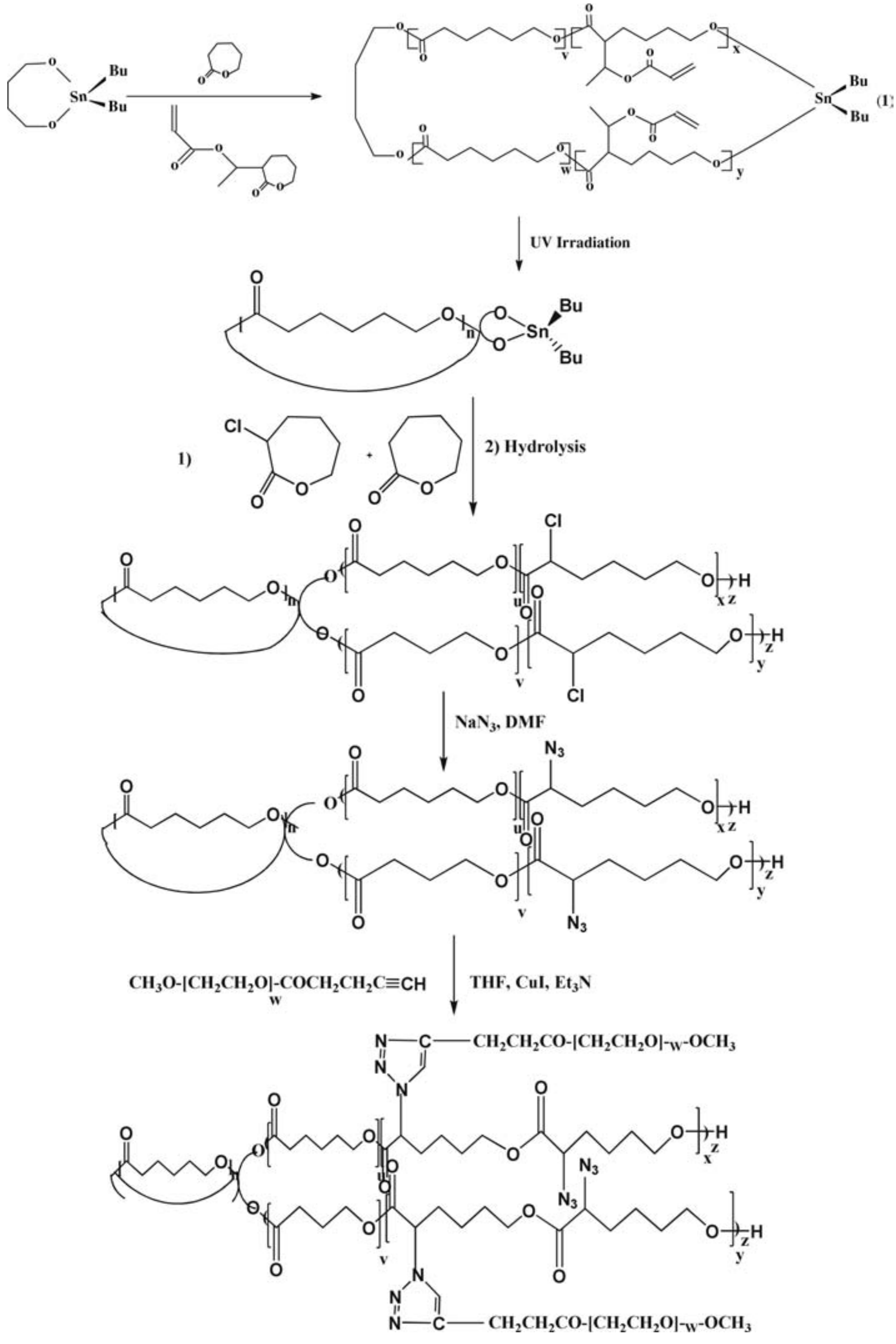
Scheme 7.82

The spirocyclic initiator **1** was employed for the polymerization of ε-CL, followed by the addition of αAεCL to form a short block. UV irradiation was then performed to cross link the acrylic pendant groups followed by the hydrolysis of the endocyclic tin alkoxides, thus providing ‘‘8’’-shaped copolyesters having four available hydroxyl groups, which can be subsequently used for the copolymerization of ε-CL and αClεCL. The chlorine moieties were converted to azides, as previously reported, and were then subjected to ‘‘click’’ reaction with alkynyl end-capped PEOs to afford the desired tadpole structures. The grafting efficiency at the final synthetic step was found to be equal to 61%. The products were characterized by rather broad MW distributions.

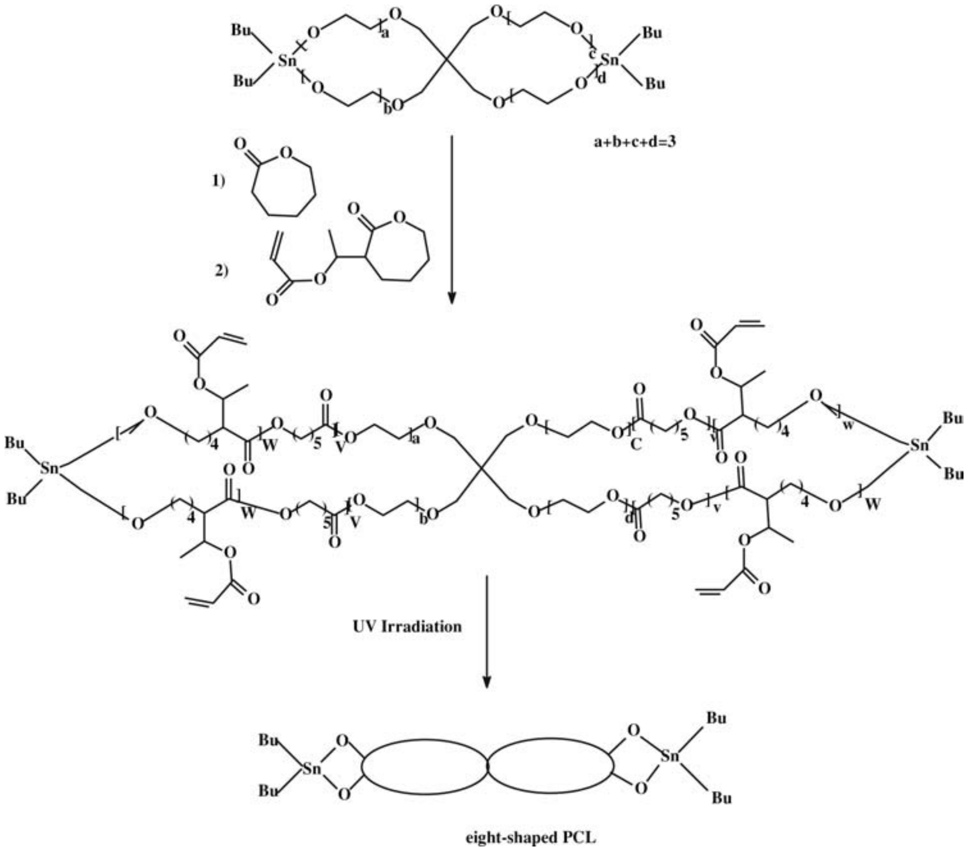
The same spirocyclic initiator 1 was used for the polymerization of ε-CL followed by the addition of a mixture of ε-CL and αClεCL. The tin alkoxides were subsequently hydrolyzed, leading to the synthesis of four-arm star-block copolymers. The pendant chlorine groups were then transformed to azides and reacted with alkynyl end-capped PEOs in a similar fashion, as previously reported, giving the final star-graft copolymers (Scheme 7.85).

7.7
Applications

The well-defined molecules presented above, with high MW, as well as structural and compositional homogeneity, could find many industrial applications, but their transfer to industrial production is difficult. The demanding synthetic procedures, in particular for living anionic polymerization, are not readily applied in industrial settings, thus justifying the limited number of industrial


Bu
Sn
Bu
v
x
w
y
(1)
UV Irradiation
n
1)
Cl
2) Hydrolysis
u
z
NaN3, DMF
N3
CH3O-[CH2CH2O]-COCH2CH2C≡CH
w
THF, CuI, Et3N
CH2CH2CO-[CH2CH2O]-W-OCH3
H

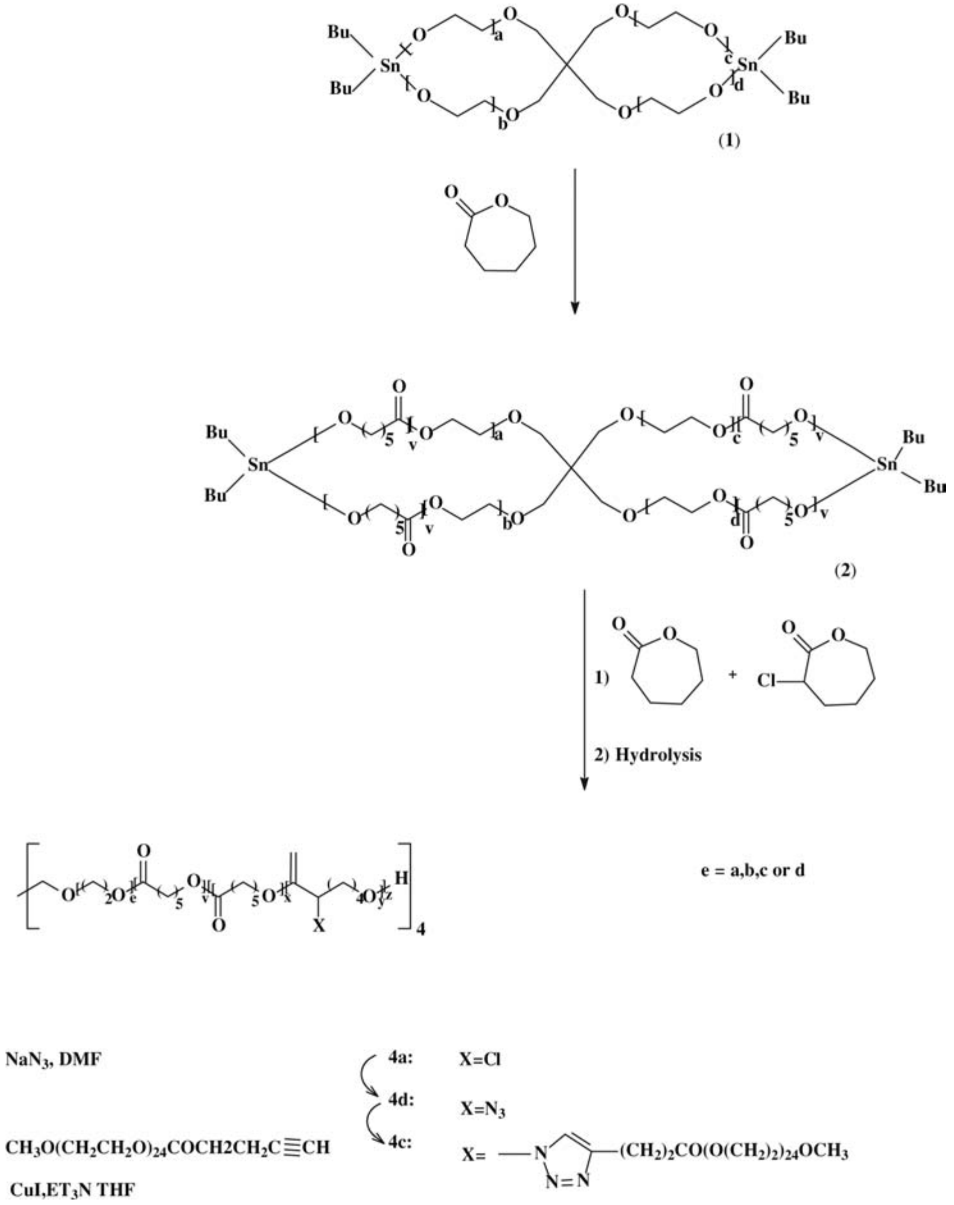
Scheme 7.83



Scheme 7.84

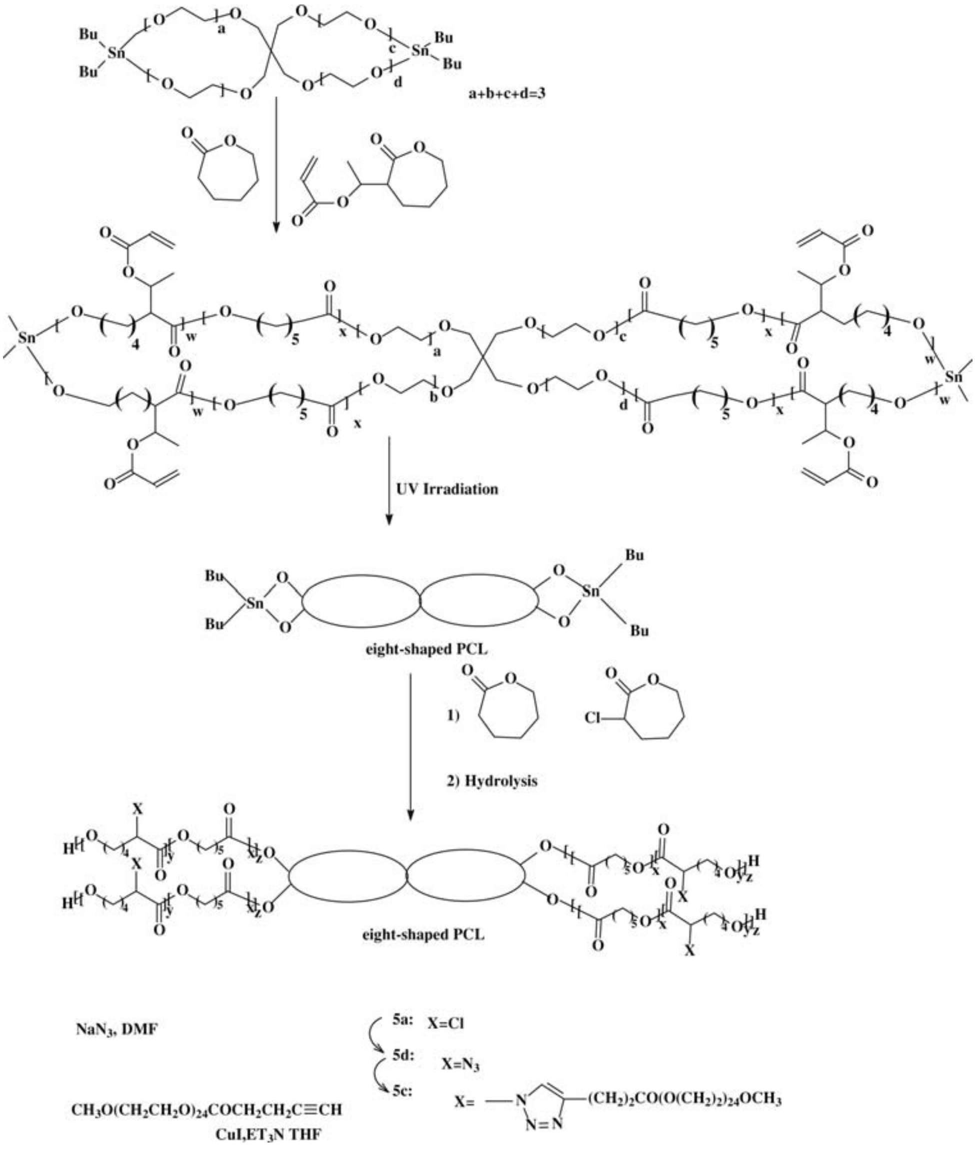
polymeric products in use. For example, star-block copolymers of butadiene and styrene, symmetric (e.g., Solprene) and asymmetric (e.g., Styrolux), have found commercial applications as adhesives and sealants, as blending agents of different homopolymers for producing materials with different properties, as surface modifiers for fillers and fibers to improve dispensability in the matrix, as surfactants for phase stabilization, as viscosity improvers of lubricating oils, as membranes for desalination, in biomedical applications, etc [196].

Well-defined molecules are mainly used to establish structure–property relationships, to select the appropriate structure for a particular application. The preparation of such selected materials is subsequently adapted to industrial conditions, by means of either a similar or different synthetic methodology. For example, low density polyethylene (LDPE), used for plastic film production, is easily processed in extruders and possesses good bubble stability, but the final film does not have the mechanical strength required for certain products. On the other hand, high density metallocene polyethylene (mPE) films are



Scheme 7.84 (*continued*).

characterized by high strength, but low processability. The question is, how can mPE processability be improved by mixing with appropriate additives? To answer this question, PBds with different macromolecular architectures (star, H-shape, super-H, pom–pom, and comb) have been synthesized by anionic



Scheme 7.85

polymerization high vacuum technique and appropriate linking chemistry, followed by hydrogenation, to produce the corresponding PEs. Shear [197] and elongational viscosity studies [198,199] were carried out on these PEs and on their mixtures with mPE (3%) to determine the shear thinning (η_0/η^*, where η_0 is the zero shear viscosity and η^* the complex viscosity at 100 rad s^{-1} at 190 °C, standard industrial film extrusion conditions) and the strain hardening ($\eta_{\text{ext}}/\eta_{\text{ext,lin.}}$ where η_{ext} is extensional viscosity and $\eta_{\text{ext,lin.}}$ the extensional viscosity predicted by linear viscoelasticity at strain rate: 1 s^{-1}; time: 3 s; and T: 190 °C). It should be noted that the higher the shear thinning, the easier the extrudability; and the higher the strain hardening, the higher the bubble stability. From these rheological studies, the mixture of mPE and PE comb (3%) was found to be the most appropriate. For the industrial synthesis of the PE comb, rather than applying anionic polymerization high vacuum techniques an alternative methodology involving the copolymerization of an ethylene-macromonomer with ethylene was used.

Thus, the ability of living and controlled/living polymerizations to produce a wide variety of well-defined architectures has made it an invaluable tool to enable us to understand the behavior and improve the properties of industrially important polymeric materials.

7.8
Conclusions

The rich variety of macromolecular architectures (star, comb, cyclic, dendritic, hyperbranched, and other complex-branched) described in this chapter represents only a small fraction of those structures achievable from living and controlled/living polymerization methods. The seed that Szwarc sowed 55 years ago gave fruit not only to developments in polymer chemistry, but also in other branches of polymer science including polymer physics and materials science, and enabled us to understand the behavior and improve the properties of industrially important polymeric materials.

List of Symbols and Abbreviations

AcOVE	Acetoxyethyl vinyl ether
AIBN	azo-α,α'-Diisobutylnitrile
BDPEP	2,2-Bis[4-(1-phenylethenyl)phenyl]propane
BDTEP	2,2-Bis[4-(1-tolylethenyl) phenyl]propane
BnBr	Bromomethylphenyl group
BPDMA	Bisphenol A dimethacrylate
CDMSS	4-(Chlorodimethylsilyl)styrene
DFM	Difunctional monomers
DLS	Dynamic light scattering
DPE	1,1-Diphenylethylene
ε-CL	ε-Caprolactone
EGDM	Ethylene glycol dimethacrylate
IR	Infrared spectroscopy
Is	Isoprene
LA	Linking agent

LALLS	Low-angle laser light scattering
LS	Light scattering
MDDPE	1,3-Bis(1-phenylethenyl)benzene
MFI	Multifunctional initiator
MFLA	Multifunctional linking agent
M_n	Number-average molecular weight
MO	Membrane osmometry
M_w	Weight-average molecular weight
M_w/M_n	Molecular weight distribution
N_A	Avogadro's number
n-BuLi	*n*-Butyllithium
NCA	*N*-carboxyanhydride
NMR	Nuclear magnetic resonance
NMP	Nitroxide mediated polymerization
P2VP	Poly(2-vinylpyridine)
P4VP	Poly(4-vinylpyridine)
PAMAM	Polyamidoamine dendrimers
PBd	Polybutadiene
PBLG	Poly(γ-benzyl-L-glutamate)
PCL	Poly(ε-caprolactone)
PDDPE	1,4-Bis(1-phenylethenyl)benzene
PE	Polyethylene
PEG	Poly(ethylene glycol)
PEO	Poly(ethylene oxide)
PI	Polyisoprene
PIB	Polyisobutylene
PIBVE	Poly(isobutyl vinyl ether)
PLL	Poly(L-lysine)
PMMA	Poly(methyl methacrylate)
PMVE	Poly(methyl vinyl ether)
P*n*BuA	Poly(*n*-butyl acrylate)
PS	Polystyrene
P*t*BuA	Poly(*tert*-butyl acrylate)
P*t*BuMA	Poly(*tert*-butyl methacrylate)
PZLL	Poly(ε-benzyloxycarbonyl-L-lysine)
RAFT	Reversible addition-fragmentation chain transfer
RI	Refractive index
ROMP	Ring opening metathesis polymerization
ROP	Ring opening polymerization
SANS	Small-angle neutron scattering
s-BuLi	*sec*-Butyllithium
s-BuOLi	*sec*-Lithium butoxide
SEC	Size exclusion chromatography
t-BuLi	*tert*-Butyllithium
TEMPO	2,2,6,6-Tetramethyl-1-piperidinyloxy stable radical

THF	Tetrahydrofuran
UV	Ultraviolet spectroscopy
VBC	Vinyl benzyl chloride
VOEM	2-(Vinyloxy)ethyl malonate

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8
Synthesis of Block and Graft Copolymers

Constantinos Tsitsilianis

8.1
Introduction

The most important achievement of the "living"/controlled polymerization methods is the synthesis of tailor-made block copolymers with specific macromolecular architecture, chemical composition/functionality, and low molecular polydispersity and heterogeneity. The beauty of these macromolecular species is that, in most of the cases, they self-assemble to nanostructured polymeric materials carrying the properties of the parent homopolymer blocks they originate from. The huge interdisciplinary endeavor dedicated to the development of block copolymers through the last decades is justified by the defensible expectations for novel applications in advanced technologies such as nanotechnology [1] and biomedicine [2].

The simplest and most widely studied type of block copolymer is the AB diblock, where only two building blocks of different nature are joined together by a single covalent bond. Very soon, just after the establishment of "living" anionic polymerization by Szwarc *et al.* [3], a new ABA triblock architecture appeared. This polymeric structure led to very interesting polymeric materials (thermoplastic elastomers, TPEs), when a relatively long elastomer such as polyisoprene (PI) is end-capped by shorter glassy polystyrene (PS) blocks. From this architecture, the concept of *topology* (i.e., from the Greek word *τόπος* meaning place, position) was introduced and consecrated as a key factor for the designing of block copolymers with specific macroscopic properties. In the ABA type TPEs, for instance, the soft block must be placed in the center.

Since then, novel macromolecular architectures constituted of more than two building blocks in linear and branched modes, such as for instance ABABA pentablock, ABC terpolymers, and/or ABCD quaterpolymers, star-shaped and graft copolymers, have been prepared. All this scientific evolution demonstrated the great importance of macromolecular engineering and motivated the polymer chemist to develop new synthetic controlled

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polymerization methods such as atom transfer radical polymerization (ATRP) [4], nitroxide-mediated polymerization (NMP) [5], group transfer polymerization (GTP) [6], reversible addition-fragmentation chain transfer (RAFT) [7], and ring-opening metathesis polymerization (ROMP) [8], targeting to create block copolymers comprising any type of monomer and prepared under less demanding polymerization conditions.

In this chapter, the synthetic strategies based on controlled/living polymerization techniques that lead to well-defined linear AB, ABA, and $(AB)_n$ multiblock copolymers, ABC and ABCBA terpolymers, ABCD quaterpolymers, as well as graft copolymers of various types are demonstrated. Other multisegmental star-shaped block copolymers/terpolymers and even more complicated architectures, such as polymeric brushes star-shaped terpolymers and dendrimers, are presented in Chapter 7. Details on the bulk and solution properties of block copolymers are given in Chapter 9. Owing to space limitations, only the basic synthetic routes and selected examples can be presented.

8.2
Principles of Block Copolymerization

The use of "living"/controlled polymerization techniques is the most convenient and efficient methodology to prepare block copolymers. Four main synthetic routes have been developed (Figure 8.1) to prepare well-defined diblock copolymers with narrow molecular weight distribution and very low compositional heterogeneity.

A straightforward method is the sequential monomer addition that can be performed in a one-pot polymerization reaction (Figure 8.1a). Provided that termination and/or transfer reactions are negligible, after the consumption of the first monomer the remaining active sites at the chain ends must be able to initiate the polymerization of the new incoming second monomer. This

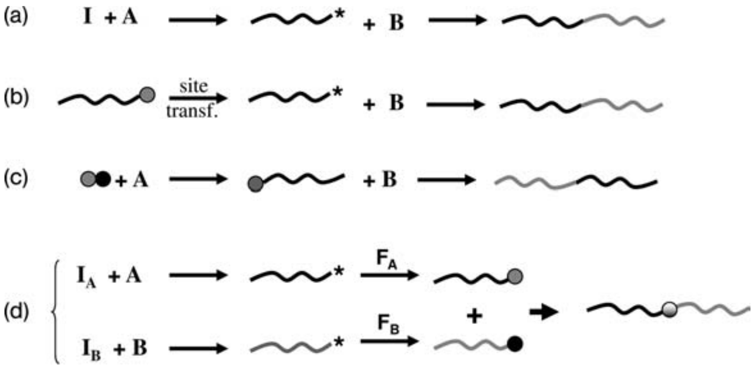


Figure 8.1 Schematic representation of synthetic strategies toward AB diblock copolymers: (a) sequential monomer addition, (b) site-transformation technique, (c) by dual initiator, and (d) by coupling ω-functional polymers. I: initiator, F: functionalization agent, $*$: active site.

crossover reaction must proceed fast and quantitatively to prevent undesirable large fluctuations in monomer composition of the growing copolymers. To achieve the latter, a specific order of monomer addition is usually required that depends on the chosen polymerization technique, i.e., anionic, radical, etc.

The second copolymerization process (a variant of sequential monomer addition) is the so-called site-transformation technique which is applied in the case when the involved monomers cannot undergo polymerization with the same type of active sites (Figure 8.1b). This strategy usually requires a sequence of transformation reactions to convert the propagation site of the first block into the suitable initiating site for the polymerization of the second monomer. Since the reaction conditions (e.g., medium nature and temperature) are specific for the different polymerization mechanisms, the copolymerization proceeds in a two-pot reaction.

The third route involves the use of a dual bifunctional initiator that is able to start simultaneously the polymerization of two monomers by different polymerization chemistries in such a way that this initiator remains attached to each type of growing chain (Figure 8.1c). The two active sites must be compatible and tolerate each other.

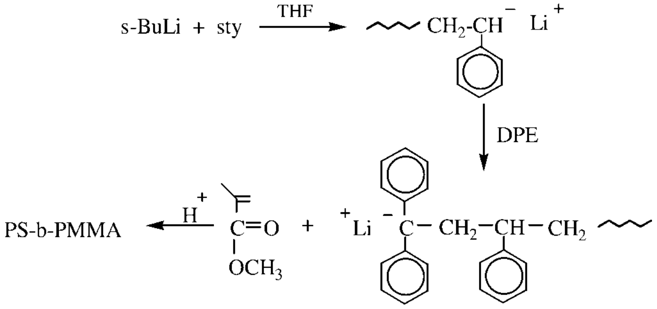
The fourth synthetic route relies on the coupling reaction of two different ω-functional homopolymers (Figure 8.1d). Apparently, the different functions of the chain ends must be highly reactive.

8.2.1
AB by Anionic Polymerization

Anionic ‘‘living’’ polymerization is the oldest polymerization method suitable for macromolecular engineering and has inspired polymer chemists to develop new controlled polymerization techniques that are carried out with different mechanisms. Anionic polymerization proceeds via organometallic sites (carbanions or oxanions) through nucleophilic reactions in aprotic media. After the wide use of protective monomers and post-polymerization chemical modifications, the versatility and potentiality of this method toward novel model block copolymers have been significantly expanded.

Two conditions have to be fulfilled to obtain well-defined diblock copolymers by anionic polymerization and sequential monomer addition: (i) the nucleophilicity of the macroanion A^- must be high enough to initiate the incoming monomer B without attacking its pendant groups (e.g., ester group of acrylates) and (ii) the initiation must be faster than the propagation rate of the second monomer. To fulfill these requirements, the monomers must be added sequentially in the order of increasing electron affinity (e.g., α-methyl styrene $<$ styrene $\approx$ butadiene $<$ vinyl pyridine $<$ methyl methacrylate (MMA)), and the nucleophilicity of the carbanion A^- should match with the incoming B monomer (though not as high) to avoid side reactions.

A nice example is the synthesis of polystyrene-*b*-poly(methyl methacrylate) (PS-PMMA) block copolymers [9]. According to Scheme 8.1, styrene is



Scheme 8.1

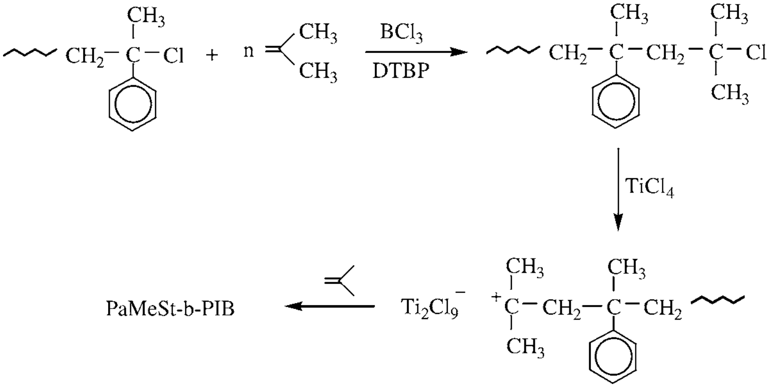
polymerized first using *s*BuLi as initiator. Since the nucleophilicity of polystyryl carbanions is very high for MMA, an intermediate addition of 1,1-diphenylethylene (DPE) is needed to avoid attack on the ester function of MMA. The advantage of DPE addition relies on the fact that is does not propagate; therefore, addition of this monomer in excess provides quantitative capping of the active sites.

Attempts to reverse the order of addition have also been reported by boosting the reactivity (nucleophilicity) of the propagating species through chemical modification. An example of this synthetic pathway is the preparation of PEO-*b*-PS block copolymer, which, however, exhibits relative broad molecular weight distribution. Thus, it was shown that living potassium poly(ethylene oxide) ($PEO^{-}K^{+}$) is capable of polymerizing styrene when converted into potassium silyl anion by reaction with 1,1,2-trimethyl-2-phenyl-1,2-disilacyclobutane functioning as an original reactivity booster of the oxyanions [10].

8.2.2
AB by Cationic Polymerization

Tailor-made block copolymers constituted of important monomeric units that cannot be polymerized by other methods such as isobutylene (IB) and alkyl vinyl ethers (VEs) can be afforded by "living" cationic polymerization (LCP) broadening hence the potentiality of macromolecular engineering [11]. Cationic polymerization proceeds through carbenion (or oxonium) sites in a controlled/living mode if appropriate conditions such as initiation/co-initiation (Lewis acid), additives, solvent, and temperature, have been chosen.

For a successful crossover reaction in the sequentially monomer addition process (i.e., fast initiation of the second monomer from the macrocations of the first one), in principle the monomers have to be added from the more reactive (more nucleophilic) to the less reactive species (e.g., VEs > α-methyl styrene > styrene > IB). The monomer reactivity order in cationic



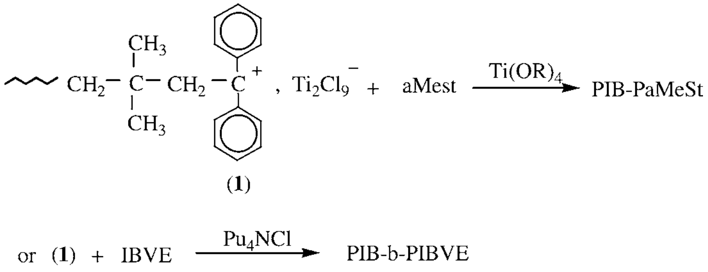
Scheme 8.2

polymerization is based on the electron-donating ability of the pendant groups of the vinylic double bond. However, this is not enough, as in anionic polymerization and in most of the cases tuning of the Lewis acidity is also required. The synthesis of poly(α-methylstyrene)-*b*-poly(isobutylene) (PαMeSt-*b*-PIB) is a characteristic example (Scheme 8.2).

As shown in Scheme 8.2, in the first step cationic polymerization of αMeSt under "living" conditions is achieved in the presence of BCl_3 in methylcyclohexane–MeCl (60 : 40, v/v) solvent mixture at −80 °C. In the second step, the addition of IB results in a fast and quantitative crossover to IB sites, which, however, are not activated enough to propagate the IB polymerization (instantaneous deactivation). Upon addition of a stronger Lewis acid ($TiCl_4$), IB propagation occurs, leading to PαMeSt-*b*-PIB diblock copolymer [12].

The aforementioned order of monomer addition in carbocationic polymerization is not inviolable. Block copolymers can be synthesized initiating with the less reactive monomer by using intermediate capping reaction of the first living block with non-homopropagating monomers such as DPE or 1,1-ditolylethylene (DTE). For instance, IB can be copolymerized sequentially with the more reactive *a*MeSt [13] or isobutyl vinyl ether (IBVE) [14]. In such cases, the capping reaction must be followed by tuning of the Lewis acidity to the reactivity of the second monomer to generate more nucleophilic counterions, which ensures fast initiation and living polymerization of the second incoming monomer (Scheme 8.3).

Efficient crossover can also be achieved in sequential LCP when the involving monomers exhibit similar reactivities. Characteristic examples can be found in the case of alkyl VEs [15]. Recently, interesting thermo-responsive double hydrophilic block copolymers comprising a lower critical solution temperature (LCST) type block has been prepared by using VE type monomers. This copolymer undergoes micellization in aqueous solutions by increasing temperature above the LCST of the responding block [16].



Scheme 8.3

8.2.3
AB by Controlled Radical Polymerization

After the advent of controlled radical polymerization techniques, new horizons have opened toward macromolecular engineering. ATRP, RAFT, and NMP are nowadays very promising controlled polymerization mechanisms that can be utilized to prepare tailor-made block copolymers bearing very important monomer units (e.g., *N*-isopropyl acrylamide, NIPAAm) that could not be achieved earlier.

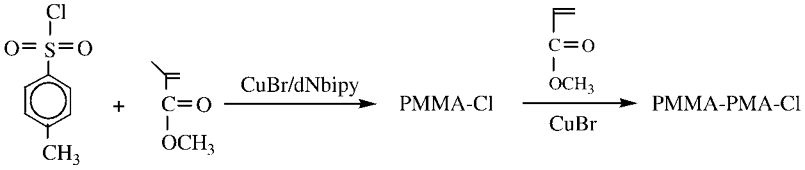
8.2.3.1 **AB by ATRP**

Polymer chain ends fitted by an alkyl halide enable ATRP to prepare AB block copolymers. This can be achieved either by reactivating the active sites of an isolated macroinitiator (dormant homopolymer) or by *in situ* addition of a second monomer (sequential monomer addition) [17]. Since it is advantageous in ATRP not to go to full conversion to minimize termination and dehydrohalogenation of chain ends, the second approach can lead to a second block that is a random copolymer of the residual first monomer and the added second monomer.

In principle, order of monomer addition is required in ATRP that follows radical stabilities (e.g., acrylonitrile > methacrylate (MAs) > styrene ≈ acrylates > acrylamides).

For instance, in the synthesis of acrylate–methacrylate block copolymers, a straightforward procedure dictates to initiate with the polymerization of the methacrylate monomer MMA. The poly(methyl methacrylate) (PMMA) macroinitiator with a chlorine terminal can efficiently initiate the polymerization of methyl acrylate (MA), resulting in a well-defined PMMA-*b*-PMA diblock copolymer (Scheme 8.4). The opposite order of monomer addition can be performed if the halogen exchange technique is employed, i.e., PMA-Br macroinitiator and CuCl as catalyst [18].

Block copolymerization within the same class of monomers such as MAs, acrylates, or styrenes can proceed regardless of the order of monomer addition, e.g., PMMA-*b*-PBMA (PBMA: poly(butyl methacrylate)) [19].



Scheme 8.4

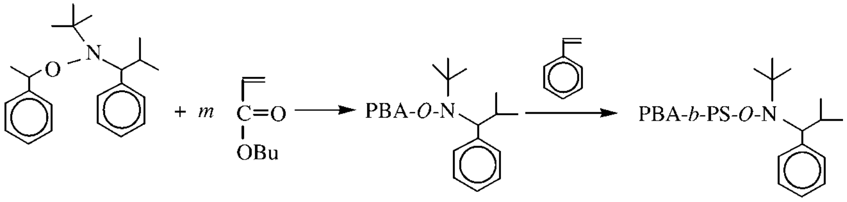
8.2.3.2 AB by NMP

The advent of second-generation alkoxyamines [20a], which are suitable for the polymerization of a range of monomer families, has enabled nitroxide-mediated controlled radical polymerization to synthesize a broad range of block copolymers [20b]. Again, the order in monomer addition is important as demonstrated in the preparation of styrene–acrylate block copolymers. Successful synthesis of such block copolymers can be achieved starting with the acrylate block (Scheme 8.5). The reverse strategy gives a block copolymer contaminated by PS homopolymers.

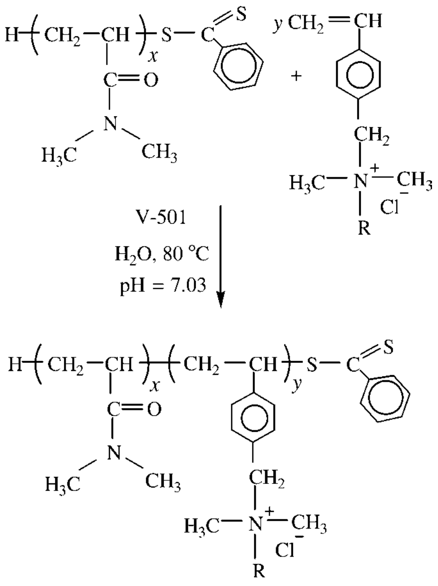
8.2.3.3 AB by RAFT

The RAFT process involves conventional free radical polymerization (FRP) of a monomer in the presence of a suitable chain transfer agent (CTA). Through careful selection of the CTA, initiator, and monomers, controlled copolymerization in aqueous media can be performed, yielding very interesting water-soluble block copolymers bearing functional moieties [21]. In contrast to all other living polymerizations involving sequential monomer addition, the RAFT process does not use a macroinitiator but a macro-CTA.

In the case that an AB diblock copolymer is constituted of monomers belonging to different families (e.g., styrenic and acrylamides), the order in monomer addition must be taken into account. A characteristic example of such a block copolymer synthesis is demonstrated in Scheme 8.6. The copolymerization reaction proceeds in two steps. First, a poly(*N*, *N*-dimethylacrylamide) (PDMA) macro-CTA was prepared. In a subsequent step, PDMA-CTA was used as macro-CTA initiator to polymerize successfully the second monomer *N*, *N*-dimethyl vinyl benzylamide (DMVBA). The



Scheme 8.5



Scheme 8.6

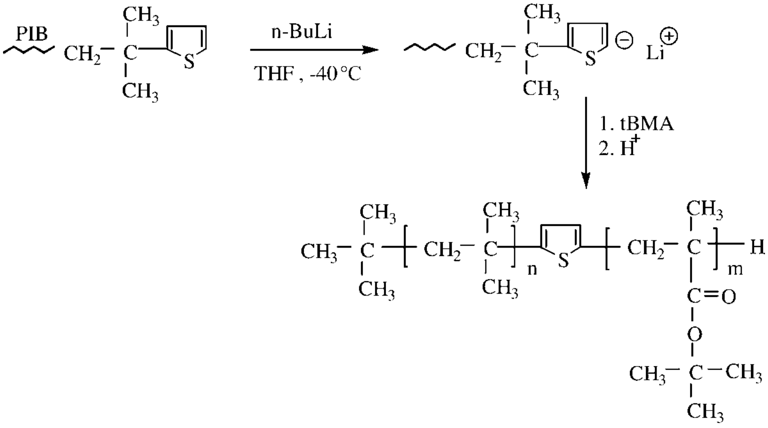
block copolymer is free from homopolymer. The opposite pathway (i.e., PDMVBA-CTA initiator for *N, N*-dimethylacrylamide (DMA)) has failed to yield monomodal copolymer distribution, which was attributed to slow fragmentation of the intermediate radical and/or to poor reinitiation efficiency of the styrenic macroradical.

8.2.4
AB by Combination of Methods

8.2.4.1 **Site-Transformation Reactions**

Block copolymers involving monomers that cannot undergo polymerization with the same type of active sites can be prepared through the so-called site-transformation technique. This technique usually requires functionalization of the first polymeric block. The prerequisite for a successful block copolymerization is that the end function of the A polymer precursor should be capable of generating a new site, the reactivity of which has to be matched with the incoming monomer, and the reaction must be carried out in a common solvent for both blocks.

A relative recent example of site-transformation method comprising living carbocationic and anionic polymerization is the synthesis of poly(isobutylene)-*b*-poly(*tert*-butyl methacrylate) PIB-*b*-P*t*BMA [22]. The synthetic route involves quantitative functionalization of living poly(isobutylene) (PIB) with thiophene and the subsequent metalation of end-groups with *n*-butyl lithium, which

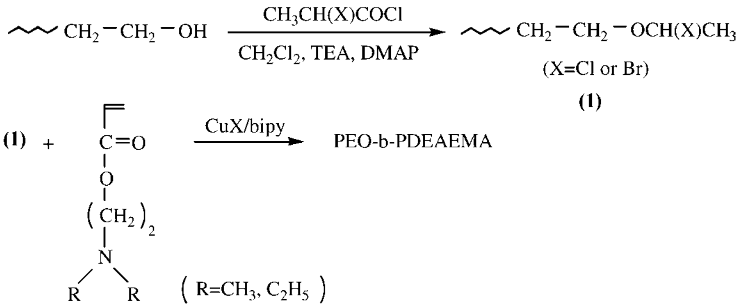


Scheme 8.7

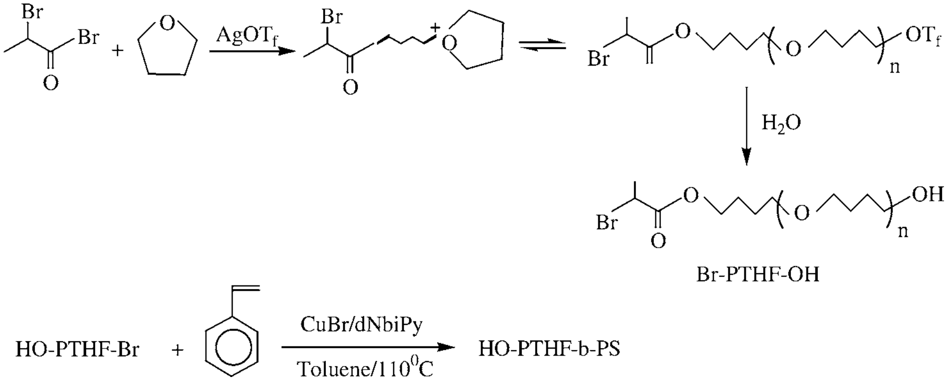
yields stable PIB macrocarbanions suitable for the polymerization of MAs (Scheme 8.7)

Interesting double hydrophilic diblock copolymers bearing a poly(ethylene oxide) (PEO) biocompatible nonionic block and a potentially cationic polyelectrolyte block are a nice example of a synthetic pathway combining anionic ring-opening polymerization (ROP) with ATRP. The monofunctional PEO made anionically is transformed to an ATRP initiator by reacting the OH end group with 2-chloropropionyl chloride in the presence of 4-(dimethylamino)pyridine (DMAP) and triethylamine (TEA) (Scheme 8.8).

The so-formed ATRP macroinitiator can be used to polymerize MA monomers bearing tertiary amine pendant groups that can be protonated in acidic aqueous systems yielding polyelectrolyte sequences of pH-tunable degree of ionization [23]. This type of reaction (i.e., OH transformation to ATRP initiator) opened opportunities for macromolecular engineering leading to graft and star-block copolymers [17].



Scheme 8.8



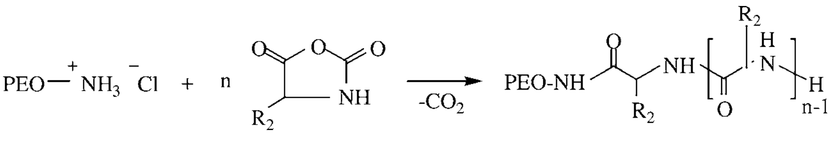
Scheme 8.9

By using bromopropionyl bromide/silver triflate initiating system, a bromopropionyl a-functionalized poly(tetrahydrofurane) (PTHF) bearing OH end function was prepared by LCP. The bromopropionate function was subsequently used for the ATRP polymerization of various monomers (e.g., styrene, MA, MMA) in the presence of CuBr/dNbipy (4,4′-di-5-nonyl-2,2′-bipyridine) catalyst, yielding the corresponding PTHF-based diblock copolymers (Scheme 8.9) [24].

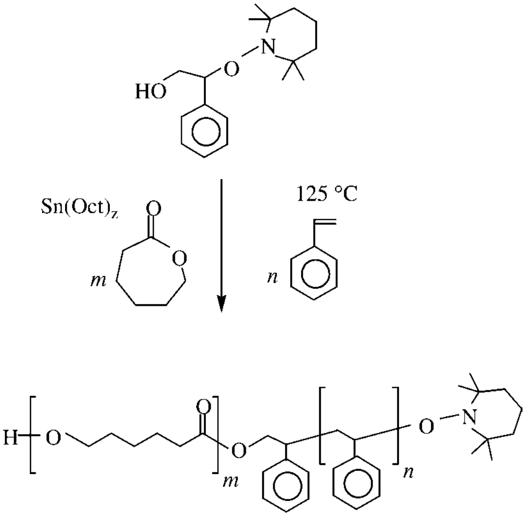
Well-defined diblock copolymers comprising polypeptide conjugates can be prepared by combining anionic ROP of oxirane with the coordinative ROP of α-amino acid *N*-carboxyanydrides (NCAs). A successful attempt was the synthesis of PEO-*b*-polypeptides using anionically synthesized PEO fitted at its end by ammonium chloride, which can polymerize γ-benzyl-L-glutamate or γ-benzyl-L-aspartate in a controlled manner (Scheme 8.10) [25].

8.2.4.2 **By Using Dual Initiator**

Simultaneous controlled polymerization of two monomers by different mechanisms (i.e., ROP and NMP) in an one-pot reaction was possible by using a double-head (dual) initiator [26]. According to Scheme 8.11, the initiator bears a single primary alcohol functionality, which is the initiation center for the anionic ROP of cyclic lactones, as well as a secondary benzyl group linked to an alkoxyamine, which is an efficient initiator for the nitroxide-mediated radical polymerization of styrene. Polymerization of styrene (S) and ε-caprolactone (CL) mixture by using this initiator in the presence of Sn(oct)$_2$ (ROP catalyst)



Scheme 8.10



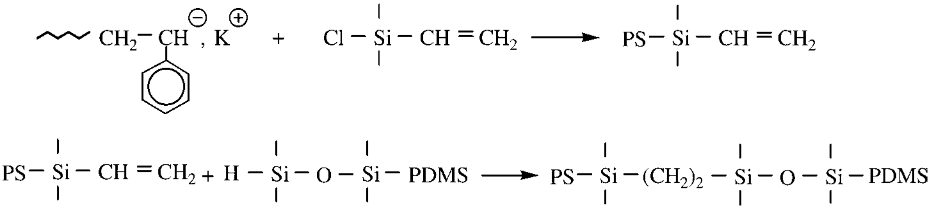
Scheme 8.11

leads to relatively well-defined PS-*b*-PCL block copolymer. Molecular weight determination at various levels of conversion reveals a linear relationship, which agrees with the "living"/controlled nature of both polymerization processes [26].

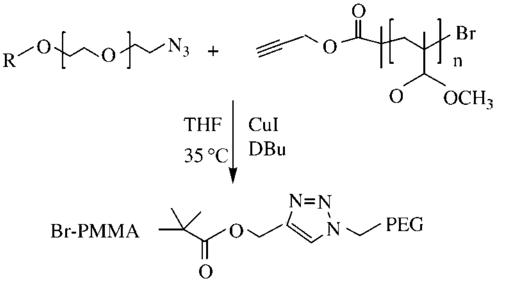
8.2.5
AB by Coupling Reactions

Reactions involving coupling of two different ω-functionalized polymer precursors have also been developed to generate block copolymers. A characteristic old paradigm is the preparation of polystyrene-*b*-polydimethylsiloxane (PS-PDMS) block copolymer that was made by reacting vinyl silane-terminated PS and PDMS fitted at chain end with a Si–H group (Scheme 8.12). Since it involves two incompatible polymers, the mixture was heterogeneous at the beginning, but as block copolymer was forming it progressively became homogeneous. It is noted that the reaction is fast although it takes place at the interface [27].

Recently "click" chemistry has been involved to macromolecular engineering. In general, this strategy relies upon suitable reactive molecular building blocks that can covalently "click" together in a highly selective, fast, and efficient way, under very mild conditions and without any side reactions. The mostly studied 1,3-dipolar cycloaddition reaction occurs between alkynes and azides, and is usually catalyzed by copper ions (being in this case highly regioselective), with the formation of a triazole ring as the cycloaddition product. The



Scheme 8.12



Scheme 8.13

above reaction is considered very suitable to be adopted in the macromolecular field, where triple bonds as well as azide groups (terminal or randomly distributed along the chain) can be easily introduced in the polymer structure as the side chain or end functional group, thus leading to a wide variety of architectures [28].

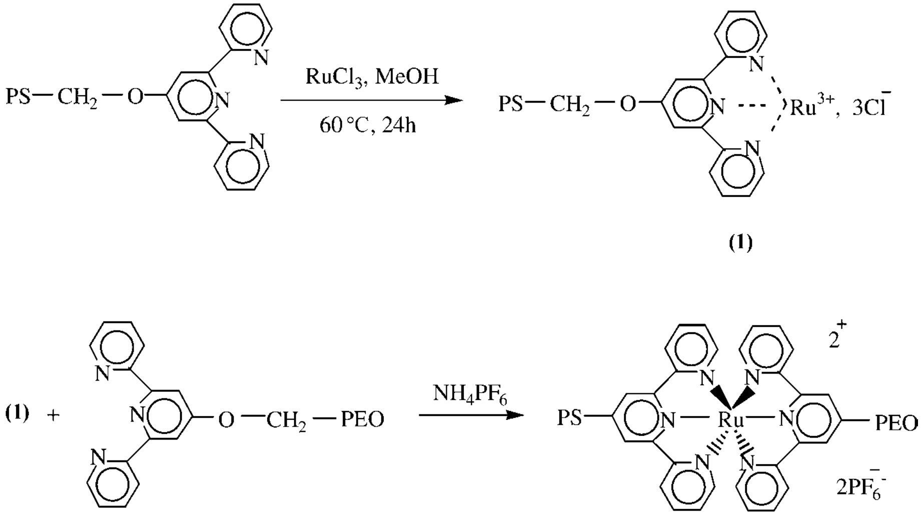
For instance, an alkyne-terminal PMMA reacting with α-azido poly(ethylene glycol) (PEG) in the presence of the CuI/1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) catalytic system afforded well-defined PMMA-*b*-PEG diblock copolymer in high yield (Scheme 8.13) [29].

The examples described above concern coupling of two different prepolymers bearing different reactive end functions. Coupling is also possible by using the same end functions and a highly reactive coupling agent (CA) in a two-step reaction. A characteristic paradigm constitutes coupling of two OH-functionalized homopolymers using diisocyanate as CA. In the first step, one of the precursors is capped with an isocyanate function upon reaction with excess of diisocyanate. In the second step, these functions react with the terminal OH group of the second precursor [30].

A very interesting new pathway to prepare block copolymers using supramolecular chemistry is coupling end/ligand-functional polymers through metal complexation reaction. This route is similar to the previous method exhibiting, however, the advantage that the metal ligand complexes can be broken under specific conditions (e.g., external stimuli) acting therefore as dormant switch [31].

2,2′ : 6′2″-Terpyridine (terPy) ligands fitted at the polymer chain end have been used with $RuCl_3$ to generate block copolymers such as PS-*b*-PEO.

As demonstrated in Scheme 8.14, the complexation reaction takes place in two steps. First, functionalized PEO-terPy was selectively complexed with $RuCl_3$ yielding the mono-complex of Ru(III) (**1**). In the second step, **1** was reacted with PS-terPy under reductive conditions for the transformation of Ru(III) to Ru(II), leading to the formation of PS-[Ru]-PEO diblock copolymer [32].



Scheme 8.14

8.3
ABA Triblock Copolymers

The simplest block copolymer architecture next to the diblock copolymer is the linear ABA triblock. By choosing the right topology of the block constituents (e.g., A hydrophobic, B hydrophilic), very interesting polymeric materials can be fabricated (e.g., associative polymers) the properties of which cannot be exhibited by the diblock counterparts. Depending on the topology of the blocks and irrespective of the chosen polymerization technique, several synthetic strategies have been developed.

8.3.1
Synthetic Strategies

The most straightforward method and widely explored so far is the use of a difunctional initiator. The middle block A is made first, bearing at both ends active sites capable of initiating the polymerization of the second monomer B,

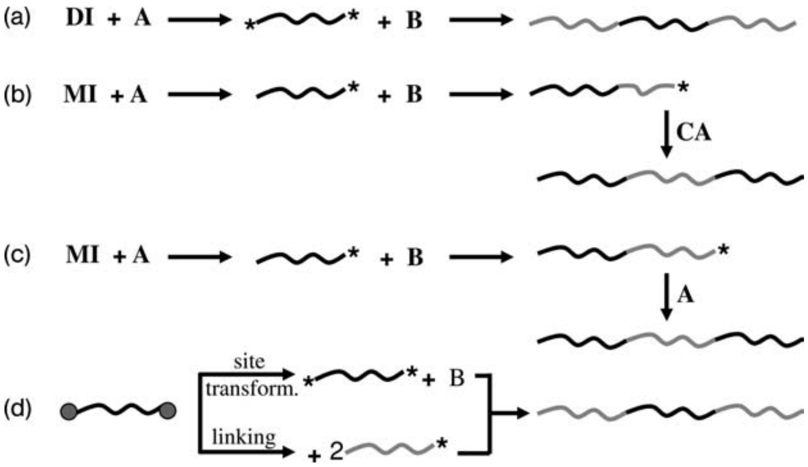


Figure 8.2 Schematic representation of synthetic strategies toward ABA triblock copolymers: (a) by difunctional initiator (DI), (b) using coupling agent (CA), (c) sequential monomer addition, and (d) through α,ω-functional polymer precursor. MI: monofunctional initiator, DI: difunctional initiator, α: active site.

which is added sequentially in the reaction medium after the consumption of the first monomer (Figure 8.2a). The advantage of this procedure is that it can be performed in an one-pot procedure. Moreover, possible A homopolymer contamination of the final product is negligible and easily removable by selective extraction.

In the case where the outer monomer B cannot polymerize the monomer A and has to be placed in the center, a CA must be used. Thus, the reaction proceeds through a monofunctional initiator (MI) and sequential addition of the monomers A and B. After the consumption of the second monomer, the living diblock copolymer is reacted in stoichiometric amount with a difunctional CA (Figure 8.2b). To attain high coupling yield, a small excess of the living diblock is required. In this case, AB diblock residual remains in the final product and can be removed by fractionation. The latter is the major drawback of this route.

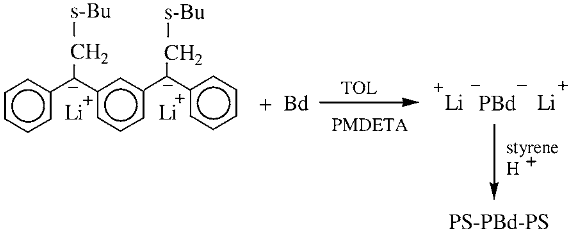
In a third method, sequential monomer addition by using a MI (Figure 8.2c) could be followed only if the electron affinity (reactivity) of both monomers is almost the same. In other words, the macroinitiator that arises from the monomer A can polymerize the monomer B and vice versa. This prerequisite is rare, and only a small number of monomer pairs fulfill this requirement in ionic polymerization. Styrene/dienes in anionic polymerization and different MAs in anionic polymerization or GTP are characteristic examples. The problem is less severe in controlled radical polymerization. The sequential monomer addition route allows, on the other hand, the synthesis of asymmetric ABA triblock copolymers (i.e., outer blocks with different degrees of polymerization).

Finally, ABA can be prepared by involving an α-ω functional polymer precursor (FPP). This procedure is needed when the two monomers cannot be polymerized by the same polymerization technique and have to be carried out in a two-pot reaction (Figure 8.2c). Two subroutes could be distinguished: (i) generation of new sites suitable for the polymerization of the incoming monomer B (site-transformation technique) [33] and (ii) use of the end functions to react with the active sites of a "living" and/or functionalized B block in stoichiometric ratio.

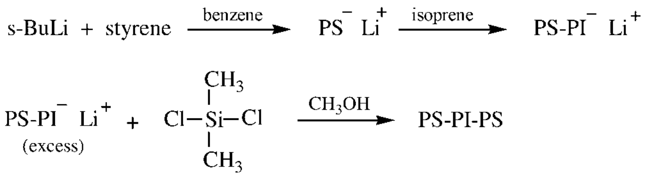
8.3.2
ABA by Anionic Polymerization

Model polystyrene-*b*-polybutadiene-*b*-polystyrene (PS-PBd-PS) or with PI as the center block (typical TPEs) has been synthesized using difunctional initiators in nonpolar media to ensure high 1–4 diene microstructure necessary for the elastomeric properties (Scheme 8.15) [34]. Diadducts of *sec*-butyllithium (*s*BuLi) with diisopropenylbenzene or 1,3-bis(1-phenyl)benzene (PEB) have been used as difunctional initiator. The latter is most advantageous since propagation of PEB during the preparation of the initiator is prevented.

Other synthetic routes have been also studied to prepare PS-PI-PS using, for example, $(CH_3)_2SiCl_2$ dichlorosilane CA (Scheme 8.16) [35]. Another type of TPE constituted of poly(dimethyl siloxane) (PDMS) central block and crystallizable polyethylene (PE) outer blocks has been synthesized by the dichlorosilane CA route and hydrogenation of polybutadiene (PBd) outer blocks of the PBd-PDMS-PBd triblock precursor [36].



Scheme 8.15



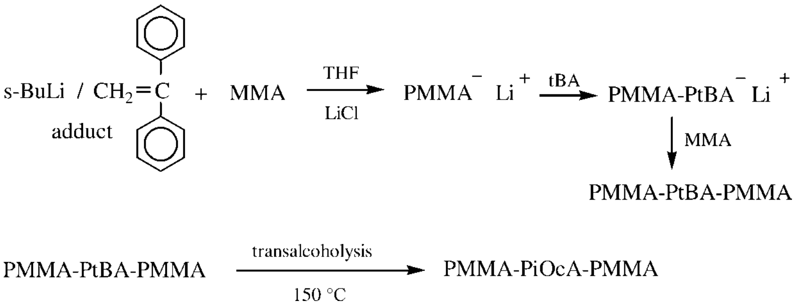
$$s\text{-BuLi} + \text{styrene} \xrightarrow{\text{benzene}} \text{PS}^{-}\,\text{Li}^{+} \xrightarrow{\text{isoprene}} \text{PS-PI}^{-}\,\text{Li}^{+}$$

$$\underset{\text{(excess)}}{\text{PS-PI}^{-}\,\text{Li}^{+}} + \text{Cl}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{Si}}}-\text{Cl} \xrightarrow{CH_3OH} \text{PS-PI-PS}$$

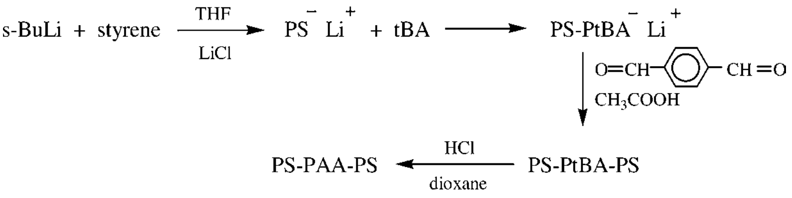
Scheme 8.16

Combination of various MAs with low and high T_g building blocks in an ABA architecture has given interesting TPEs exhibiting better stability against oxidation and better optical properties than the dienic analogs. A representative type is PMMA-PiOcA-PMMA, which was synthesized by the sequential monomer addition route using 1,1,-diphenylhexyllithium and subsequent additions of MMA, *t*-butyl acrylate (*t*BA), and MMA. The final product, with the low T_g poly(*iso*-octyl acrylate) (PiOcA) central block, resulted by post-polymerization transalcoholysis at 150 °C in the presence of *p*-toluenesulfonic acid according to Scheme 8.17 [37].

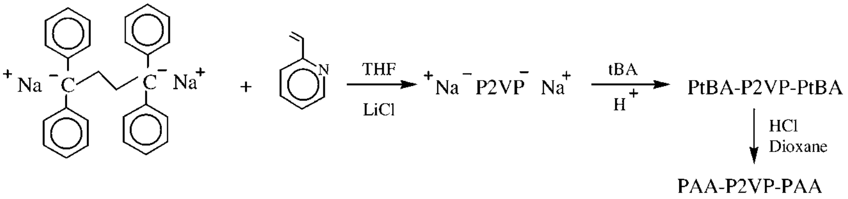
Amphiphilic ABA triblock copolymers capable of forming reversible hydrogels useful in waterborne formulations have been prepared by anionic polymerization and explored in aqueous media. Telechelic polyelectrolytes, e.g., poly(acrylic acid) (PAA) end-capped by PS short blocks, were prepared by the CA route using *t*BA and post-polymerization hydrolysis to obtain the desired PAA central block (Scheme 8.18) [38]. The reaction was carried out in tetrahydrofuran (THF) in the presence of LiCl to ensure control of *t*BA polymerization [39]. Terepthaldialdeyde was used as CA, yielding more than 95% coupling. Owing to the weak polyelectrolyte character of the PAA bridging chains, the rheological properties of the formed physical gel can be tuned by pH. The same route has been applied for the synthesis of a similar PS-PMAA-PS telechelic polyelectrolyte using 1,4-di(bromomethyl)benzene as CA [40].



Scheme 8.17



Scheme 8.18



Scheme 8.19

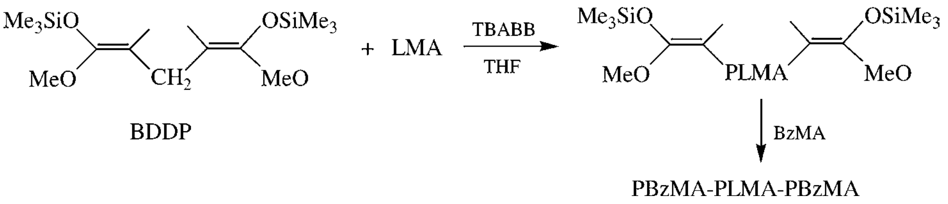
Nonionic amphiphilic triblocks with PEO as the hydrophilic part and PS as the hydrophobic part have been synthesized with PEO either in the middle or in the outer block topology [41]. These copolymers have been studied also in the bulk since they are constituted of glassy and crystallizable segments. The recent interest in the case of PS-PEO-PS was to investigate polymer crystallinity in confined geometries [42].

Recently, an ionizable double hydrophilic triblock copolymer comprising of poly(2-vinylpyridine) (P2VP) and PAA was synthesized by the difunctional initiator route and post-polymerization hydrolysis as described in Scheme 8.19 [43].

The water-soluble PAA-P2VP-PAA triblock copolymer may exist in different states as a result of protonation–deprotonation equilibrium tuned by pH of the solution. At high pH, it behaves as amphiphilic at intermediate pH as segmented polyampholyte, where positively charged protonated P2VP segments coexist with negatively charged PAA segments, and finally at low pH as a cationic polyelectrolyte capped with AA moieties capable of developing H-bonding. This unique multifunctionality allows it to self-assemble through different interactions, (electrostatic or hydrophobic) forming either physical networks (pH 3.5) or compact micelles (pH 8), respectively.

8.3.3
ABA by GTP

GTP is a controlled "living" polymerization method suitable for preparation of block copolymers composed from meth(acrylic) repeating units (Chapter 1). It has been applied in industrial scale (DuPont) for the fabrication of amphiphilic block copolymer dispersing agents for pigmented-water based inks. According to recent considerations, GTP seems to proceed through a dissociative (anionic) mechanism (proposed by Quirk) [44] in the presence of nucleophilic anions (catalysts) [45]. One of the advantages of GTP versus classical anionic polymerization out of experimental conditions (polymerization at room temperature) consists of the easy block copolymerization by sequential monomer addition irrespective of the monomer addition order. Therefore, ABA triblock copolymers can be synthesized by either the difunctional initiator or the sequential monomer addition routes (Figure 8.2).



Scheme 8.20

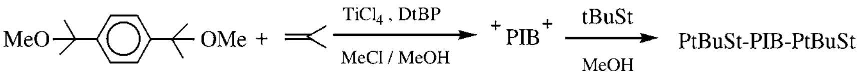
Poly(benzyl methacrylate)-*b*-poly(lauryl methacrylate)-*b*-poly(benzyl methacrylate) (PBzMA-PLMA-PBzMA) was synthesized using 1,5-bis(trimethylsiloxy)-1,5-di-methoxy-2,4-dimethyl-1,4-pentadiene (BDDP) initiator and tetrabutylammonium bibenzoate (TBABB) catalyst following the difunctional initiator route (Scheme 8.20) [46].

Cationic telechelic polyelectrolytes bearing poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) as the stimuli-sensitive, hydrophilic central block and PMMA hydrophobic outer blocks were prepared through the same synthetic approach and explored in aqueous media as a function of pH [47, 48]. Owing to protonation of the tertiary amine groups of the PDMAEMA block at low pH, the copolymer self-associates, forming a stiff physical gel at relative low concentration (1 wt%), functioning as a very efficient thickener useful for aqueous formulations.

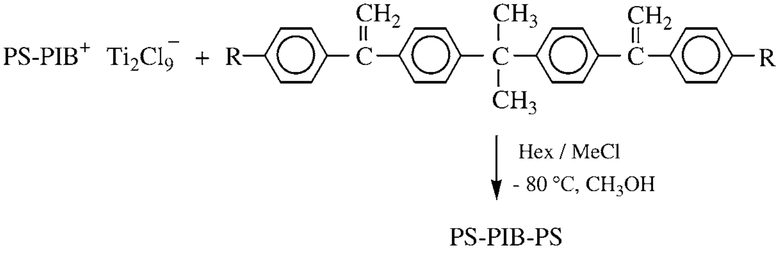
8.3.4
ABA by Cationic Polymerization

Interesting polymeric materials such as TPEs based on PIB, associative amphiphiles based on poly(vinyl ether) (PVE), and telechelic ionomers have been prepared by cationic polymerization. A typical example is the preparation of poly(*tert*-butyl styrene)-*b*-poly(isobutylene)-*b*-poly(*tert*-butyl styrene) (P*t*BuSt-PIB-P*t*BuSt) synthesized by the difunctional initiator method [49]. *p*-Dicumyl methyl ether (DicumOMe)/$TiCl_4$ was used as the difunctional initiating system, which polymerized sequentially IB and P*t*BuSt in the presence of 2,6-di-*tert*-butylpyridine (D*t*BP) to prevent side reactions (Scheme 8.21).

Ionomer-like ABA triblocks with good elastomeric properties constituted of PTHF middle block end capping with linear polyethylenimine (LPEI) short blocks are another example involving ring-opening oxetane polymerization by cationic polymerization. The synthetic strategy involves polymerization of THF



Scheme 8.21



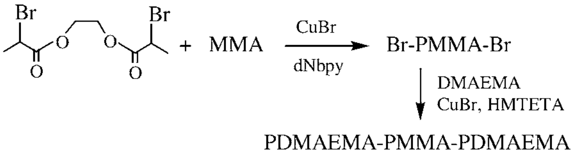
Scheme 8.22

by trifluoromethane sulfonic anhydride difunctional initiator followed by the addition of 2-methyl-2-oxazoline in a different solvent and post-polymerization hydrolysis with concentrated HCl. Complexation of the LPEI block ends by $CuCl_2$ leads to a physical network structure behaving as a tough TPE [50].

PS-PIB-PS synthesis has also been conducted through the CA route, using bis-diphenyl ethylene as CA, according to Scheme 8.22. It has to be mentioned that IB must be added at $\leq$95% styrene (St) conversion to obtain living PS-PIB diblocks with negligible PS homopolymer contaminations. Owing to the PS-PIB diblock residual in the final product, the mechanical properties were inferior to the best triblocks made by the difunctional initiator route [51]. On the other hand, PαMeSt-PIB-PαMeSt was synthesized successfully since *in situ* coupling of the living diblocks with 2,2-bis[4-(1-phenylethenyl)phenyl]-propane (BDPEP) was rapid and nearly quantitative. Note that the difunctional initiator pathway for the preparation of this copolymer cannot be followed because of unfavorable crossover from living PIB to αMeSt [52].

8.3.5
ABA by Controlled Radical Polymerization

Early examples using controlled radical polymerization were the synthesis of symmetric PMMA-PBMA-PMMA and PBMA-PMMA-PBMA by the sequential monomer addition route through ATRP [53]. Amphiphilic copolymers constituted of PMMA and PDMAEMA, both of which can be located as the middle block, were synthesized through the FPP route (Figure 8.2c), yielding symmetric triblocks (Scheme 8.23) [54].



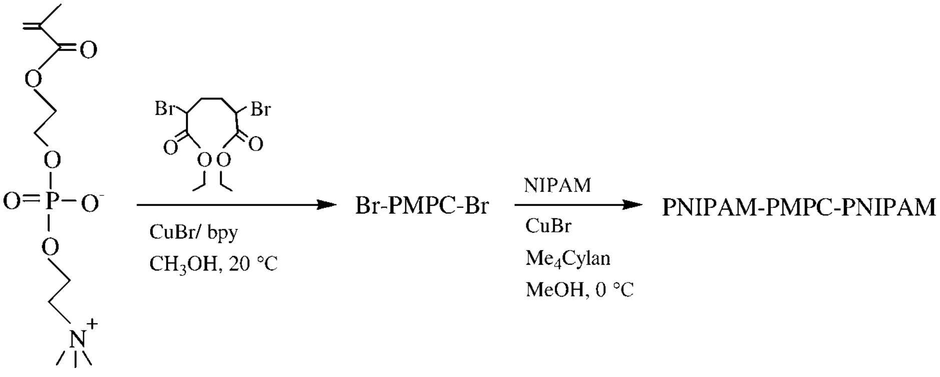
Scheme 8.23

The polymerization of MMA was conducted first, using 1,2-bis(2-bromopropionyloxy) ethane as initiator in the presence of CuBr and bidentate ligand. In the second step, the difunctional Br-PMMA-Br macroinitiator was utilized to polymerize 2-(dimethylamino)ethyl methacrylate (DMAEMA) in the presence of CuBr/1,1,4,7-10,10-hexamethyltriethylene-tetramine (HMTETA).

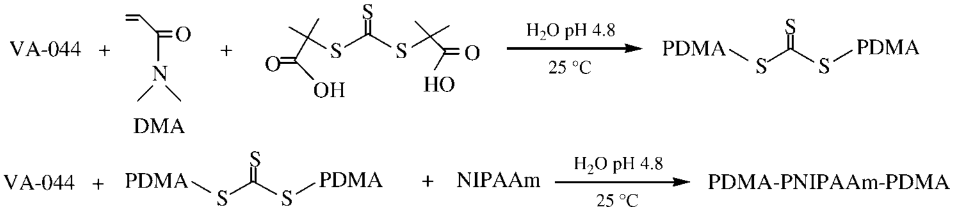
ABA triblocks capable of forming biocompatible responsive physical gels have also been synthesized by ATRP. A two-step FPP route was followed using diethyl-*meso*-2,5-dibromoadipate (DEDBA) as initiator. In the first step, an α,ω-difunctional macroinitiator of 2-methacryloyloxyethyl phosphoryl choline (MPC) was prepared in the presence of CuBr/2bpy catalyst. The Br-PMPC-Br after isolation and purification was used in the second step to polymerize NIPAAm under CuBr/Me$_4$cyclam, yielding the triblock PNIPAAm-PMPC-PNIPAAm (Scheme 8.24) [55].

The fact that the reaction is carried out at room temperature is very advantageous. The phosphoryl choline motif is an important component of cell membranes, and polymers based on this component could offer materials for potential applications in biomedicine. The double amphiphilic PNIPAAm-PMPC-PNIPAAm block copolymer exhibits interesting thermosensitive properties because of the poly(*N*-isopropyl acrylamide) (PNIPAAm) building blocks. At low temperatures, the copolymer is molecularly dissolved, whereas above the LCST of PNIPAAm, it self-assembles forming a physical gel.

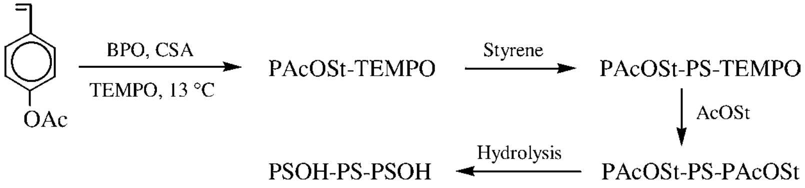
Another attempt to incorporate PNIPAAm segments into the ABA architecture has been achieved very recently through the RAFT mechanism [56]. PDMA-PNIPAAm-PDMA copolymers were synthesized at room temperature in water using a novel water-soluble trithiocarbonate RAFT agent. These conditions with ecological impact are very advantageous and promising from a technological point of view. According to Scheme 8.25, 4,4′-azobis(2-(imidazolin)-2-yl)propane) dihydrochloride (VA-044) was employed as the radical source, and 2-(1-carboxy-1-methylethylsulfanyl trithiocarbonyl sulfanyl)-2-methylpropionic acid (CMP) as the RAFT CTA.



Scheme 8.24



Scheme 8.25



Scheme 8.26

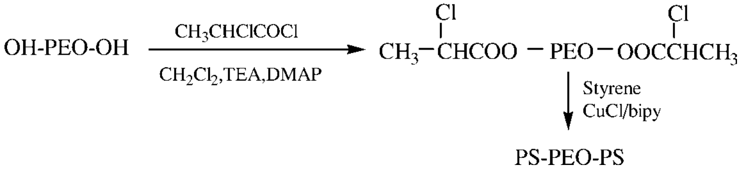
Thermo-sensitive reversible micelles are obtained at temperatures above the LCST of PNIPAAm by hydrophobic association, showing that these triblock are promising candidates for drug delivery applications.

Finally, NMP has been used for ABA triblock preparation using the sequential monomer addition route. Benzoyl peroxide (BPO) as initiator, 2,2,6,6-tetramethylpiperidinoxy (TEMPO) as the nitroxide stabilizer, and camphorsulphonic acid as the accelerator were used to polymerize sequentially 4-acetoxystyrene, styrene, and again 4-acetoxystyrene. The obtained PAcOSt-PS-PAcOSt can be subjected to hydrolysis to yield the corresponding amphiphilic copolymer (Scheme 8.26) [57].

8.3.6
ABA by Combination of Methods

While attempting to design block copolymers having specific properties for targeting applications many times the involving monomers cannot be polymerized by the same controlled/living polymerization mechanism. To overcome this difficulty, site-transformation techniques have been used. For the case of ABA triblock synthesis, the FPP pathway (Figure 8.2d) is used by transforming the functional end-groups of the A polymer precursor to suitable active sites capable of initiating the polymerization of the monomer B (macroinitiator approach).

α,ω-Hydroxy-poly(ethylene oxide) prepared by anionic polymerization can be transformed to an ATRP macroinitiator by a functionalization reaction according to Scheme 8.27. The conversion of OH groups was performed by reacting with 2-chloropropionyl chloride in methylene dichloride (CH_2Cl_2) in



$$\text{OH-PEO-OH} \xrightarrow[\text{CH}_2\text{Cl}_2\text{,TEA,DMAP}]{\text{CH}_3\text{CHClCOCl}} \text{CH}_3-\overset{\text{Cl}}{\overset{|}{\text{C}}}\text{HCOO}-\text{PEO}-\text{OOC}\overset{\text{Cl}}{\overset{|}{\text{C}}}\text{HCH}_3 \xrightarrow[\text{CuCl/bipy}]{\text{Styrene}} \text{PS-PEO-PS}$$

Scheme 8.27

the presence of DMAP and TEA. This ATRP macroinitiator was used in a subsequent step for the polymerization of styrene, yielding the PS-PEO-PS triblock copolymer [23b].

Biocompatible and biodegradable amphiphilic triblock copolymers bearing PEO in the center and end-capped at both ends by poly(ε-benzyloxy carbonyl L-lysine) (PLL(Z)) were synthesized by anionic ROP of *N*-carboxyanhydride of ε-benzyloxy carbonyl L-lysine (L-Lys(z)-NCA) using H_2N-PEO-NH_2 as initiator in dimethyl formamide (DMF) [57]. The resulting PLLZ-PEO-PLLZ triblock copolymer exhibits amphiphilic character and forms aggregates with interesting morphologies, which are attributed to the ability of the PLLZ segments to form different secondary structures such as α-helix and β-sheet.

8.4
$(AB)_n$ Linear Multiblock Copolymers

Linear multiblock copolymers comprising A and B sequential blocks more than three of the same degree of polymerization have been prepared following two routes: sequential monomer addition, in which the monomers exhibit similar reactivity, and condensation polymerization of the α,ω-functionalized A and B building blocks. The former method leads to well-defined $(AB)_n$ multiblock copolymers, whereas in the second one the total number of the blocks cannot be controlled (polydisperse sample).

Representative species of this class of materials, composed of perfectly alternating PS and PI segments $(S\text{-}I)_n$, were synthesized by anionic polymerization using *sec*-butyllithium as the initiator and sequential addition of styrene and isoprene in cyclohexane at 60 °C. On exploring the effect of architecture on their microstructural characteristics and bulk properties, it was observed that increasing n generally promoted reductions in both the lamellar period and upper (styrenic) glass transition temperature, but noticeably increased in tensile modulus and yield strength. These observed trends are more pronounced in the copolymer series with constant chain length because of the coupled relationship between n and molecular weight of the blocks [59].

8.5
ABC Triblock Terpolymers

Linear triblock terpolymers consisting of three segments of different nature, each one conferring different functions to the polymer, are of increasing interest due to their ability to form a rich variety of novel functional nanostructures with potential applications in nanotechnology. The large morphological diversity, observed either in solution or in the bulk by the ABC architecture, is due to the large number of involved variables governing the phase separation/self-assembly of these novel materials, i.e., three interaction parameters in bulk (x_{AB}, x_{AC}, x_{BC}), or six in solution (plus $\chi_{AS}, \chi_{BS}, \chi_{CS}$) as well as composition (f_A, f_B, f_C) and topology (ABC, ACB, BAC). The synthesis of ABC terpolymers was initiated from the early 1970s using anionic polymerization, but in recent years an impressive increase of new ABCs has appeared reflecting the new possibilities of macromolecular engineering after the important development of the new controlled/living polymerization techniques and the new challenges the ABCs offer toward potential advanced applications [60, 61].

8.5.1
Synthetic Strategies

It is obvious that the synthesis of ABC block terpolymers can be accomplished in a straightforward way if all the monomers can be polymerized sequentially under the same polymerization mechanism (sequential monomer addition) (Figure 8.3a). However, the need to prepare ABCs with specific block combination and topology has led to the development of other synthetic pathways (Figure 8.3). Therefore, depending on the nature of the monomer (which defines the mechanism) and the topology of the blocks (ABC versus ACB versus BAC), three more strategies can be designed considering that the order of monomer addition is A + B + C.

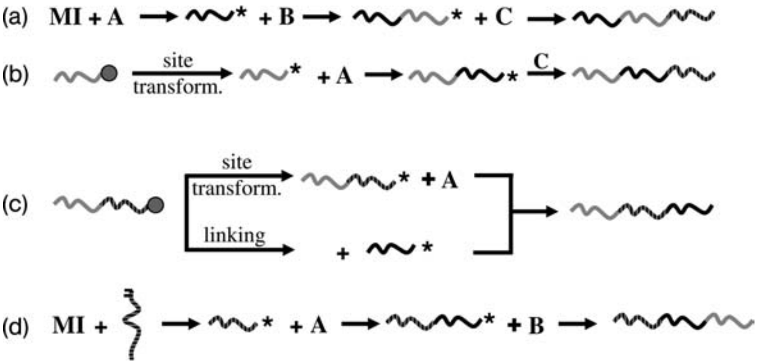


Figure 8.3 Schematic representation of synthetic strategies toward ABC triblock terpolymers: (a) sequential monomer addition, (b) by macroinitiator, (c) by ω-functional diblock precursor (FDB), and (d) through macromonomer. MI: monofunctional initiator, *: active site.

The end function of a ω-functionalized polymer precursor is transformed into an active site capable of initiating the polymerization of monomer B. After the consumption of B, the monomer C is added (Figure 8.3b). This method named the *macroinitiator approach* can incorporate two different polymerization mechanisms; for instance, OH-terminated PEO synthesized by anionic polymerization can be transformed to an ATRP macroinitiator (Scheme 8.27).

When the C block is desired to be in the middle, an ω-functionalized diblock copolymer, prepared by sequential monomer addition of B and C, has to be prepared in the first step. Two subroutes can be followed: either to use the diblock precursor as macroinitiator by a site-transformation reaction to polymerize the monomer A; or to use the end function for linking a living polymer A (Figure 8.3c). Again, two different polymerization mechanisms can be involved.

Nonpropagating macromonomers can also be used. The double bond can react with an organometallic compound to create an active site, which will be used for the sequential polymerization of A and B monomers. This route is alternative to the macroinitiator approach, in the case that the monomer A cannot polymerize monomer C.

8.5.2
ABC by Anionic Polymerization

A large variety of ABC block terpolymers has been synthesized by anionic polymerization using in most cases sequential monomer addition as described recently [62]. Here, only some selective examples concerning the various pathways and recent results dealing with important solution properties will be demonstrated.

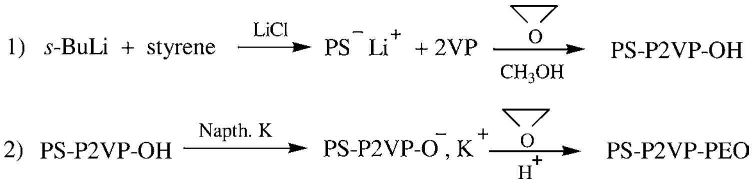
PS-P2VP-PBd triblock copolymer cannot be synthesized straightforwardly by sequential monomer addition. This problem was overcome by the FDB method in a two-step anionic polymerization procedure. In the first step, an ω-functionalized PS-P2VP-CH_2-Cl diblock was prepared by sequential monomer addition using *s*BuLi as initiator and a large excess of *p*-xylene dichloride to terminate the reaction. In cases in which difunctional reagents are used, a large excess is needed to prevent coupling. In the second step, living butadiene capped by DPE is deactivated by the PS-P2VP-CH_2-Cl (Scheme 8.28) [63]. DPE serves to lower the nucleophilicity of the active sites to avoid attack to the pyridine rings.

The preparation of PS-P2VP-PEO was accomplished through the macroinitiator subroute. In the first step, OH ω-functionalized PS-P2VP was synthesized by capping the 2VP active sites with ethylene oxide. Since Li was used as the counter anion (from *s*BuLi initiator), propagation of ethylene oxide (EO) is prevented, and the excess EO can be used to ensure quantitative functionalization. In the second step, potassium alcoxides were generated by reacting potassium

$$1)\ s\text{-BuLi} + \text{styrene} \longrightarrow \text{PS}^{-}\,\text{Li}^{+} + 2\text{VP} \xrightarrow{\text{Cl-CH}_2\text{-Ph-CH}_2\text{-Cl}} \text{PS-P2VP-CH}_2\text{-Cl}$$

$$2)\ s\text{-BuLi} + \text{Bd} \longrightarrow \text{PBd}^{-}\,\text{Li}^{+} \xrightarrow[\text{PS-P2VP-CH}_2\text{-Cl}]{\text{DPE}} \text{PS-P2VP-PBd}$$

Scheme 8.28



Scheme 8.29

naphthalene with the OH functions of PS-P2VP-OH. This macroinitiator polymerized EO to yield the final product (Scheme 8.29) [64]. This triblock bearing two different hydrophilic segments self-assembles in water, forming three-layer micelles comprising a PS hydrophobic core and a pH-sensitive P2VP inner layer surrounded by a PEO soluble corona.

Water-soluble double hydrophilic ABC terpolymers constituted of two ionogenic segments, which can be charged positively (P2VP) or negatively (PAA) depending on pH, and a hydrophobic poly(*n*-butyl methacrylate) (P*n*BMA) were synthesized by sequential monomer addition and post-polymerization reaction according to Scheme 8.30. The central P*t*BA block was selectively hydrolyzed by HCl in dioxane at 85 °C. ^{1}H-NMR inspection showed that the P*n*BMA segment remains intact under the reaction conditions chosen.

A rich polymorphism was observed for the P2VP-PAA-P*n*BMA aqueous solution as a function of pH. Among others, it forms three-compartment centrosymmetric micelles at pH 1 and a three-dimensional network at pH 7, functioning as a potential carrier and/or as a gelator, respectively [65, 66].

The topology of the hydrophobic block is critical in the double hydrophilic ABC terpolymers. By manipulating MAs that have very similar reactivity, one can use the same route as above just by changing the sequence of the monomer addition. For instance, the synthesis of P2VP-PMMA-PAA can be accomplished by the sequential monomer addition route using MMA as the

$$s\text{-BuLi} + 2\text{VP} \xrightarrow{\text{LiCl}} \text{P2VP}^{-}\,\text{Li}^{+} + t\text{BA} \longrightarrow \underset{(\mathbf{1})}{\text{P2VP-PtBA}^{-}\,\text{Li}^{+}}$$

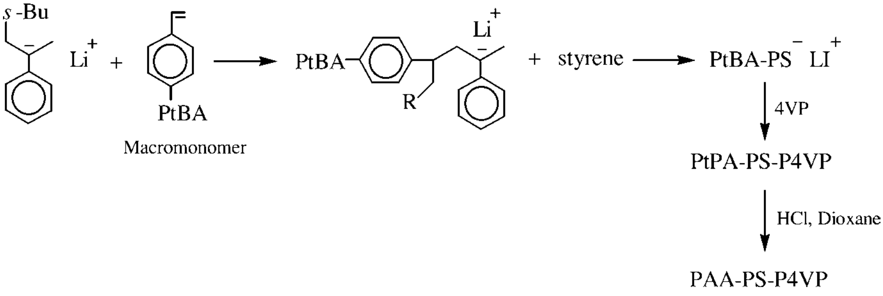
$$(\mathbf{1}) + \text{nBMA} \xrightarrow{\text{H}^{+}} \text{P2VP-PtBA-PnBMA} \xrightarrow[\text{Dioxane}]{\text{HCl}} \text{P2VP-PAA-PnBMA}$$

Scheme 8.30

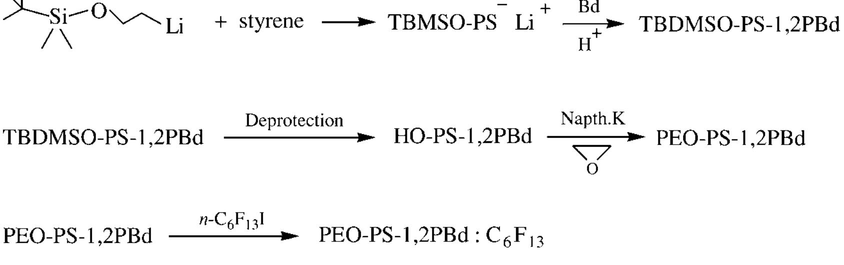
second monomer. This polymer forms now micellar self-assemblies bearing oppositely charged corona chains (P2VP, PAA). These "living" self-assemblies, called *heteroarm starlike micelles*, are sensitive to pH changes and can further associate in a second level of hierarchy [67].

Another PAA-PS-P4VP terpolymer bearing blocks with similar functionalities as in the previous cases but with a long PS in the middle was synthesized according to the macromonomer pathway. A P*t*BA macromonomer with a styryl unsaturation was first prepared. In the second step, α-methylstyryllithium reacted with the macromonomer, generating an active site that initiated the polymerization of styrene and subsequently of 4-vinyl pyridine, Scheme 8.31 [68]. Acidic hydrolysis yielded the final double hydrophilic terpolymer, which forms vesicular nanostructures that can interchange the outside and inside soluble chains (P2VP or PAA) by changing the pH of the solution [69].

An interesting monohydrophilic ABC terpolymer with highly incompatible hydrophobic segments was designed and explored in aqueous media. PBd-PS-PEO was prepared in several steps by the FDB route (Figure 8.3c and Scheme 8.32). An HO-PS-PBd α-functionalized diblock precursor was prepared first using 3-(*t*-butyldimethylsiloxy)-1-propyllithium as initiator. By deprotection of the t-butyl dimethylsiloxy (TBDMS) group and reacting the resulted OH function with naphthalene potassium, the diblock was transformed to a macroinitiator suitable for the polymerization of oxirane. Finally, the PBd block was modified into



Scheme 8.31



Scheme 8.32

a fluorinated (F) segment by reacting the pendant double bonds with *n*-perfluorohexyl iodide. The resulted ABC triblock forms multicompartment micelles in water with a well-segregated PS and F compartment in the core and PEO in the corona [70].

Shell-cross-linked micelles are another representative example of nano-objects. PEO-PDMAEMA-PMEMA was prepared by the MI approach and sequential monomer addition of DMAEMA and (morpholino)ethyl methacrylate (MEMA). The macroinitiator was generated by reacting OH-PEO with the potassium salt of dimethylsulfoxide (DMSO) [71]. These terpolymers self-assemble in aqueous media forming three-compartment micelles with a poly(morpholino)ethyl methacrylate (PMEMA) hydrophobic core PDMAEMA inner layer and PEO corona. The inner layer was cross-linked by a quaternization reaction of DMAEMA moieties [72].

Noncentrosymmetric compartmentalized micellar nanoparticles constituted of cross-linked PBd core and PS, PMMA hemispheres named ‘‘Janus micelles’’ were prepared using PS-PBd-PMMA terpolymers synthesized by sequential anionic polymerization and cross linking of the PBd spherical mesophase in the solid state. After solubilization and alkaline hydrolysis of PMMA to poly(methacrylic acid) (PMAA), amphiphilic Janus micelles were obtained, which further self-assembled in water, forming supermicelles [73].

8.5.3
ABC by GTP

GTP is a versatile polymerization method to prepare ABC terpolymers using the sequential monomer addition route. The advantage of the method relies on the fact that no order of addition of the monomers is needed since methacrylic types usually are used. Therefore, all the topological isomers ABC, ACB, and BAC can be made by just changing the monomer addition order under the same initiator and conditions. A representative example is the synthesis of all isomer terpolymers with PMMA, PDMAEMA, and tetrahydropyranyl methacrylate (THPMA) segments of about equal degrees of polymerization. It was shown that the block topology determines the type of micelles formed in selective solvent (onion, heteroarm starlike) and therefore their size [74].

Another type of terpolymer but in diblock architecture, A-*b*-(B-*co*-C), is possible by GTP because of the similar reactivity of the methacrylic monomers. Tailor-made poly(2-(diethylamino)ethyl methacrylate)-*b*-poly[(oligo(ethylene glycol) methacrylate)-*co*-methyl methacrylate], PDEAEMA-*b*-P(EGMA-*co*-MMA), responsive diblock terpolymers were designed bearing thermosensitive blocks P(EGMA-*co*-MMA) of tunable LCST. The idea was to incorporate statistical copolymer building blocks, since their LCST depends on the nature and the composition of the monomers and therefore can be tuned at will by macromolecular chemistry [75].

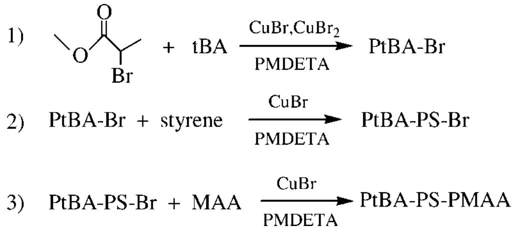
8.5.4
ABC by Cationic Polymerization

ABC terpolymers bearing three different VE monomers have been synthesized by carbocationic polymerization using the sequential monomer addition pathway. A very interesting recent paradigm is the nonionic triple hydrophilic poly(2-ethoxyethyl vinyl ether)-*b*-poly(2-methoxyethyl vinyl ether)-*b*-poly(2-ethoxyethoxyethyl vinyl ether) (PEOVE-PMOVE-PEOEOVE). It was synthesized by using 1-(isobutoxy)ethyl acetate in the presence of $Et_{1.5}AlCl_{1.5}$ in toluene/THF mixture at 0 °C and adding 2-ethoxyethyl vinyl ether (EOVE), 2-methoxyethyl vinyl ether (MOVE), 2-ethoxyethoxyethyl vinyl ether (EOEOVE), sequentially. The unique behavior of this copolymer is due to the different LCST of the building blocks the middle of which exhibits the higher LCST (most hydrophilic block). A multistage association occurs in aqueous media upon heating as the temperature is passing through the LCSTs of the different segments. Three reversible sequential states were observed: a molecularly dissolved state, a core–shell–corona micelles state, and a physical gel [76].

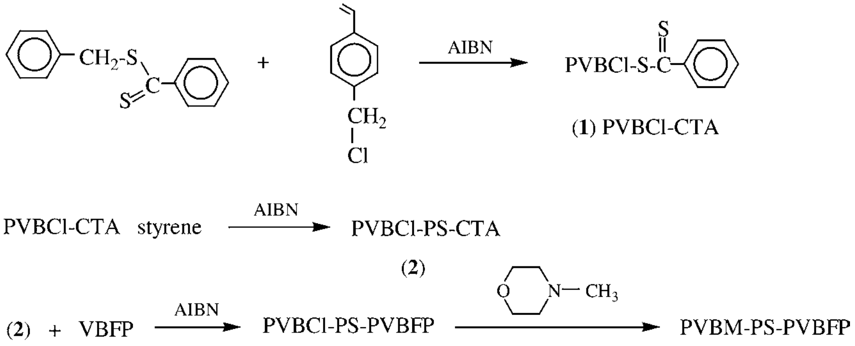
8.5.5
ABC by Controlled Radical Polymerization

Controlled radical polymerization has also been employed to design ABC terpolymers, mainly through the ATRP and more recently the RAFT polymerization mechanism. P*t*BA-PS-PMAA was synthesized by ATRP using a three-pot sequential monomer addition route in which the second and the third monomers were polymerized by the macroinitiator prepared in the previous steps, respectively. The macroinitiators were purified before use. In the first step, the reaction was performed by 2-bromopropionate, CuBr/*N*, *N*, *N*′, *N*″, *N*″-pentamethyldiethylenetriamine (PMDETA) initiating system, and *t*BA, yielding the P*t*BA-Br macroinitiator. In the second step, a P*t*BA-PS-Br diblock macroinitiator was generated, which was used in the third step to give the final product according to Scheme 8.33 [77].

The macroinitiator approach is often used to prepare ABC terpolymers utilizing PEO-Br macroinitiator. A very nice example for its unique properties is in the preparation of PEO-PDEAEMA-PHEMA. The synthesis was performed in a one-pot reaction with sequential addition of monomers DEAEMA and



Scheme 8.33



Scheme 8.34

2-hydroxyethyl methacrylate (HEMA). In a second step, the poly(2-hydroxyethyl methacrylate) PHEMA block was converted by esterification, using excess succinic anhydride in pyridine, yielding the final PEO-PDEAEMA-PSEMA (PSEMA=poly(2-succinyloxyethyl metacrylate)). This triple hydrophilic block terpolymer exhibits a rich association behavior as a function of pH. It forms three types of micelles, the corona of which changes its nature from cationic protonated PDEAEMA (low pH) to natural PEO (intermediate pH) and to anionic neutralized PSEMA (high pH), simply by adjusting the solution pH [78].

RAFT polymerization has been employed recently in the synthesis of ABC terpolymers. Poly(vinylbenzyl chloride)-*b*-polystyrene-*b*-poly(pentafluoro phenyl 4-vinylbenzyl ether) (PVBCl-PS-PVBFP) was synthesized by a three-step sequential monomer addition route, using benzyl dithio benzoate as CTA (Scheme 8.34). The PVBCl block was quaternized by *N*-methylmorpholine, yielding the cationic amphiphilic PVBM-PS-PVBFP (PVBM=poly(4-methyl-4-(4-vinyl benzyl)morpholin-4-iumchloride)) terpolymer comprising two highly incompatible hydrophobic blocks. The interest for this terpolymer arises from its ability to form multicompartment micelles of a novel nanostructure in aqueous media [79].

8.5.6
ABC by Combination of Methods

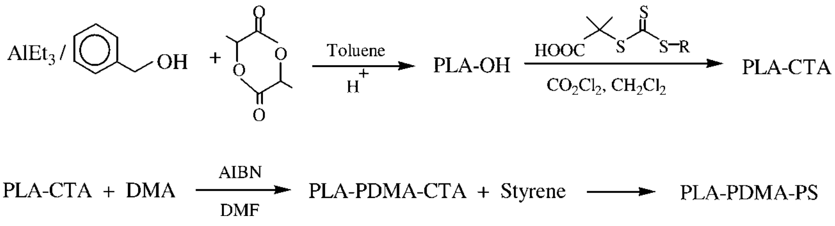
Combination of different methods, although are carried out in a multipot procedure and are of high cost since many reagents and solvents are involved, may offer quite interesting polymeric materials. Nanoporous PS containing hydrophilic pores can be fabricated from a suitable ABC terpolymer bearing the polylactide (PLA) etchable segment, PDMA as the hydrophilic middle block, and PS as the matrix material. This can be achieved by designing the composition of the terpolymer to form a centrosymmetric cylindrical morphology in a continuous matrix. The pores will be formed by selective degradation of the inner PLA core cylinders. The polymer was prepared by a combination of controlled ROP and RAFT polymerization according to Scheme 8.35 [80].

8.6
Synthesis of ABCA Tetra- and ABCBA Pentablock Terpolymers

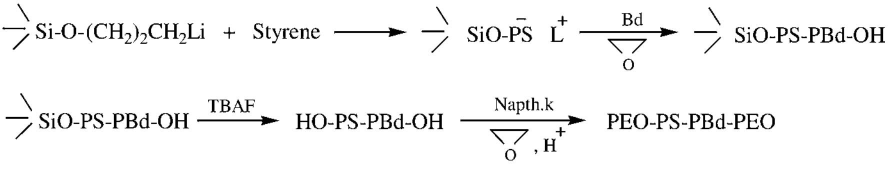
Linear terpolymers comprising three different segments of more than three units (i.e., ABCA and ABCBA) have been designed and investigated in solution and in the bulk.

A very interesting synthetic methodology was applied to prepare PEO-PS-PBd-PEO in a multistep anionic polymerization. Firstly, an α,ω-hydroxy PS-*b*-PBd was synthesized using the protected initiator 3-*tert*-butyldimethylsiloxy-1-propyllithium and sequential monomer addition of styrene and butadiene. The reaction was terminated by ethylene oxide. After deprotection with tetrabutylammonium fluoride (TBAF), both OH ends were converted to potassium alkoxides and used to polymerize ethylene oxide (Scheme 8.36). These ABCA amphiphiles form vesicles or wormlike micelles in water depending on the length of the outer PEO segments [81].

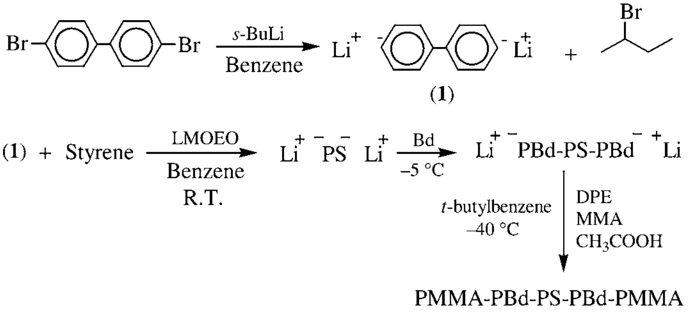
An amphiphilic ABCA terpolymer has been prepared by the sequential monomer addition route and modified by post-polymerization reactions. PS-PI-PBd-PS synthesized by anionic polymerization was first hydrogenated using a Ni–Al catalyst and accordingly the PS outer blocks were sulfonated and neutralized with NaOH. A novel aggregate morphology was obtained in water, showing influence of the ABCA asymmetric architecture in copolymer self-assembly [82].



Scheme 8.35



Scheme 8.36



Scheme 8.37

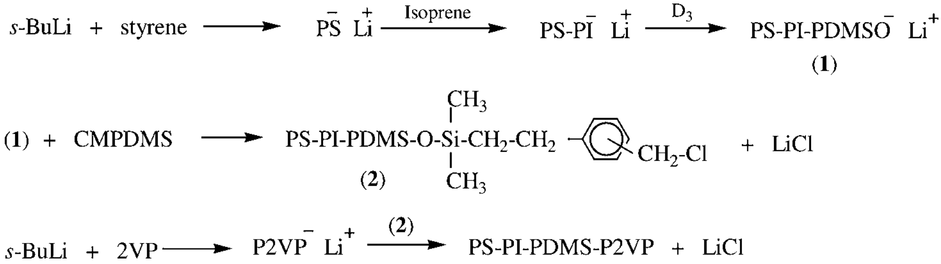
Symmetric ABCBA terpolymers can be made by using a difunctional initiator and sequential monomer addition. PMMA-PS-PBd-PS-PMMA is a characteristic example prepared by anionic polymerization. It was initiated by the *t*BuLi/*m*-diisopropenyl benzene diadduct and butadiene, styrene, and MMA sequential addition in cyclohexane to ensure 1–4 microstructure of the central PBd block. The last MMA block was polymerized in the presence of THF at low temperature [83].

A novel approach to prepare multifunctional initiating systems soluble in apolar organic media susceptible for anionic polymerization was developed recently. For the synthesis of PMMA-PBd-PS-PBd-PMMA, bis(aryl halide) was metalated by a lithium/halide exchange reaction. The resulting initiator was used to polymerize sequentially styrene, butadiene, and MMA (Scheme 8.37). To ensure solubilization of the initiator in benzene, lithium 2-methoxyethoxide (LMOEO) σ/μ coordinating ligand was added to the reaction medium prior to monomer addition. This novel route was applied also to the preparation of well-defined star-shaped $(ABC)_n$ block terpolymers [84].

ATRP synthesis has been utilized for the preparation of PDEMAEMA-PEO-PPO-PEO-PDEAEMA (PPO=poly(propylene oxide)) pentablock terpolymers following the macroinitiator approach. A HO-PEO-PPO-PEO-OH (pluronic) triblock precursor was transformed to a bifunctional ATRP initiator according to the method described in Scheme 8.27 and was used to polymerize DEAEMA. A reversible gelation at around physiological temperatures and pH makes this pentablock a potential candidate for use in injectable drug delivery devices [85].

8.7
Synthesis of ABCD Quaterpolymers

Four different building blocks incorporated in a single linear macromolecule, named *ABCD quaterpolymers*, have recently appeared, increasing our expectations for even higher diversity and functionality toward multifunctional nanostructured polymeric materials.



Scheme 8.38

A novel honeycomb morphology, which has arisen from phase separation of all the incompatible blocks of a PS-PI-PDMS-P2VP quaterpolymer, was observed in the bulk. This macromolecule was synthesized by anionic polymerization in two steps: A sequential monomer addition was applied in the first step to prepare ω-functionalized PS-PI-PDMS terpolymer precursor capping the living sites of the terpolymer with the heterofunctional linking agent chloromethyl phenyl ethenyl dimethyl chlorosilane (CMPDMS). In the second step, living P2VP was deactivated on the chloromethylene function of the ABC precursor (Scheme 8.38) [86].

Reactive ABCD quaterpolymers bearing glycidyl methacrylate (GMA) was designed to control the morphology in epoxy-amine networks. PS-PBd-PMMA-PGMA was synthesized straightforwardly by anionic polymerization through sequential monomer addition. It was shown that the use of reactive block copolymers of well-defined composition permitted adjustment of the final morphology of block copolymer/thermoset nanocomposites [87].

8.8
Graft Copolymers

Graft copolymers constitute a family of nonlinear, branched segmented copolymers of special interest because of their high segment density and specific architecture. They comprise a backbone macromolecular chain bearing a number of side chains (branches) of different chemical nature. The nomenclature is poly(A)-*g*-poly(B) or A-*g*-B, where poly(A) is the backbone and poly(B) stands for the side chains. Graft copolymers are characterized by the grafting density, i.e., the number of branch points (side chains) over the number of monomers units of the backbone chain, which is usually relatively low (<10%). Alternatively, the spacing can be used, i.e., the average distance between the side chains in terms of monomer units. In the special case of every (or nearly every) repeating unit of the backbone bearing a side chain (grafting density close to 100%), the graft copolymers are referred to as *molecular brushes, bottlebrushes,* or *cylindrical polymer brushes* [88].

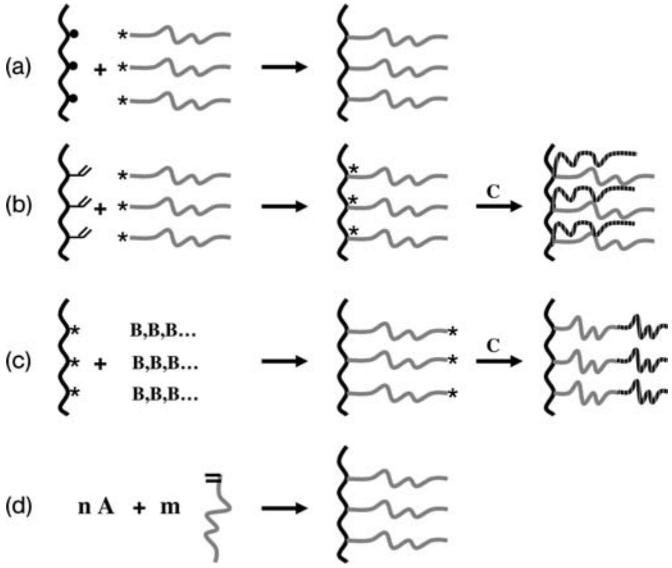


Figure 8.4 Schematic representation of synthetic strategies toward graft copolymers: (a and b) "grafting onto," (c) "grafting from," and (d) "grafting through." $*$: active site.

8.8.1
Synthetic Strategies

Three main synthetic routes have been developed for the preparation of graft copolymers as depicted in Figure 8.4:

1. The "grafting onto" method involves the reaction of living macromolecular (B) chains with specific pendant functional groups distributed along the backbone (A) chain (synthesized independently) (Figure 8.4a and b), In this method, two synthetic pathways could be distinguished: (i) the active chains are deactivated onto the backbone (e.g., anionic sites reacting with electrophilic groups); (ii) the living chains react with unsaturations and therefore the active sites are preserved in the branch points. The latter cases allow further copolymerization by adding a C monomer. Possibilities of undesired bridging between backbone chains are the major drawback of this pathway. In general, the "grafting onto" route leads to well-defined graft copolymers with molecular control of the backbone and the side chains since precise characterization of the side chains can be performed by sampling out prior grafting. To determine the grafting density, the overall molecular weight of the brush must be determined.
2. In the "grafting from" synthetic route, a number of active sites are generated along the backbone (A) chain, which are used to initiate the polymerization of monomer B creating the side chains (Figure 8.4c).

The significant drawback of this route is the inability to characterize directly the molecular features of the branches and therefore the grafting density. An average molecular weight of the grafts can be estimated from the overall molecular weight of the copolymer and the number of sites per backbone chain assuming that all the sites have been involved to the polymerization of the incoming monomer. More precise results are obtained by cleaving the side chains from the backbone to determine their length separately.

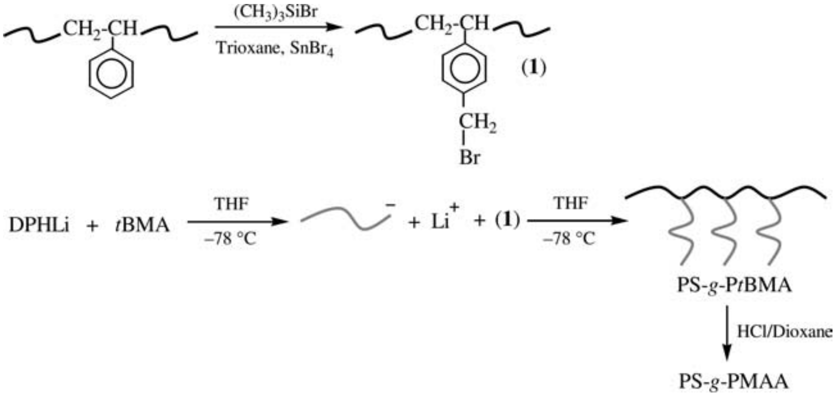
3. Macromonomers, i.e., ω-functionalized polymers bearing a polymerizable group [89], are involved in the "grafting through" method. A given mixture of monomer A and macromonomer B is copolymerized to yield the graft copolymer (Figure 8.4d). This route is suitable for polymerization methods that permit random copolymerization such as FRP. After the establishment of controlled/living radical polymerization, this method seems to be more promising as one can control the length of the backbone chain and the grafting density from the monomer feed ratio. However, the copolymerization of macromonomers is often complicated by excluded volume effect and the incompatibility between the growing backbone chain and the incoming macromonomer [90a,b].

8.8.2
A-*g*-B Graft Copolymers

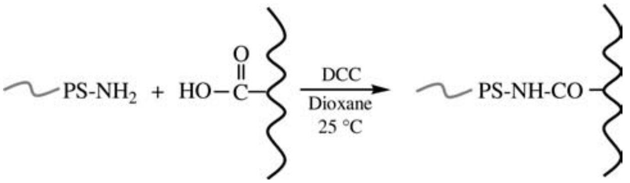
Graft copolymers have been synthesized by anionic polymerization very early in the 1960s [90c]. In this chapter, some recent examples and new developments will be presented.

The most common synthetic strategy is the "grafting onto" route. Amphiphilic PS-*g*-PMAA with ionizable PMAA branches were prepared and studied in selective media. First, a linear PS of known degree of polymerization was partially bromomethylated by trimethylbromosilane and trioxane with the aid of tin tetrabromide catalyst. In the grafting step, 1,1-diphenylhexyllithium (DPHLi) was used to prepare the *t*-butyl methacrylic branches (poly(*tert*-butyl methacrylate), P*t*BMA) in THF at low temperature. After the monomer consumption, the bromomethylated PS backbone was introduced to the reaction medium and the living P*t*BA ends were deactivated by the bromo-electrophiles, yielding the graft copolymer. Hydrolysis of the branches in acidic media gives graft copolymers with PMAA side chains (Scheme 8.39) [91]. The main conclusion from their association behavior in selective solvents was the low aggregation numbers attributed to the graft architecture.

A reverse type graft copolymer with a polyacid as the backbone bearing PS short side chains was prepared through the "grafting onto" route but using a condensation reaction instead of deactivation as described above. The reaction was carried out in dioxane at 25 °C between amino-functionalized PS ($PS\text{-}NH_2$)



Scheme 8.39

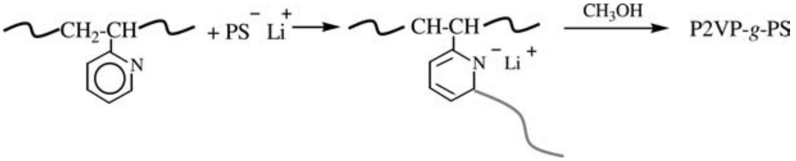


Scheme 8.40

and PAA in the presence of 1,3-dicyclohexyl carbodiimide (DCC) as promoter (Scheme 8.40) [92].

The same reaction has been used to prepare the so-called hydrophobically modified polyelectrolytes constituted of PAA grafted with hydrocarbon or fluorocarbon pendant hydrophobes. These amphiphilic polymers have been used as associative thickeners forming physical gels in aqueous formulation [93].

Poly(vinyl pyridines) (P2VP or P4VP) can be used in anionic polymerization as a backbone chain to generate graft copolymers following the ''grafting onto'' approach. Living PS and/or PI react with the pyridine rings forming P2VP-*g*-PS copolymers as shown in Scheme 8.41. The anion at the PS end is preserved on the nitrogen atom and is deactivated by CH_3OH addition [94].



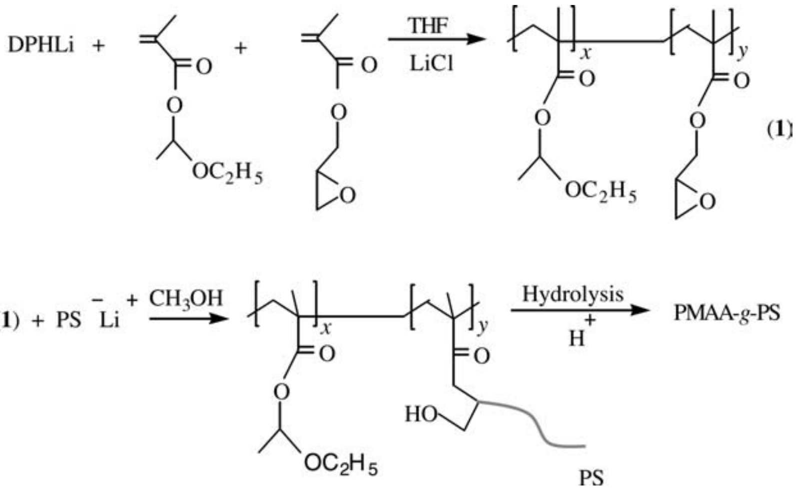
Scheme 8.41

Anionic random copolymerization is a relatively rare case since the reactivity of the monomers has to be very similar. However, it has been applied for the preparation of the backbone chain in PMMA-*g*-PS graft copolymers. 1,1-Diphenylhexyllithium (DPHLi) was used as initiator to copolymerize 1-ethoxyethyl methacrylate (EEMA) and GMA. The resulting random copolymer exhibits narrow molecular weight distribution. In a subsequent step, living PS was reacted with the epoxy pendant groups of P(EEMA-*co*-GMA) and the generated alkoxide anions were protonically deactivated. Finally, the EEMA moieties were hydrolyzed to yield the amphiphilic graft (Scheme 8.42). This ''grafting onto'' method leads to well-defined graft copolymers since it allows control of the grafting density and the length of backbone and branches [95].

A double hydrophilic and stimuli-responsive graft copolymer comprising a PAA backbone and PNIPAAm side chains constitutes a very interesting example. Two synthetic methods were applied to prepared PAA-*g*-PNIPAAm: (i) by reacting α-functionalized H_2N-PNIPAAm onto PAA as in Scheme 8.40 and (ii) Using the ''grafting through'' route by conventional radical copolymerization of AA and PNIPAAm macromonomer [96].

This graft copolymer represents a characteristic paradigm of a polymer comprising pH-sensitive backbone (PAA is a weak polyelectrolyte) grafting by temperature-sensitive side chains due to the LCST of PNIPAAm. It undergoes marked solubility changes in water in response to temperature and/or pH changes, exhibiting potential applications in medicine and biotechnology.

A similar double hydrophilic graft copolymer in which the branches are of *N*, *N*-dimethylacrylamide (PDMA) was accomplished by the same route [97]. Interpolymer complexation through hydrogen bonding between



Scheme 8.42

AA and DMA moieties governs the aqueous solution properties of this polymer.

In both previous cases, the "grafting through" strategy was applied by using the conventional free radical copolymerization of monomer/macromonomer, which fails to control the molecular characteristic of the backbone chain. Controlled radical polymerization is now used to overcome this problem.

A well-defined P*n*BA-*g*-PMMA graft copolymer was obtained by the macromonomer approach using the ATRP method [98]. In this investigation, it was indicated that the relative reactivity of the methacryloyl functional PMMA is much closer to that of MMA in ATRP with respect to the conventional radical copolymerization because of a longer time scale of monomer addition, i.e., seconds for ATRP vs. milliseconds for conventional radical polymerization.

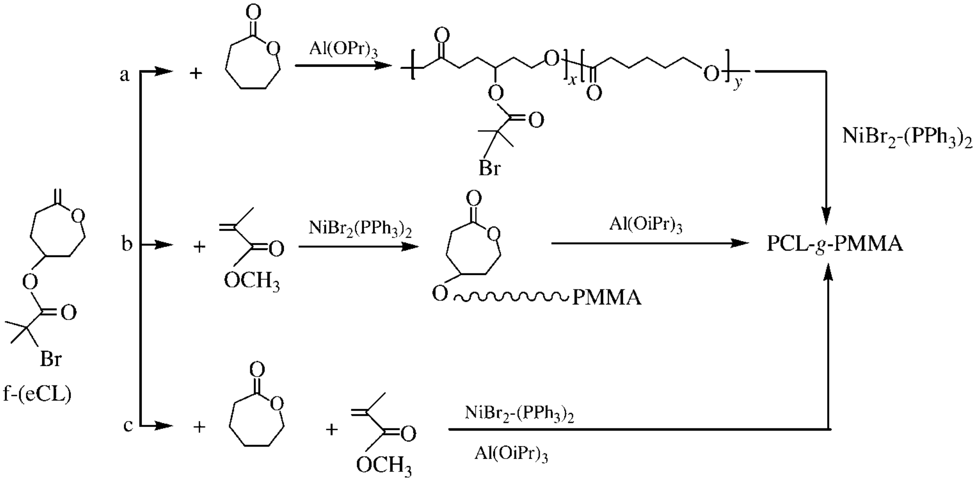
A similar macromonomer approach was used to synthesize PMMA-*g*-PDMS graft copolymers in which again the reactivity ratio of PDMS macromonomer was determined to be much closer to MMA in ATRP mechanism. The consequence of this fact is that the branches are constantly incorporated into all copolymer chains at a certain rate according to the macromonomer/comonomer composition in feed. Therefore, it was shown that the "grafting through" approach performed by ATRP is most beneficial and effective at controlling the graft copolymer structure in terms of main chain length/polydispersity and branch distribution/homogeneity [99].

As shown later, the effect of graft copolymers microstructure on mechanical properties is significant. Comparing the tensile elongation ε of three samples with the same overall M_w and PMMA composition but exhibiting different branch distribution, the following results were observed. The tapered graft (RAFT) had ε of 30%, the irregular product (FRP) 120%, and the regular structure (ATRP) the highest, 280% [100].

Graft copolymers with poly(ε-caprolactone) (PCL) as the backbone and PMMA branches constitute a special case as prepared by combination of ROP and ATRP. Three synthetic approaches were followed: (i) by "grafting from" route, (ii) by "grafting through" using PMMA macromonomer with lactone functionality, and (iii) by one-step/one-pot route in which ROP and ATRP polymerization procedures occur at the same time. The method relies on the synthesis of γ-(2-bromo-2-methylpropionyl)-ε-caprolactone ATRP (initiator)-functionalized lactone monomer f(ε-CL), which can be copolymerized with ε-CL to build the backbone chain (Scheme 8.43) [101].

The most pronounced difference was between the one-step/one-pot and the macromonomer route. The control of molecular weight and polydispersity was clearly compromised in the one-step procedure.

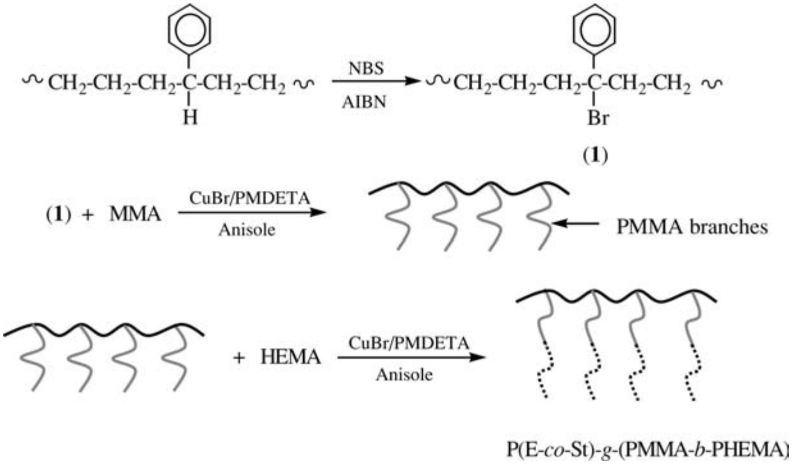
The "grafting from" synthetic route has also been applied in ATRP polymerization to prepare graft copolymers using suitably modified (e.g., brominated monomeric units) macromolecular chains or statistical copolymers (Figure 8.4c) as macroinitiators [102]. Although this method seems to lead to a less well-defined graft copolymer, it permits the generation of di-block grafts. A nice example is the preparation of a PE-based graft copolymer.



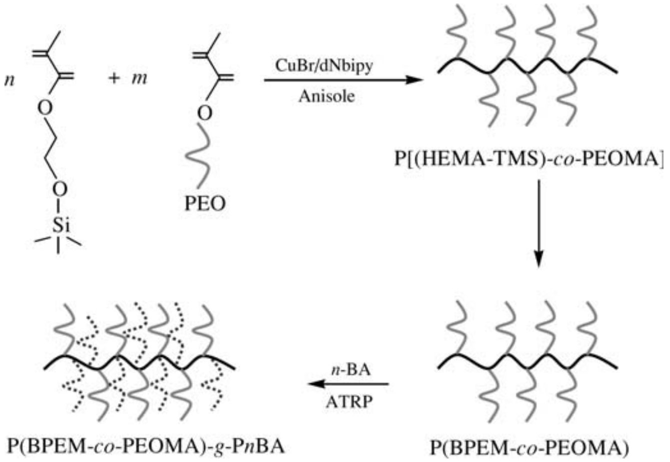
Scheme 8.43

Poly(ethene-*co*-styrene) was brominated using *N*-bromosuccinimide (NBS) to create benzyl bromide moieties randomly distributed along the chain. These functions were used to initiate MMA and, in a subsequent step, HEMA (Scheme 8.44) [101].

Heterografted block copolymers, i.e., graft copolymers comprising two types of pure branches of different nature, have been synthesized by ATRP following two synthetic strategies. In the first case, a two-step "grafting through" followed by "grafting from" procedure was proposed. In the first step, a graft copolymer precursor is prepared by the macroinitiator approach.



Scheme 8.44



Scheme 8.45

Copolymerization of 2-(trimethylsilyloxy)ethyl methacrylate (HEMA-TMS) and PEO macromonomers (poly(ethylene glycol)methylether methacrylate, PEOMA) was conducted under typical ATRP conditions, yielding P[(HEMA-TMS)-*co*-PEOMA)]. This graft copolymer precursor was transformed to ATRP macroinitiator by cleavage of the trimethylsilyloxy (TMS) protecting groups and esterification with 2-bromopropionyl bromide. A new set of poly(*n*-butyl acrylate) (P*n*BA) branches was grown from the active sites along the backbone chain (Scheme 8.45) [104].

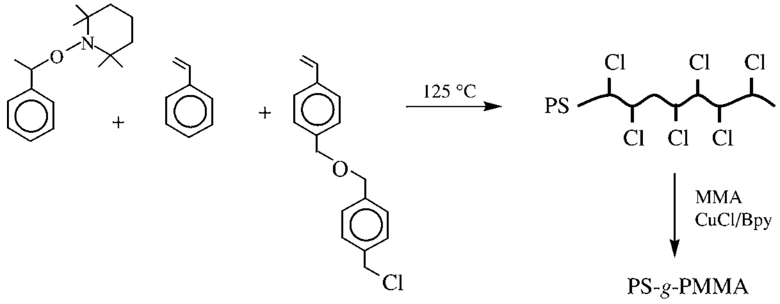
Copolymerization of two different macromonomers constitutes an alternative route to prepare heterografted copolymers. This was exemplified by the synthesis of PDMS-PEO heterograft copolymers by ATRP one-pot procedure [105]. In both cases described above, the final products are densely grafted copolymers belonging to the category of molecular brushes that exhibit unique properties.

Nitroxide-mediated controlled radical polymerization has been employed to afford graft copolymers. For example, a mixture of styrene and *p*-(4′-chloromethylbenzyloxymethyl) styrene initiated by TEMPO produces the PS backbone chain bearing latent ATRP initiating sites. In a second step, PMMA branches can grow under ATRP standard conditions (Scheme 8.46) [106].

If *p*-chloromethylstyrene is used in the above procedure, then TEMPO-based initiating groups can be generated along the PS backbone by reacting with the sodium salt of the hydroxyl functionalized alkoxyamine derivative [107].

8.8.3
Model Graft-Like Architectures

The establishment of structure–property relationships and test of theoretical concepts require precise control of the macromolecular characteristics.



Scheme 8.46

This motivated the design of model graft-like block copolymers of specific architectures in which the grafting distance between adjacent grafts and the number of branches per chain and grafting center are well defined (Figure 8.5) [108].

The synthetic routes toward these model branched macromolecules comprise mainly anionic polymerization under high vacuum and chlorosilane chemistry.

The synthesis of regular PI-*g*-PS graft copolymers was conducted according to Scheme 8.47 [109]. Excess of $MeSiCl_3$ is needed to prevent dimerization of PSLi. The statistical nature of the final linking (in other words, number of

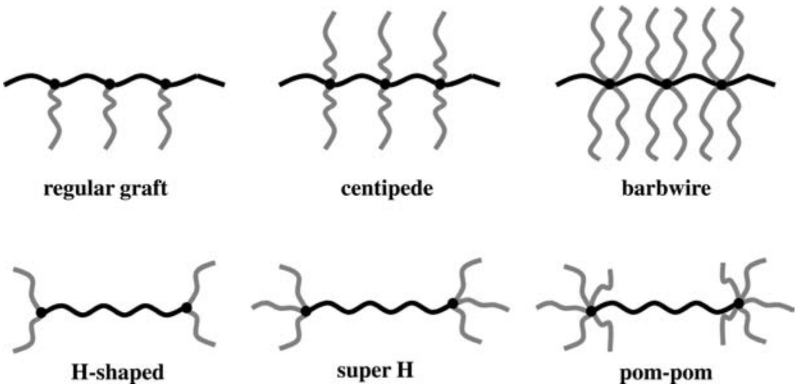


Figure 8.5 Schematic representation of graft-like complex architectures.

$$\overset{-}{PS}\,\overset{+}{Li} + \text{Excess } MeSiCl_3 \longrightarrow (PS)(Me)SiCl_2 + LiCl + MeSiCl_3\uparrow$$

$$\overset{+}{Li}\,\overset{-}{}\!PI\overset{-}{}\,\overset{+}{Li} + (PS)(Me)SiCl_2 \xrightarrow{\text{Polycondensation}} PI\text{-}g\text{-}PS + LiCl$$

Scheme 8.47

branching points mean value) is not strictly controlled, but its average value can be targeted through the Si–Cl/living ends ratio.

Centipedes (tetrafunctional) and barbwire (hexafunctional) multigrafts were accomplished by using tetrachlorosilane and hexachlorosilane CAs, respectively (Schemes 8.48 and 49) [110, 111].

It is known that the mechanical properties of styrene/diene-based TPEs depend on the morphology they adopt in solid state after microphase separation. It was shown recently that the PI-*g*-PS$_2$ centipede with 10 branch points and 22% PS exhibits an exceptional combination of high strength and very high elongation at break as compared with the commercial ABA triblock copolymer TPEs Kraton (20% PS) and Styroflex (58% PS) [112].

The chlorosilane approach has also been utilized to prepare H-shaped, super H, and pom–pom PS/PI block copolymers according to Scheme 8.50 [112–114]. In all these cases, fractionation is necessary to isolate the targeting final product. This fact, together with the difficulties of the high vacuum technique and the long reaction times, limits the use of these interesting materials in basic research.

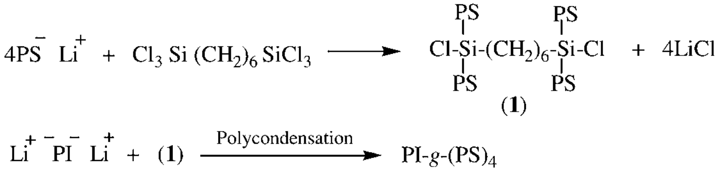
Very recently, amphiphilic H-shaped (PS)$_2$-PEO-(PS)$_2$ block copolymers were synthesized by ATRP using the tetrafunctional PEO macroinitiator (2,2-bis(methylene α-bromopropionate)propionyl terminated PEO) and studied in selective media. In the PS-selective solvents, wormlike structures were observed by atomic force microscopy (AFM). In contrast, in the PEO-selective solvents the wormlike aggregates were transformed into spheres coexisting with unimers [115].

Even more complex branched topologies have been proposed through an iterative multistep synthetic procedure using anionic polymerization. A rich variety of such multisegmental copolymers have been reported in a recent review [116].

$$\mathrm{2PS^{-}\,Li^{+} + SiCl_4 \longrightarrow (PS)_2SiCl_2 + 2LiCl}$$

$$\mathrm{Li^{+}\,{}^{-}PI^{-}\,Li^{+} + (PS)_2SiCl_2 \xrightarrow{\text{Polycondensation}} PI\text{-}\mathit{g}\text{-}(PS)_2 + LiCl}$$

Scheme 8.48

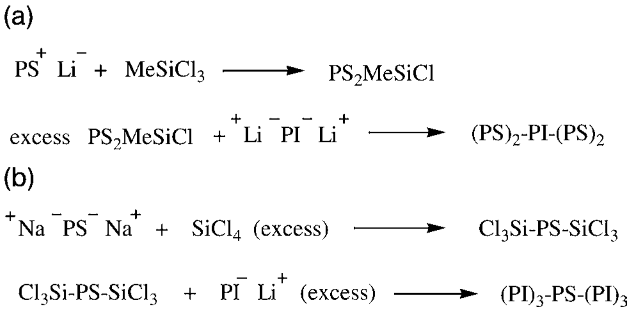


$$\mathrm{4PS^{-}\,Li^{+} + Cl_3\,Si\,(CH_2)_6\,SiCl_3 \longrightarrow Cl\text{-}\underset{PS}{\overset{PS}{Si}}\text{-}(CH_2)_6\text{-}\underset{PS}{\overset{PS}{Si}}\text{-}Cl + 4LiCl}$$

(**1**)

$$\mathrm{Li^{+}\,{}^{-}PI^{-}\,Li^{+} + (\mathbf{1}) \xrightarrow{\text{Polycondensation}} PI\text{-}\mathit{g}\text{-}(PS)_4}$$

Scheme 8.49



(a)

$$\overset{+}{\mathrm{PS}}\ \overset{-}{\mathrm{Li}} + \mathrm{MeSiCl_3} \longrightarrow \mathrm{PS_2MeSiCl}$$

$$\text{excess}\ \mathrm{PS_2MeSiCl} + \overset{+}{\mathrm{Li}}\ \overset{-}{\mathrm{PI}}\ \overset{-}{\ }\overset{+}{\mathrm{Li}} \longrightarrow \mathrm{(PS)_2\text{-}PI\text{-}(PS)_2}$$

(b)

$$\overset{+}{\mathrm{Na}}\ \overset{-}{\mathrm{PS}}\ \overset{-}{\ }\overset{+}{\mathrm{Na}} + \mathrm{SiCl_4}\ \text{(excess)} \longrightarrow \mathrm{Cl_3Si\text{-}PS\text{-}SiCl_3}$$

$$\mathrm{Cl_3Si\text{-}PS\text{-}SiCl_3} + \overset{-}{\mathrm{PI}}\ \overset{+}{\mathrm{Li}}\ \text{(excess)} \longrightarrow \mathrm{(PI)_3\text{-}PS\text{-}(PI)_3}$$

Scheme 8.50

8.9 Applications

In principle, the block copolymer applications rely on their ability to self-organize in nanostructures (characteristic dimension 10–100 nm) since two or more incompatible homopolymer blocks are obliged to coexist through covalent bonding. Moreover, the specific properties exhibited from each block are preserved into the nanostructured self-assembly, creating therefore an advanced property that could not be afforded before. This fact was recognized from the very beginning of block copolymer history with the styrene–diene systems. TPEs are one of the oldest examples of commercialized applications, which still dominate the market for block copolymers. A typical TPE exhibits the ABA triblock copolymer topology constituted of a long and flexible central chain, such as PI (soft component), and two glassy shorter PS outer blocks (hard component). The rubberlike properties of TPEs rely on the 3D nanostructured network comprising distinct PS domains (physical cross-links) bridged by PBd chains [117].

ABC triblock terpolymers have emerged as a promising class of nanostructured plastics since their industrial production is possible nowadays [118]. They can be used as surfactants (compatibilizers) and nanostructured agents of many commercial polymers and epoxy thermosets. The industrially prepared copolymers often contain large amounts of residuals, which, however, do not constitute a drawback, as demonstrated recently in styrene-butadiene-methylmetacrylate (SBM) terpolymers, which may contain as much as 30 wt% SB diblock copolymer. Together with triblock chains, these SBs participate in the formation of stable core–shell nanostructures when melt-blended in twin-screen extruders with various matrices miscible with PMMA. In amorphous poly(styrene-*co*-acrylonitrile) or poly(vinylidene fluoride), the resulting nanostructured aggregates with multiple soft shells lead to a unique balance between toughness and stiffness [119].

The formation of reversible hydrogels (physical gels) by amphiphilic ABA triblock copolymers through hydrophobic interactions of the outer A blocks, in analogy to the networks formed in TPE or micellar AB diblock hydrogels, is another property that has been utilized in a large variety of applications. The nonionic PEO/PPO amphiphilic block copolymer family has been commercialized very early and is used in aqueous formulations in cosmetics, pharmaceutics, and lifestyle products [120]. Recently, more sophisticated double hydrophilic block copolymers bearing responsive blocks to various stimuli such as temperature, pH, ionic strength, and light have been explored and developed targeting to be used in biomedical applications. Indeed, injectable hydrogels suitable for tissue engineering can be fabricated by block copolymers comprising biocompatible and biodegradable polymeric blocks.

Diblock polymeric amphiphiles have been investigated intensively, especially those that are able to self-assemble forming polymeric vesicles named also *polymersomes* (in analogy to liposomes) for their potential applications in biomedicine as drug and DNA carriers [121]. A recent promising paradigm is the biomimetic pH-responsive poly(2-(methacryloyloxy)ethyl phosphorylcholine)-poly(2-(diisopropylamino)ethyl methacrylate (PMPC-PDPA) polymersomes, which can encapsulate plasmid DNA during the self-assembly process at neutral pH. These polymersomes show very low cytotoxicity and can deliver their cargo in primary human dermal fibroblast cells [122].

The broad development of block copolymer nanostructures inevitably leads to their intersections with nanotechnology. Tunable in size and morphology, the periodic ordered nanostructures afforded by block copolymers in the bulk are promising candidates for nanopatterning [123]. Ultralight density storage media could be made by transferring a simple 2D periodic block copolymer pattern into a magnetic film substrate. The block copolymer lithographic mask was created by reactive ion etching of poly(ferrocenyl-dimethylsilane) (PFS) nanospheres formed from a nanostructured PS-*b*-PFS film in an oxygen plasma. The resulting cobalt dots were small enough for single-domain magnetic nanoparticles having an area density of 3×10^8 dots cm^{-2}. The experimental coercivity of these patterned magnetic dots arrays can be attributed to their in-plane shape anisotropy as well as nonzero crystalline anisotropy [124].

Distinct domains of block copolymer micelles can be used as "nanoreactors" for the synthesis of inorganic nanoparticles. For instance, titania nanoparticles are interesting for applications in catalysis, water purification, and ultraviolet (UV) blocking. They can be prepared within the PEO core of PS-PEO micelles formed in a nonpolar solvent. HCl within the micelle cores was reacted with titanium alkoxides, leading to the formation of TiO_2 nanoparticles [125].

The ABC triblock terpolymer is the simplest and best suited architecture for the stabilization of self-assemblies, which leads to structured nano-objects with potential application in nanotechnology. This can be achieved when one of the three segments affords cross-linkable moieties. A good paradigm is the fabrication of organic nanotubes made by poly(isoprene-*b*-cinnamoylethyl methacrylate-*b-tert* butyl acrylate) PI-PCEMA-PtBA terpolymers that form three-compartment centrosymmetric cylindrical micelles in methanol. These micelles were stabilized by photo-cross-linking of the poly(cinnamoylethyl methacrylate) PCEMA-intermediated shell and consequentially they were subjected to ozonolysis, which decomposes the PI core yielding nanotubes. The central block was made from 2-trimethylsiloxyethyl methacrylate (P(HEMA-TMS)), which was modified by deprotection and reaction with cinnamoyl chloride [126].

There is of course a plethora of examples, which cannot be incorporated in such a limited chapter, showing the numerous potential applications that can be offered by the use of block copolymers toward semiconducting and magnetic materials, nanoparticles and nanocapsules, nanoporous materials, photonic crystals, and so forth. The endeavor for real advanced applications based on block copolymers is continuing unceasingly.

8.10
Concluding Remarks

The rapid progress of controlled/living polymerization methods in recent years, together with the possibility to use combined synthetic strategies and post-polymerization selective chemical modifications, has opened new opportunities for synthesizing novel polymeric materials with fascinating properties. Macromolecular architecture is one of the key factors for designing block copolymers that have become nowadays more complex by incorporating an increasing number of building blocks, differing in chemical nature (ABA to ABC to ABCD, etc.), to a large variety of topologies (linear, graft, star, dendrimers, etc.). This chemical diversity and multifunctionality of block copolymers are generating new challenges in polymer physics in terms of phase behavior, self-assembly, and nanostructured morphology, which lead to the establishment of molecular structure–property relationships and in turn to novel potential applications. With the enlargement of collaboration of polymer science with biology, physics, materials science, etc., tailor-made novel advanced materials based on macromolecules are very likely to emerge in the coming years.

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9

Morphologies in Block Copolymers

Volker Abetz, Adriana Boschetti-de-Fierro, and Jean-François Gohy

9.1

Introduction

Block copolymers are polymers, in which different homo- or random copolymer segments are connected into one macromolecule. Block copolymers not only combine the properties of the constituting blocks, but may display new properties depending on the way the different blocks are combined into one macromolecule, the strength of incompatibility between different blocks, and their respective molecular weights. For the synthesis of block copolymers the reader is referred to Chapter 7.

Besides their use as compatibilizers in polymer blends [1, 2], block copolymers have also a wide range of other potentials. Examples are their use as surfactants [3–5], light-emitting [6] or photovoltaic devices [7], or photonic crystals on optical length scales [8, 9]. Block copolymers have been also used as templates for ceramic structures [10, 11] and as hosts for colloidal metals [12] and transition metal complexes [13, 14]. The formation of vesicular structures in solution makes block copolymers also interesting as carriers of drugs or for cosmetic applications [15]. Thermoplastic elastomers based on hard and soft blocks are prominent examples, where block copolymers also received importance as bulk materials [16]. Among multiblock copolymers with hard and soft segments, polycondensates like polyesters-urethanes, polyether-urethanes, or polyester-amides should be mentioned. Also thermoplastic elastomers based on poly(butylene terephthalate) as hard segments and poly(ethylene oxide)-*b*-poly(ethylene-*co*-butylene)-*b*-poly(ethylene oxide) triblock copolymers as soft segments have been reported [17].

In this chapter we want to consider three different scenarios for this self-assembly of block copolymers: (i) morphology in the bulk, (ii) morphology under confinements, i.e., in thin films, and (iii) morphology in solution.

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9.2
Block Copolymers in Bulk State

Concerning the morphological behavior of block copolymers, we just mention some fields of research, which will not be discussed further in this chapter. Crystallization within microdomains and the interplay between crystallization and morphology formation is an ongoing topic since the beginning of research on block copolymers [18–20]. Also, block copolymers with liquid–crystalline blocks have been investigated [21–23]. The self-assembling process leading to microphase-separated morphologies may be influenced by external parameters, like mechanical or electric fields [24–32]. We will not deal with these issues, but rather concentrate on the bulk morphological behavior of block copolymers, which have been cast from a solution to achieve an equilibrium structure. However, to cover all these different aspects is beyond the scope of this contribution. There are many reviews on the morphological behavior of block copolymers in general, for example, Refs [33–36]. Therefore, we will address only briefly, the basic theoretical concepts of microphase separation, and then give an overview of the rich morphological behavior of binary, ternary, and more complex block copolymers of various architectures with a special focus on the developments during the last few years.

Different from polymer blends, chemically well-defined block copolymers, self-assemble into regular crystal-like lattices when microphase separation occurs, as shown in Figures 9.1–9.3 for diblock copolymers, linear triblock terpolymers, and 3-miktoarm star terpolymers, respectively.

These regular structures lead to a typical scattering behavior (as monitored by small-angle X-ray scattering (SAXS) or small-angle neutron scattering (SANS)). Here, the critical concentration fluctuation wavelength occurs on a finite length scale directly related to the macromolecular chain dimensions, which leads to a maximum in the scattering curve in the equilibrium state, while a phase-separating blend will be macroscopically demixed in equilibrium, which corresponds to an infinite value of the fluctuation wavelength.

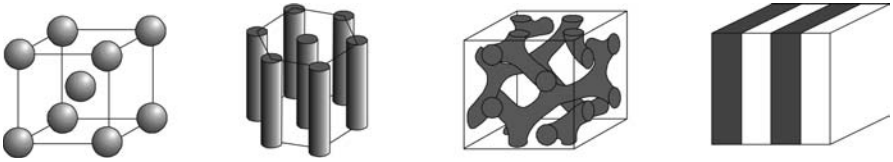


Figure 9.1 Microphase-separated morphologies of diblock copolymers for increasing amount of the dark component up to $f = 0.5$. From left to right: spheres, cylinders, double gyroid, lamellae. (Reprinted with permission from Ref. [37].)

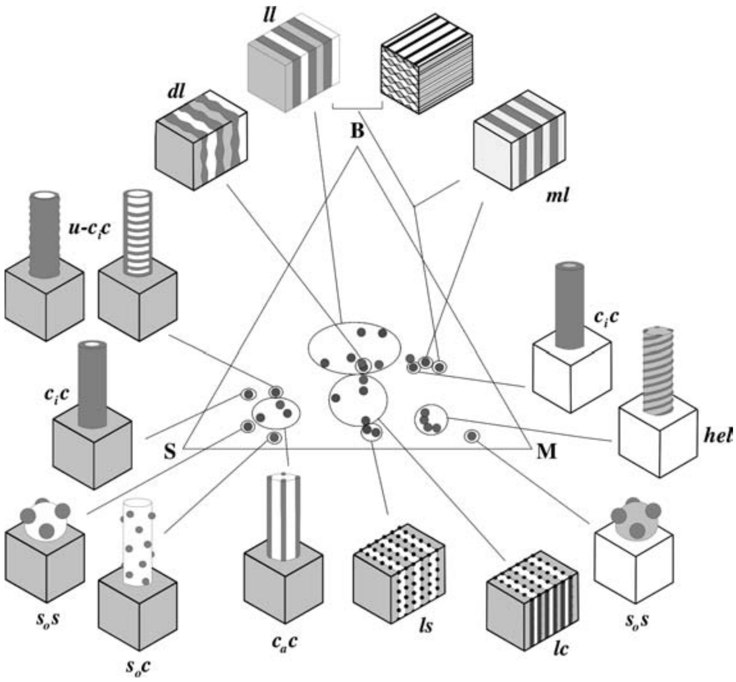


Figure 9.2 Microphase-separated morphologies in the example of polystyrene-*b*-polybutadiene-*b*-poly(methyl methacrylate) (SBM) triblock terpolymers. S, gray; B, black; and M, white (corresponds to bright-field TEM with OsO_4-staining). (Reprinted with permission from Ref. [37].)

9.2.1
Theoretical Descriptions of Block Copolymer Morphologies in the Bulk State

The theoretical works on the morphological behavior of block copolymers have been reviewed before [35, 36]; thus, only the basic concepts are presented here. Owing to the connectivity of different blocks, block copolymers can only undergo a microphase separation, when the different blocks become incompatible with each other [38, 39]. The incompatibility between different blocks is often expressed by the product of the Flory–Huggins–Staverman segmental interaction parameter, χ, and the degree of polymerization (DP), N. It should be noted that there are ongoing discussions on the influence of the junction point between blocks and the end groups on the interaction parameter, which is found to differ between blends of A and B homopolymers on one side, and the corresponding AB block copolymer [40]. There are two different contributions to the free energy of a given microphase-separated block copolymer. On one hand, the system tends to minimize the interface between connected blocks, on the other hand the conformational entropy tends to a random coil conformation of the blocks leading to a weak segregation (or large and diffuse)

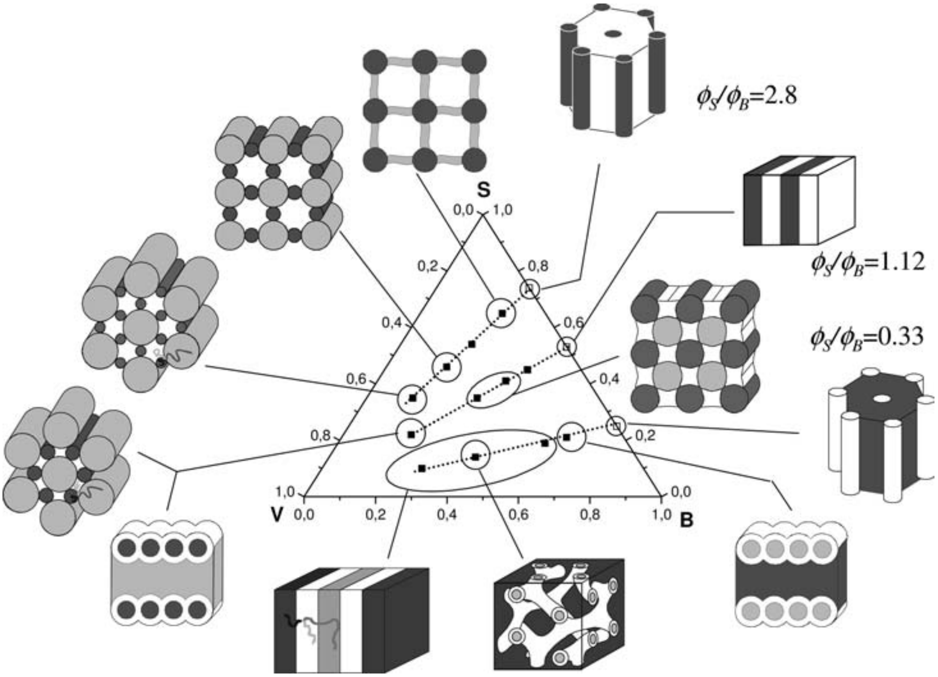


Figure 9.3 Microphase-separated morphologies in the example of polystyrene-*arm*-polybutadiene-*arm*-poly (2-vinylpyridine) (SBV) 3-miktoarm star terpolymers. S, white; B, black; and V, gray (corresponds to bright-field TEM with OsO_4/CH_3I staining). (Reprinted with permission from Ref. [36].)

interface between the blocks. As a result, a morphology forms with a larger interface between blocks than the minimal interface. Thus, depending on the degree of incompatibility as expressed by χN, the connected blocks interdiffuse with each other, less or more. For high χN, block copolymers adopt a sharp interface between strongly stretched blocks in different microdomains (strong segregation limit, SSL), while for low χN, there is broad interphase between the two microdomains (weak segregation limit, WSL). The two situations are schematically shown in Figure 9.4.

Let us first consider equilibrium structures of diblock copolymers in the liquid (melt) state. Within the SSL, the following contributions to the free energy of a block copolymer chain are considered: the interfacial energy originating from the interfacial tension between the incompatible blocks and the elastic contributions of the different blocks. The SSL theory was mostly developed by Meier [42], Helfand [43, 44], and Semenov [39].

The WSL approach for the description of the order–disorder transition, i.e., the transition between the microphase-separated block copolymer and the disordered melt, where the two blocks mix with each other, was developed by Leibler [38] and Erukhimovich [45] using the random phase approximation.

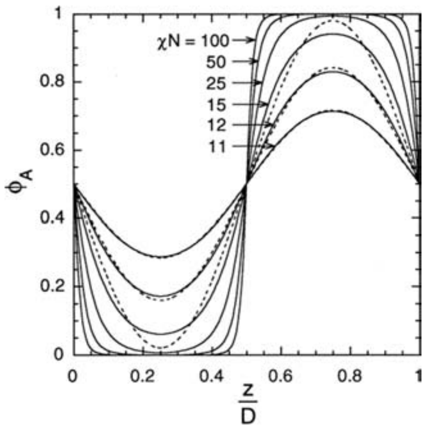


Figure 9.4 Concentration profile of one segment type (A) perpendicular to the interface, over one period of a lamellar block copolymer phase ($f = 0.5$) for various degrees of incompatibility (χN), ranging from the weak segregation limit (WSL) ($\chi N = 11$) to the strong segregation limit (SSL) ($\chi N = 100$). Dashed lines denote first-harmonic approximations for the profiles at $\chi N = 11$, 12, and 15. (Reprinted with permission from Ref. [41]. Copyright (1996) by the American Chemical Society.)

In this scenario, the system is described by a so-called order parameter, which is related to the space-dependent volume fraction or segment density the components. Again, the system is considered to be incompressible. The order parameter is then given by the deviation of the local segment density from the mean composition value. While in the disordered state, the order parameter vanishes, it takes finite values in the ordered phases. In the Fourier transform of the pair correlation function, the order parameter is called the *structure function* and is directly related to the scattering intensity observed by SAXS or SANS. The scattering curve shows a maximum at a scattering vector q^*, which is related to the radius of gyration of the block copolymer. For a symmetric diblock copolymer, a second-order transition between lamellar and disordered phase was predicted, while at all other compositions a first-order transition between disordered state and a body centered cubic phase of spherical domains formed by the minority component was predicted, which changes into hexagonally packed cylinders and finally into lamellae upon further increasing χN. Leibler himself already noted that his approach does not account for fluctuation effects, which become important for finite degrees of polymerization [38]. Corrections for these fluctuations were introduced by Fredrickson and Helfand [46], which prevent the structure factor at q^* from divergence to infinity at the microphase separation transition, but reaches a finite value leading to a first-order phase transition for the symmetric diblock copolymer also. Moreover, there is a finite composition region where a direct transition between disordered and lamellar phases is predicted and the fluctuation effects disappear for infinite large N.

For these calculations, the order parameter of the system was developed as a function of characteristic wave vectors, which correspond to the scattering vectors of reflections observable in a scattering experiment. These phase diagrams only considered the classical microphase morphologies (spheres, cylinders, and lamellae), which are characterized by interfaces with a constant

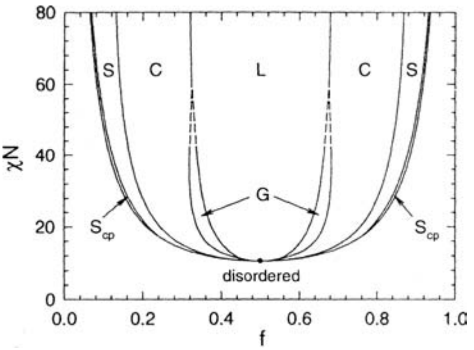


Figure 9.5 Phase diagram of a diblock copolymer composed of components with similar statistical lengths, based on SCFT. (Reprinted with permission from Ref. [47]. Copyright (1997) by the American Institute of Physics.)

mean curvature. However, nonclassical morphologies are also discussed in the vicinity of the hexagonal and lamellar phases, which show a nonconstant mean curvature, even for the ideal case (large matrix forming block). These are the double gyroid, the double diamond, and the hexagonally perforated lamellae [47]. The double gyroid morphology was investigated theoretically by different groups in the WSL [48, 49]. This particular morphology belongs to a whole class of structures, the free energies of which differ only slightly, and have not been distinguished experimentally so far [50, 51]. Only the double gyroid is considered to be a stable morphology, while the other two are metastable, as follows from the self-consistent field theory (SCFT) calculations. Matsen and Bates also used SCFT to cover the bridge between the WSL and the SSL leading to the phase diagram shown in Figure 9.5 [47].

Within the SCFT, the free energy is described by contributions of the internal energy and entropy contributions by the junction points and the different blocks [47]. We just note here that binary block copolymers of other topologies, like linear ABA triblock [52–54] or star copolymers of different numbers of arms [55–57] have also been studied theoretically.

While the phase behavior of amorphous binary block copolymers, in particular diblock copolymers, has been investigated for a long time and most of the fundamental problems seem to be explored, more complex block copolymers like ternary triblock or star copolymers have been addressed much later, motivated by the increasing number of experimental results [58]. For example, in contrast to the morphology of AB diblock copolymers, which is mainly determined by one interaction parameter, χ, and one independent composition variable like the volume fraction ϕ_A, the morphology of ternary triblock copolymers (triblock terpolymers) is controlled mainly by three interaction parameters, χ_{AB}, χ_{BC}, χ_{AC} and two independent composition variables ϕ_A, ϕ_B. Also, the topology is important. Owing to the larger number of independent parameters, it is not surprising that triblock terpolymers show a huge variety of morphologies.

Different groups studied the phase behavior of triblock terpolymers by application of the strong segregation theory [59–63], Birstein *et al.* used the

SSL theory also for the description also for miktoarm star terpolymers [64]. Matsen *et al.* used SCFT also for ABC triblock terpolymers, where he compared different compositions ($\phi_A = \phi_C$) [65]. It was shown that here also, a gyroid morphology with interpenetrating A and C tripod networks in a B matrix is more stable than a corresponding diamond lattice with interpenetrating A and C tetrapod networks in a B matrix. For such triblock terpolymers also, tetragonally packed A and C cylinders in a B matrix were described as well as cubic lattices of spheres. Also, the core–shell double gyroid morphology was described by this method [66].

The phase behavior of ABC triblock terpolymer melts was calculated by SCFT, also by Tyler *et al.* [67]. They focused on "nonfrustrated" ABC triblock terpolymers, in which the χ_{AC} between the end blocks is significantly larger than that between the middle and either end block, i.e., $\chi_{AC} > \chi_{AB} = \chi_{BC}$. Such systems tend to form ordered structures with no AC interface, which is consistent with experimental findings on polyisoprene-*b*-polystyrene-*b*-poly(ethylene oxide).

However, with the exception of the co-continuous morphologies, which are mostly considered to be stable (in the case of gyroids) or metastable in weak or intermediate segregation regime, SSL theory gives qualitatively, a good understanding of various morphologies and, therefore, it is often used for more complex structures. In comparison to SCFT, it is much less intensive in terms of numerical calculations.

When comparing ABC triblock with AC diblock copolymers, an interesting question is the influence of the middle block on the miscibility of the two outer blocks, i.e., how the miscibility of A and C in an ABC triblock terpolymer differs from the miscibility of these two blocks in an AC diblock copolymer. To answer this question, the phase diagram of a diblock copolymer was calculated in the SSL by setting the free energy of a microphase-separated morphology equal to the free energy of the homogeneous phase [68]. From these calculations, the volume fractions where spheres transform into cylinders and cylinders into lamellae were obtained in good agreement with experimental data on diblock copolymers. Also, the critical value of the product χN where a symmetric lamellar diblock copolymer transforms into the disordered phase, was obtained in good agreement with the theory of Leibler [38] in the WSL. Also, the influence of a short but strongly interacting middle block on the miscibility behavior of the two outer blocks was investigated theoretically by Erukhimovich *et al.* [69], and stimulated experiments on the order–disorder transition of an ABC triblock terpolymer, by Pispas *et al.* [70]

All these approaches still suffer from the principal problem that to calculate the free energy of a given morphology, its corresponding symmetry needs to be put into the calculation. In other words, from such calculations, a new morphology never will be predicted [87]. In principle, Monte Carlo simulations could overcome this problem, but have limitations due to finite size effects. Drolet and Fredrickson proposed an SCFT without assuming a symmetry by solving self-consistent equations in real space to find the minimum of the free energy [71]. Bohbot-Raviv and Wang minimize an approximate free energy functional using an arbitrary unit cell, where both the local volume fraction and the unit cell can vary [72]. Especially, the possibility for the unit cell to vary during minimization of the free energy avoids the determination of wrong equilibrium structures.

9.2.2

Experimental Results on the Morphological Properties of Block Copolymers in the Bulk State

The lattice sizes of block copolymer morphologies being typically in the range of approximately 10–100 nm, SAXS [73–77] or SANS [78], in many cases, are powerful tools to investigate the morphology of these materials and the chain conformations of individual components. Also, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) [79, 80], and scanning force microscopy (SFM) [81] have been widely used to directly image the bulk and surface structures of block copolymers.

A challenging question is: what are the conformational properties of a block copolymer in the bulk state? Mostly, scattering experiments, namely, SANS experiments were used to ''visualize'' individual, labeled chains in a matrix of nonlabeled similar chains by taking advantage of the huge scattering contrast between ^{1}H and ^{2}H. While scattering experiments monitor the reciprocal space, and need to be Fourier transformed to get a ''real'' picture with the help of models due to the lack of the phase information, microscopy techniques directly give a ''real'' picture. Jinnai's group used TEM tomography in combination with computer simulation to show the single-chain distribution in a polystyrene-*b*-polyisoprene copolymer in the bulk state [82]. The local frustration of the blocks on a nanoscale can be analyzed using the size of the gyration radius. Flat and bent lamellae were compared and they could show that the single polymer chains in the bent lamella are more stretched out than those in the flat lamella.

Using chiral monomers, a new spectacular morphology for diblock copolymers was found, which is a helical morphology [83]. Thus, chirality of repeating units is another segmental parameter besides segmental stiffness, affecting the morphological behavior, which has not been addressed yet by theory.

Among the block copolymers being composed of more than two different monomers, we restrict our discussion here on systems with three types of monomers. In most of the experimental research carried out, the morphological behavior of linear ABC triblock terpolymers, the dependence on the composition for given sets of monomers was investigated. Depending on the relative values of χ between different blocks, various types of chain frustration occur in linear block copolymers, which allow the definition of several groups of block copolymers, as was first outlined by Bailey *et al.* for ABC triblock terpolymers on the example of block copolymers of polyisoprene

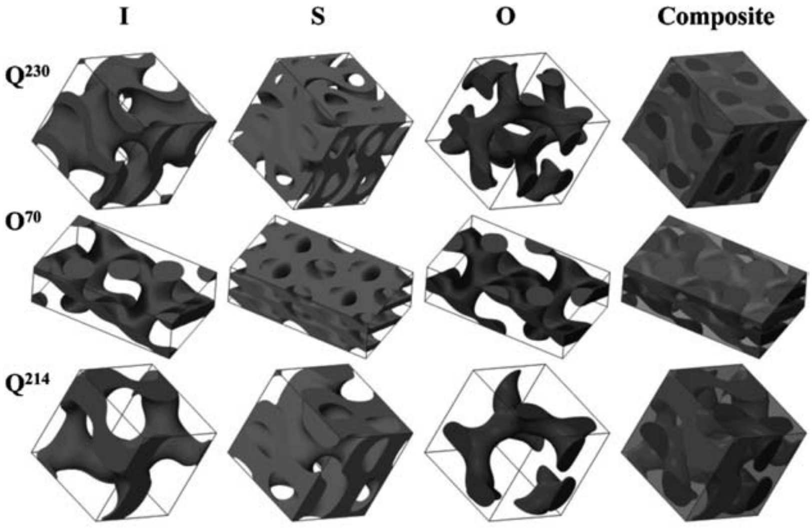


Figure 9.6 Different co-continuous morphologies for polyisoprene-*b*-polystyrene-*b*-poly(ethylene oxide) triblock terpolymers. (Reprinted with permission from Ref. [93]. Copyright (2004) by the American Chemical Society.)

(PI), polystyrene (PS), and poly(ethylene oxide) (PEO) [84]. If $\chi_{AC} > \chi_{AB}$, χ_{BC}, the block copolymer is showing no frustration, as the most incompatible blocks are topologically separated, and therefore, can avoid a common interface for most compositions. Matsushita's group presented a systematic study on such a system, polyisoprene-*b*-polystyrene-*b*-poly(2-vinylpyridine) (ISV), with $\phi_I \approx \phi_V$. Starting from $\phi_I \approx \phi_V \approx \phi_S$ and then increasing ϕ_S, they obtained lamellae, cylinders of both I and V arranged on a tetragonal lattice and finally I and V spheres on a cubic lattice [85]. Between the lamellar and cylindrical region also, a co-continuous morphology was found, which was assigned to an ordered tricontinuos double diamond (OTDD) structure, in which one of the tetrapod-lattices is formed by I and the other one by V, separated by the S matrix. However, a few years later, the OTDD was ruled out as it happened to the corresponding ordered bicontinuous double diamond (OBDD) lattice discussed for binary block copolymers before [65, 86]. Instead of the OBDD, the double gyroid structure was found to fit all experimental data for binary block copolymers [87]. A similar system, polybutadiene-*b*-polystyrene-*b*-poly(methyl methacrylate), was studied by Stadler's group. In this case, the end blocks also self-assembled into cylindrical domains $\phi_B \approx \phi_M \approx 0.2$; however, in a rather disordered, glassy structure on a mesoscopic length scale [88]. For the same type of triblock terpolymer with approximately $\phi_B \approx \phi_S \approx \phi_M$, a coexistence between lamellae and a core–shell gyroid structure was found [37]. Lamellar structures were also found for asymmetrically composed polybutadiene-*b*-polystyrene-*b*-poly(2-vinyl pyridine) triblock terpolymers [89].

In another class of triblock terpolymers, the interaction parameters are like $\chi_{AB} < \chi_{AC} < \chi_{BC}$. Polystyrene-*b*-polyisoprene-*b*-poly(2-vinyl pyridine) and polystyrene-*b*-polybutadiene-*b*-poly(2-vinyl pyridine) are examples of this type. These triblock terpolymers show a rich morphological behavior; again, a strong tendency for the formation of core–shell type of morphologies and a rather strong tendency to avoid direct interfaces between the two end blocks [89–91]. Bates' group showed also a new noncubic structure for another system belonging to this group, a polyisoprene-*b*-polystyrene-*b*-poly(ethylene oxide) triblock terpolymer with $\phi_I \approx \phi_S \approx \phi_{EO}$ [92, 93] (see also Figure 9.6).

A third class of triblock terpolymers has interaction parameters following the rule: $\chi_{AC} < \chi_{AB}, \chi_{BC}$. Such systems allow for a common interface between the outer blocks, as their relative incompatibility is the smallest. Such an interface will be formed if the volume fraction of the middle block is significantly smaller than the volume fractions of the outer blocks; otherwise also, core–shell and other morphologies will be found. Fujimoto's group reported on polystyrene-*b*-polyisoprene-*b*-poly(4-vinylbenzyl)dimethylamine (SIA) triblock terpolymers, where they found a strong influence of the casting solvent on the morphology of the investigated films [94]. The first core–shell morphologies in ABC triblock terpolymers were reported by Riess *et al.* in polystyrene-*b*-polyisoprene-*b*-poly(methyl methacrylate), which was blended either with poly(methyl methacrylate) (PMMA) or with PS [95]. For lower ratios of ϕ_B/ϕ_A, core–shell spheres and core–shell cylinders with a C matrix and lamellae of all three components were proposed, while at larger ratios of ϕ_B/ϕ_A, the A component forms many little spheres within a B sphere surrounded by C matrix or, in the case for lamellae, A forms spheres within a B lamella. Stadler's work in the field of linear ABC triblock terpolymers based on polystyrene (S), polybutadiene (B), and poly(methyl methacrylate) (M), led to the discovery of a number of new morphologies [59, 88, 96–100]. The first studies dealt with systems, where also the volume fractions of the outer blocks, ϕ_S and ϕ_M, were kept approximately similar. However, in contrast to Matsushita's work, the volume fraction of the middle block, ϕ_B, was decreased, and only lamellar morphologies were obtained, where between the S and M lamellae either B spheres, B cylinders, or a B lamella were embedded with increasing ϕ_B [59]. The finding of a helical morphology, where the middle block forms helices around a cylinder formed by one outer block while the other forms the matrix [96] and a new hexagonal morphology [100] were probably the most fascinating new structures in this system. The chemical modification of blocks by transition metal complexes [101] or hydrogenation led to other spectacular morphologies like rings surrounding a cylinder [102] or the knitting pattern morphology [103–105] (Figure 9.7, see also the book cover). The knitting pattern morphology is probably a result of sequential microphase separation of the different blocks from solution, and thus, a kinetically trapped structure, similar to the hexagonal structure found in a polystyrene-*b*-polybutadiene-*b*-poly(methacrylic acid) triblock terpolymer [106]. While the knitting pattern was only found in hydrogenated polystyrene-*b*-polybutadiene-*b*-poly(methyl methacrylate), i.e., polystyrene-*b*-poly(ethylene-*stat*-butylene)-*b*-poly(methyl methacrylate), a blend of two different polystyrene-*b*-polybutadiene-*b*-poly(methyl methacrylate)s showed also a knitting pattern morphology [107].

Compared to linear block copolymers, less work has been reported on miktoarm star copolymers, which is also due to their rather difficult synthesis. Among the different publications in this field, there are only a few dealing with a systematic investigation of the morphology dependending on composition [108–113]. Owing to the topology, in miktoarm star copolymers, a strong tendency for the formation of columnar (cylindrical) morphologies is found, with the junction points being located on parallel lines rather than interfaces. Abetz' group reported on such 3-miktoarm star terpolymers [111] and their blends [114]. Matsushita's group carried out studies on a similar system and gave an interpretation of these morphologies in terms of Archimedian tiling patterns, as shown in Figure 9.8 [112].

However, lamellar and core–shell type of morphologies have also been observed in cases with $\chi_{AC} > \chi_{AB}, \chi_{BC}$. In this case, there is the tendency to form a separating B layer between A and C, if the volume fractions allow for that. In the B-domain, a certain intermixing with A and C segments occurs, due to the chain topology [64, 115].

A symmetric linear polystyrene-*b*-poly((4-vinylbenzyl)dimethylamine)-*b*-polyisoprene triblock terpolymer reported by Matsushita *et al.*, [116] which showed a similar morphology like in some polyisoprene-*arm*-polystyrene-*arm*-poly(methyl methacrylate) miktoarm star terpolymers from Hadjichristidis' group [109], when being cast from a selective solvent [117, 118]. This example underlines the influence of the preparation conditions on the bulk morphology of block copolymers.

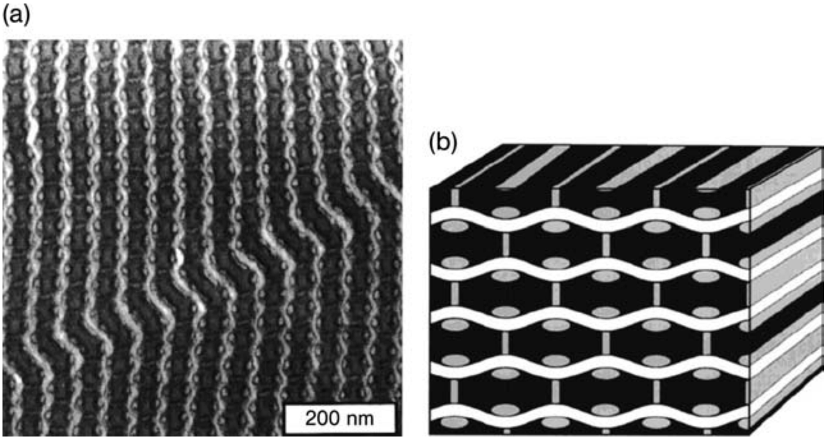


Figure 9.7 The knitting pattern morphology of a polystyrene-*b*-poly(ethylene-*stat*-butylene)-*b*-poly(methyl methacrylate) cast from chloroform. (Reprinted with permission from Ref. [105]. Copyright (2001) by the American Chemical Society.)

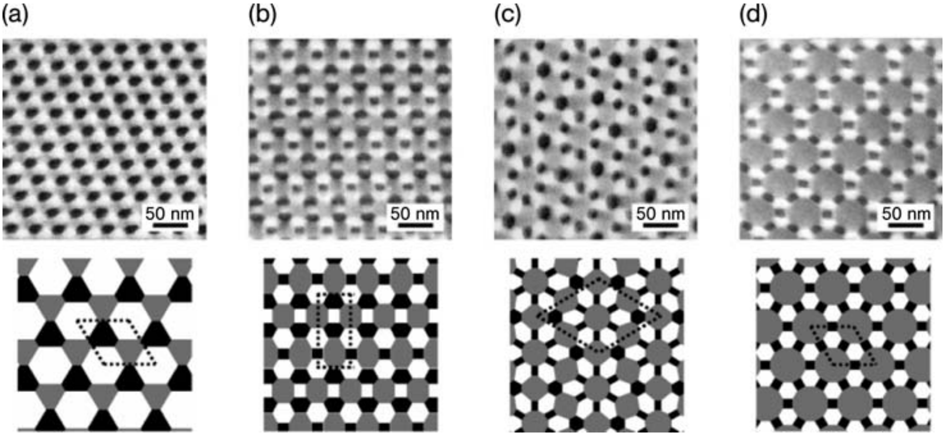


Figure 9.8 Archimedian tiling patterns in polyisoprene-*arm*-polystyrene-*arm*-poly(2-vinylpyridine) miktorarm star terpolymers of various compositions: (a) $I_{1.0}S_{1.8}P_{1.0}$, (b) $I_{1.0}S_{1.8}P_{1.6}$, (c) $I_{1.0}S_{1.8}P_{2.0}$, and (d) $I_{1.0}S_{1.8}P_{2.9}$. (Reprinted with permission from Ref. [112]. Copyright (2006) by the American Chemical Society.)

In general, blending of various block copolymers is a way to a range of morphologies, which are often not found in the corresponding pure block copolymers at any composition. Besides the example of the knitting pattern morphology, this was demonstrated on a range of other structures based on these particular triblock terpolymers [37, 119, 120]. Although in these blends, different block copolymers with a low polydispersity were mixed together, another type of block copolymer blends are systems, where a block copolymer shows a certain polydispersity by itself. Strictly speaking, this is always true for synthetic polymers, but usually not considered that way. Meuler *et al.* investigated the effect of polydispersity on the morphology for a triblock terpolymer. They found that a core–shell gyroid structure was found in a wider compositional (with respect to the type of repeating units) range compared to a monodisperse (or narrow disperse) sample [121]. Also, attractive interactions between different block copolymers have been used as a tool to generate common superstructures between linear and star copolymers [114, 122]. Specific interactions like hydrogen bonds were used to generate novel superstructures, which are often kinetically trapped structures due to the strong interactions between the attracting blocks [123, 124].

Matsushita's group investigated blends of miktoarm star terpolymers with homopolymers and could show the universality of self-assembling symmetries by finding a CsCl-type morphology [125] and a quasi-crystalline 12-fold symmetry [126, 127].

Using multiblock terpolymers, morphologies with several parallel characteristic, periodic length scales can also be generated, as was shown for an undecablock terpolymer [128], and a noncentrosymmetric lamellar structure similar to the one observed for a blend of ABC and AC block copolymers [120] was found for an ABCA tetrablock terpolymer [129].

9.3
Block Copolymer Thin Films

Block copolymer thin films are a very active research field that attracts interest both from the academic and the industrial areas. The reasons for such interest are manifold: (i) self-assembly ability inherent in block copolymers that leads to a variety of morphologies; (ii) influence of the confined dimensions associated with thin films on the structure generation process; (iii) importance of the substrate and the surface on the final morphology; (iv) wide range of novel morphologies not observed in bulk systems; (v) fabrication possibilities by well-known thin film techniques; and (vi) they require only small amounts of usually expensive material.

The extensive activity in the block copolymer thin film area can be appreciated by the increasing number of research articles and reviews being published. Among the many interesting articles and reviews, we would like to arbitrarily highlight two contributions. The article from Li *et al.* [130] presents a summary of the experimental reports related to alignment of block copolymer domains in thin films. The contribution from Park *et al.* [131] also addresses the control of block copolymer structures, and offers a comprehensive overview including a section that deals with morphology control on thin film applications. As some of the first comprehensive contributions to the area of block copolymer thin films, the work of Matsen [132] in 1998 offers an overview of the pioneer research activities, while Fasolka and Mayes [133] reviewed in 2001, the physics of structure formation in block copolymer thin fims.

Despite the observed and potential advantages, there are still some barriers to overcome to strengthen the use of block copolymers for thin films applications. The most important obstacle to hurdle is related to the control of the obtained structure, and usually over long ranges. Therefore, this section presents some general concepts on block copolymer thin films and focuses further on strategies used to control the self-assembly process, i.e., the final morphology, in block copolymer thin films.

9.3.1
General Concepts of Block Copolymer Thin Films

Material layers with thicknesses in the micrometer or nanometer range are addressed as *thin films*, although the term is mostly restricted to films where thicknesses are up to 1 μm. These thin films usually show physical properties, e.g., hardness, electrical conductivity, etc., that are different from the material bulk properties. Therefore, it is possible to achieve new properties not characteristic for the bulk material. Owing to those particular properties, thin films have gained importance in many applications, such as optical filters, mirrors, reflective surfaces, permeation barriers, and solar cells, among others. Additionally, the increasing interest in thin films is enhanced by economical advantages gained by the small amount of material required for the fabrication and the well-developed fabrication processes [134, 135].

Block copolymers have also gained interest for thin films applications thanks to their self-assembly ability. The expected equilibrium or metastable morphologies from bulk systems are affected by the confined thickness, as well as by the interaction of each block with each interface. This means that in block copolymer thin films, the microphase separation occurs relative to the surfaces, so that the block copolymer domains form with a given orientation related to the substrate and/or the surface. For morphologies with continuous domains, i.e., lamellae or cylinders, the orientation of the long axes is a major characteristic of the film.

The phase behavior of block copolymers in thin films is richer and more complex than in bulk as a result of the many effects of the interfaces with both the substrate and the surface. Molecular weight, Flory–Huggins–Staverman interaction parameters, temperature, and volume fraction of each component are the factors that determine the structure formation of block copolymers in the bulk. In thin films, additional factors are involved in the resultant morphology, since usually the block with lowest surface energy will migrate toward the surface, while the block with the lowest interfacial energy will locate itself at the substrate. The thickness itself plays also an important role, since it introduces an additional confinement: if the film thickness is a noninteger multiple of the bulk periodicity, the thin film structure will deviate from the bulk morphology. This added driving force can adjust the structure formation and finally stabilize novel structures not present in the bulk system [133, 136–138].

From different experimental results, it can be concluded that the structure formation in block copolymer thin films is governed by an interplay of two factors [138, 139]. First, the surface field orients the bulk structure or it stabilizes a nonbulk structure, also known as *surface reconstruction*. Second, for films with variations in thickness, the film thickness uses interference and confinement effects to bridge the stability regions of different phases.

The segregation of a different block to the substrate and to the surface generates the so-called asymmetric wetting, with the thickness of a uniform film is described by $(n + 1/2) \cdot d$, where d is the domain spacing. If the thickness is not described by $(n + 1/2) \cdot d$, then depressions or valleys will form in quantized steps of height d to maintain the volume. Symmetric wetting occurs when the same block is segregated to the substrate and the surface. In this case, a uniform film has a thickness of $n \cdot d$ [140, 141].

Owing to the possibility of obtaining highly ordered two-dimensional patterns, block copolymer thin films are of great interest. Applications are mainly focused on nanolithography [136], nanoreactors [140], and nanofabrication [142, 143]. To obtain high aspect ratio uniform structures, self-assembled block copolymers as lithographic masks are used as a sacrificial layer to transfer a set of nanoscale patterns with high density into the desired material. To date, such uniform structures are widely used in the semiconductor industry, among others, capacitors and transistors, due to the increased number of bits per unit area.

Beyond the traditional applications, block copolymer thin films are being developed in other fields such as nanofilters and nanoreactors. In block copolymer thin films it is possible to introduce functionalities contained within one of the nanodomains. For instance, the domain can be loaded with nanoparticles for nanofabrication or with catalysts to work as nanoreactors. In addition, such functionality can produce thin films with stimuli-responsive behavior for nanoseparation.

9.3.2
Controlled Self-Assembly in Block Copolymer Thin Films

For most of the applications of block copolymer thin films, a regular periodic array is required in the long scale range. Even though the self-assembly of block copolymers produces uniform nanostructures, these usually need to be optimized for a complete spatial and orientational control of the nanodomains. Additionally, the natural domain orientation generated during structure formation in thin films (e.g., lamellae lying parallel to the substrate) might not be desirable for a given application. Therefore, to achieve the desired pattern, various techniques have been developed for controlling the self-assembly in block copolymer thin films.

9.3.2.1 Interactions with Air and Substrate Interfaces

When compared to bulk morphologies, block copolymer thin films present highly oriented domains. This phenomenon is the result of surface and interfacial energy minimization, explained by the energetic compatibility of each block toward the surface and the substrate boundary conditions. As previously mentioned, in addition to the short-range interactions of the bulk system, in block copolymer thin films there are short-range interactions of each block with the surface and the substrate. For an A–B lamellae forming block copolymer thin film, parallel lamellae will generate in the case that the substrate or air interfacial tension against A and B are different, as schematically described in Figure 9.9 [142]. On the other hand, the lamellae will orient perpendicular to the substrate if the substrate and the surface are neutral toward A and B.

On the basis of this principle, Huang *et al.* [144] found a way to control the orientation of lamellae or cylinder nanodomains in diblock copolymers of polystyrene-*b*-poly(methyl methacrylate). They anchored polystyrene-*ran*-poly

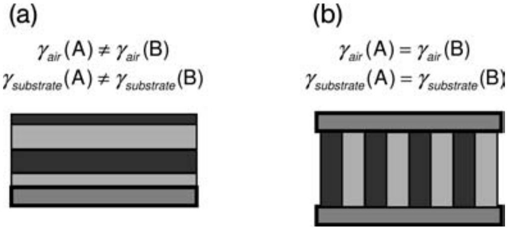


Figure 9.9 Schematic representation of parallel (a) and perpendicular orientation (b) of block copolymer domains in thin film caused by short-range interactions of block chains A and B with surface and substrate surface and long-range interactions of block chains A and B in a confined space inherent in the thin film thickness. γ_{air} and $\gamma_{\mathrm{substrate}}$ denote interfacial tension between air and block chain and that between substrate and block chain, respectively.

(methyl methacrylate) copolymers to both interfaces of the film, and were able to eliminate all preferential interfacial segregation of the components by tailoring the composition of the random copolymer, so that the interactions between the blocks and the interfaces were balanced. The presented model system was a PS-*b*-PMMA symmetric diblock copolymer showing a lamellar morphology in bulk with a periodicity of 36 nm, and a PS-*r*-PMMA random copolymer with a PS fraction of 0.60 was anchored to the surfaces.

The morphology control achieved by means of the adjustment of the interactions with the substrate interface was analyzed by SEM images. The effect of one neutral substrate interface and one preferential interface (air) is observed in the featureless film, where the PS block forms lamellae parallel to the air interface owing to its lower surface energy. However, when the film is confined between two neutral surfaces, the block copolymer lamellae align perpendicularly to the surfaces, over the entire surface of the film and across the full film thickness.

Besides the constrictions imposed by the substrate and surface interactions, thin films are also restrained by the film thicknesses themselves. Knoll *et al.* [145] have shown that the thin film structure formation of a cylinder-forming block copolymer is dominated by the so-called surface reconstructions, where the stability is determined by both the surface field and the film thickness. The employed model system was a polystyrene-*b*-polybutadiene-*b*-polystyrene triblock copolymer swollen in chloroform vapor to equilibrate the generated structure. Chloroform is considered as a nonselective solvent for the two different polymers, and therefore, it acts as plasticizer in the film. The vapor annealing treatment generates terraces of different thicknesses along the film, whose height and domain distribution has been characterized by SFM (Figure 9.10).

The results presented in Figure 9.10 show that the structure formed by the block copolymer changes as a function of the film thickness and the boundaries between different domain arrangements correspond to thickness

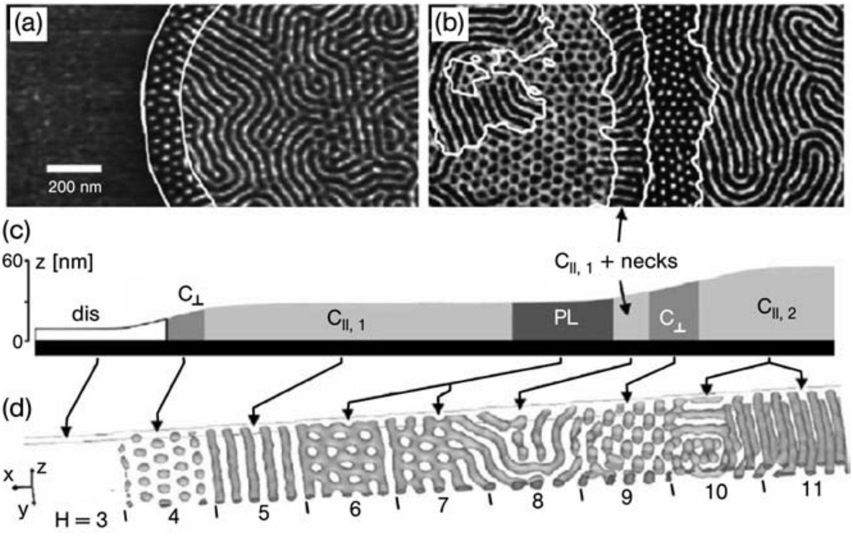


Figure 9.10 (a and b) Scanning force microscopy phase images of PS-*b*-PB-*b*-PS thin films after annealing in chloroform vapor. Contour lines calculated from the corresponding height images are superimposed. (c) Schematic height profile of the phase images shown in (a) and (b). (d) Simulation of an $A_3B_{12}A_3$ block copolymer film in one large simulation box of [$352 \times 32 \times H(x)$] grid points, with increasing film thickness $H(x)$, $\varepsilon_{AB} = 6.5$, and $\varepsilon_M = 6.0$. The latter corresponds to a preferential attraction of B beads to the surface. The isodensity surface $\rho_A = 0.5$ is shown. (Reprinted with permission from Ref. [145]. Copyright (2002) by the American Physical Society.)

variations. The structure formed by PS cylinders oriented parallel to the substrate dominates the film (indicated as $C_{\parallel}$). Perforated polystyrene lamellae (PL) and PS cylinders oriented perpendicular to the substrate ($C_{\perp}$) were also found in the thinner regions. Therefore, the authors concluded that the deviations from the bulk structure in thin films are surface reconstructions, where the stability regions of the different phases (domain arrangements) are modulated by the film thickness by interference and confinement effects.

Roughness of the Substrate Surface The structure formation process in thin films is not only affected by the interaction to the substrate interface, but also by the substrate roughness. The domain orientation by this strategy has received only moderate attention, although some studies have been carried out on ideal grating-like substrates (of $q_s R \sim 0.15$, where R is the (root mean square) vertical displacement of the surface topography about a mean horizontal plane and $q_s = 2\pi/\lambda_s$, with λ_s as the characteristic lateral periodicity in the surface topography) [146] and substrates with larger aspect ratio grating

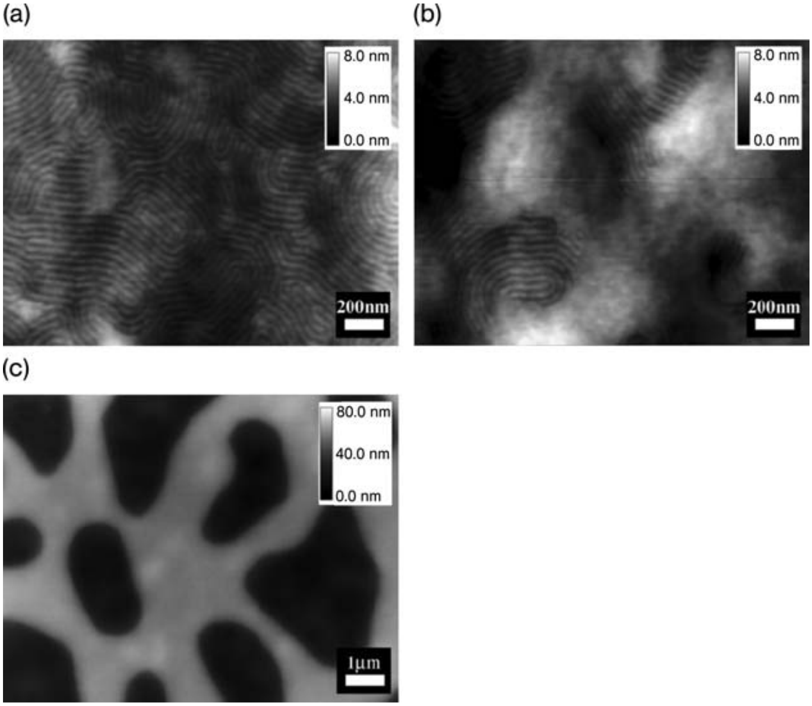


Figure 9.11 Scanning force microscopy height images of 38K-36.8K PS-PMMA block copolymers on a (ITO) replicated polyimide substrate thermally smoothed to $q_s R = 0.25$. Images show typical surfaces after annealing at 200 °C for increasing times: (a) 60 min; (b) 70 min; and (c) one day. (Reprinted with permission from Ref. [149]. Copyright (2005) by the American Chemical Society.)

[147, 148]. Sivaniah *et al.* have done extensive research on lamellar orientation in thin films of polystyrene-*b*-poly(methyl methacrylate) diblock copolymers on e-beam deposited indium tin oxide (ITO) coatings on glass [149–151]. The results showed that a rough ITO substrate (or its polyimide replica) produced thin films where the orientation of the lamellae was perpendicular to the surface. A smooth substrate was obtained by annealing the polyimide replica above its glass transition temperature, and parallel oriented lamellae were obtained on this substrate.

Further experiments were carried out to determine the critical roughness that dictates the transition from parallel- to perpendicular-oriented lamellae. For this propose, 250-nm thin films of polystyrene-*b*-poly(methyl methacrylate) diblock copolymers were spin cast on polyimide substrates of different roughness, and the film structure was followed with SFM after annealing at 200 °C for a range of times (Figure 9.11). Perpendicular lamellae orientation was observed for the thin films on all the rough substrates after the initial annealing. For substrates with a $q_s R$ value smaller than a critical value, the perpendicular orientation persisted for a time $t_{q_s R}$. After this time, a disappearance of the perpendicular lamellae is observed as well as the eventual formation of parallel lamellae orientation. The lag time $t_{q_s R}$, before the transition of lamellae orientation was observed to be longer for polyimide substrates with higher $q_s R$ values. The authors assume that these results can be extended to block copolymer systems with small differences in the attraction of each block to the air and substrate surfaces.

9.3.2.2 **Alignment by External Fields**

The long-range alignment of block copolymer domains has been widely approached by the application of external fields. These techniques achieve directional control of the block copolymer domains based on the ability to match an external field to some molecular or supermolecular feature. In the following, the use of electric fields and temperature gradients for controlling the self-assembly of block copolymer thin films will be presented.

Electric Fields It has been suggested that the final oriented morphology is the result of simultaneous orientation and ordering of the domains when starting from a disordered state, while the alignment mechanism of randomly oriented domains is by translation of grain boundaries [29, 152, 153]. The electric field alignment of the cylindrical structure in block copolymer thin films was studied by Xu *et al.* by means of SANS and TEM [154]. A polystyrene-*b*-poly(methyl methacrylate) diblock copolymer thin film was annealed at 185 °C under 40 $\mathrm{V \cdot \mu m^{-1}}$, and the cross-sectional TEM images of the films after 9, 12, and 16 h are shown in Figure 9.12. The original poorly ordered state was initially driven into cylindrical domains oriented parallel to the film surface by the applied surface field. Further annealing disrupted the cylinder and formed elliptical domains that eventually connected into cylindrical domains oriented in the field direction. The initial domain orientation parallel to the surface is attributed to the interfacial interactions, while the applied electric field orients the domain along the field direction. The transition occurs by a local rearrangement and alignment.

Thurn-Albrecht *et al.* [155, 156] used electric fields to align a cylinder-forming polystyrene-*b*-poly(methyl methacrylate). They have shown that out-of-plane electrodes can force PMMA cylinders to orient perpendicular to the substrate and that these ordered arrays can be used to grow nanowires either by electrodeposition through the porous template or by using it as a mask for etching or patterning the underlying substrate.

The effect of the interfacial interactions on the electric field induced sphere-to-cylinder transition was recently studied by Wang *et al.* [157] for a polystyrene-*b*-poly(methyl methycrylate) diblock copolymer thin film on two different substrates. One substrate was pristine silicon, which has a strong

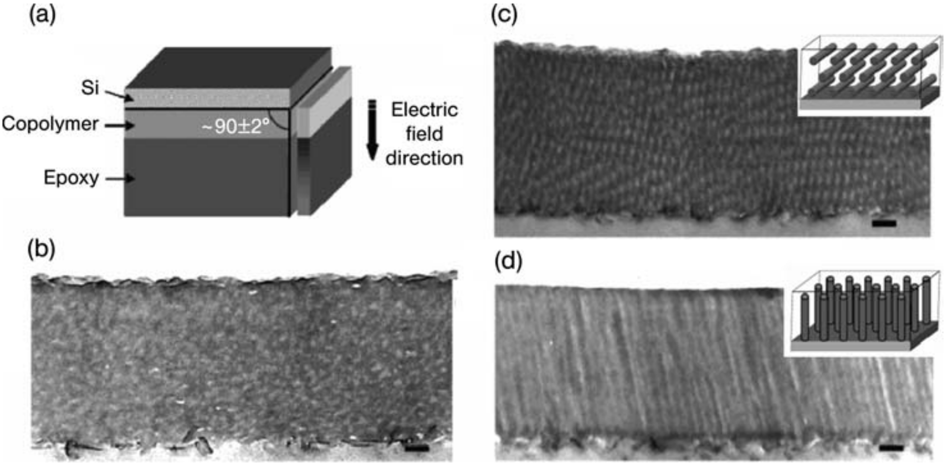


Figure 9.12 (a) Schematic diagram of sample preparation. (b)–(d) Cross-sectional transmission electron microscopy images of PS-*b*-PMMA films after annealing at 185 ± 5 °C under a 40 V μm^{-1} electric field for (b) 9, (c) 12, and (d) 16 h (scale bar: 100 nm). (Adapted and reprinted with permission from Ref. [154]. Copyright (2005) by the American Chemical Society.)

preferential interaction with the methyl methacrylate block; and the other is a poly(styrene-*ran*-(methyl methacrylate)) copolymer anchored to a silicon substrate, so that the interfacial interactions of the blocks are balanced. By applying an electric field of 40 V·μm^{-1} for 24 h under annealing at 170 °C, they have shown that the interfacial energies can increase the critical electric field strength and slow down the kinetics of the electric field induced sphere-to-cylinder transition. Very strong preferential interfacial interactions suppress the mentioned transition, while moderate interfacial interactions allowed the electric field induced sphere-to-cylinder transition, but under longer timescales.

Temperature Gradients The use of an applied temperature gradient to orient domains in block copolymer thin films has been reported by Hashimoto *et al.* [158, 159]. Samples of polystyrene-*b*-polyisoprene were prepared in a so-called zone heating device, where the heating blocks were set at 210 °C (above the order–disorder transition temperature of the copolymer) and the cooling blocks at 5 °C, thus, generating a sharp temperature gradient along the normal axis. Owing to the slow speed of the moving temperature gradient and its large magnitude, the grain growth that starts from the surface in the normal direction is favored over the nucleation of new grains. Therefore, a single lamellar large grain is able to grow when the appropriate experimental conditions are met. A representative transmission electron micrograph is shown in Figure 9.13.

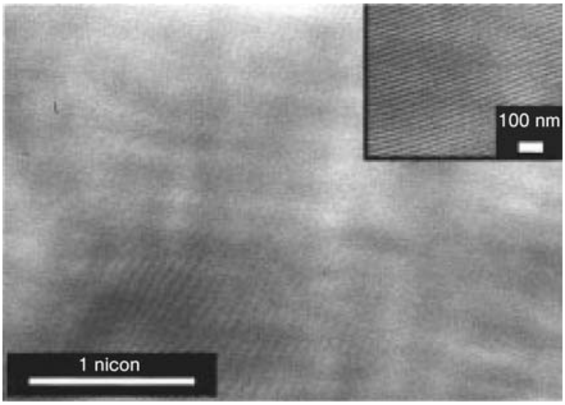


Figure 9.13 Representative transmission electron microscopy image of a single lamellar grain prepared by the zone heating process (scale bar: 1 μm, insert: 100 nm). (Reprinted with permission from Ref. [159]. Copyright (1999) by the American Chemical Society.)

9.3.2.3 **Crystallization**

The morphology of semicrystalline block copolymers is determined by a competition between two factors: [160–166] the block copolymer's ability to self-assemble, which is based on the interactions among the different blocks (organization of incompatible blocks into separated microphases), and the crystallization of the crystallizable block(s). The final morphology has been found to be path-dependent, based on whether the crystallization occurs from a homogeneous state or a microphase-separated one [167–169]. Since crystallization is a basic process of self-organization, it can be used to control the self-assembly in block copolymer thin films. However, attention must be paid to the slow kinetics that governs polymer crystallization. Kinetic effects are responsible for the lack of long-range order in polymer crystals, even if thermodynamics would predict much more ordered crystalline states.

During polymer crystallization, the nucleus is selected as the starting point and the preferred direction is determined by the crystal growth. In block copolymers, the growth direction can also be influenced by the different morphologies [170–172]. Furthermore, boundaries like three-phase contact lines offered by wetting and dewetting processes in thin films can influence the growth direction, as well as the probability to nucleate [173].

The combination of the previously mentioned phenomena in one process has been approached by Reiter *et al.*, [174] as a tool for the generation of patterned structures of block copolymer thin films on different length scales. They studied the behavior of a hydrogenated polybutadiene-*b*-poly(ethylene oxide) diblock copolymer, where only the PEO block was able to crystallize. Thin films were prepared from toluene or methylcyclohexane solutions by spin-coating, and the morphology evolution was followed in real time by light microscopy.

After crystallization, more detailed information was obtained by SFM, and the results are shown in Figure 9.14. It was observed that, after crystallization, the surface was rough compared to the initially smooth surface (before crystallization). The periodic distance measured from the phase images, i.e., periodicity formed by soft and hard regions, was 22 ± 1 nm. This means that the lamellae are oriented perpendicular to the substrate, and this orientation was lost upon heating. It was observed, as shown in Figure 9.14c and d that the presence of a three-phase contact line caused the preferential alignment of perpendicular lamellae.

The results presented by Reiter *et al.* show that microphase separation and a dewetting process can produce long-range order during crystallization of block copolymer thin films due to directed crystal growth. The lamellae are oriented perpendicular to the surface, and the overall structure is well aligned over macroscopic distances. The process was found to be driven by chain folding of the crystallizable block confined between two layers of the amorphous block. Aligned lamellae oriented perpendicular to the surface were also found by De Rosa *et al.* [175, 176] for a semicrystalline polyethylene-*b*-poly(ethylene-*alt*-propylene)-*b*-polyethylene triblock copolymer. In this case, the controlled organization was approached by epitaxial crystallization.

The epitaxial crystallization of polyethylene (PE) has been extensively studied on various inorganic, polymer and organic substrates, from which well-oriented PE crystals have been grown [177–179]. In their work, De Rosa *et al.* approach the epitaxial crystallization of the PE block onto the surface of crystals of benzoic acid. They showed that high orientation of the crystals and the block copolymer domains is achieved through crystallization from the homogeneous melt. The long-range orientation of the crystalline unit cell of the substrate induces excellent alignment of the domains, because the microphase separation process is driven by the crystallization of the PE block. As a consequence, the final structure consists of long lamellae domains perpendicular to the surface. The high orientation obtained for the PEO block is attributed to strong surface interaction due to a crystallographic match of the unit cells between the PE crystals and the benzoic acid substrate.

The influence of crystallization temperature and annealing treatments on the domain size in block copolymer thin films has been studied by Boschetti-de-Fierro *et al.*, [180]. Thin films of polyethylene-*b*-polystyrene-*b*-poly(ethylene oxide) were spin cast from toluene solutions onto silicon wafers, and the thin film morphology was studied by SFM after the application of thermal protocols at different crystallization and annealing temperatures. It was observed that the domain size of the disk-like dispersed domains (where the crystallizable blocks are located) varied with the applied crystallization conditions in a manner similar to that the lamellar thickness is known to vary, i.e., at higher crystallization temperatures thicker crystals are formed, and also bigger dispersed domains are found.

The increase in domain size is attributed to more uniform microphase separation due to higher chain mobility at higher temperatures, despite the

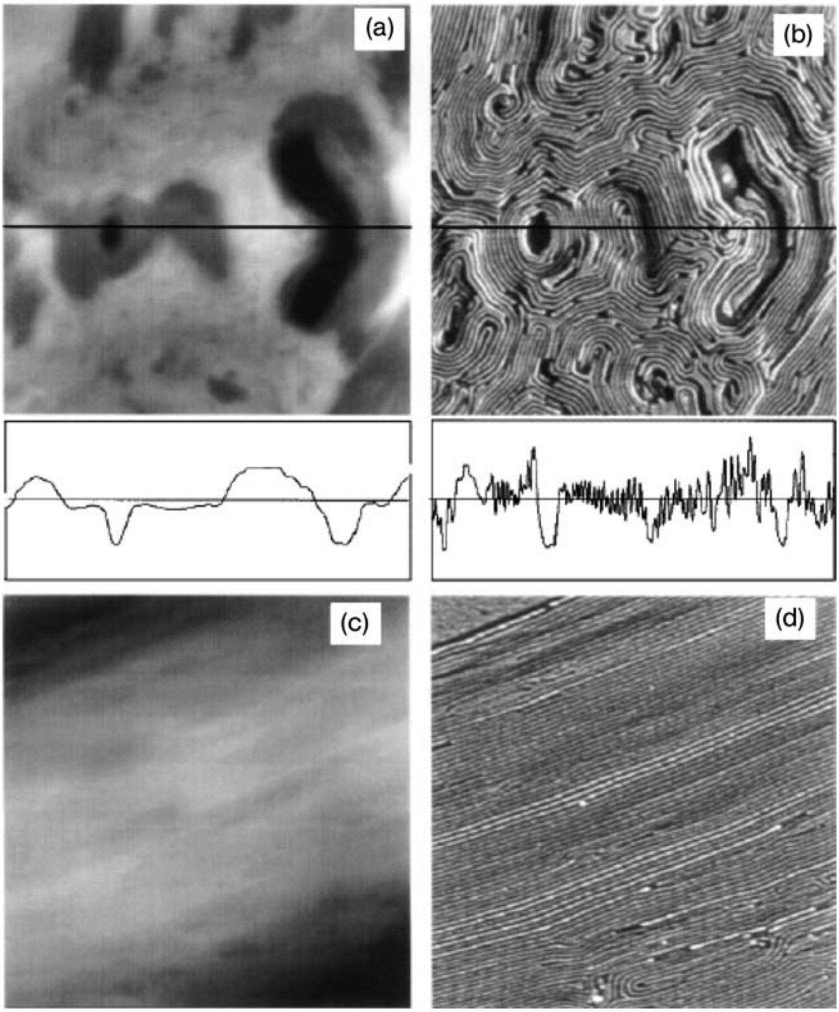


Figure 9.14 Typical tapping mode scanning force microscopy images from a diblock copolymer thin film crystallized at 35 °C. Images were taken (a and b) from an area in the middle of the sample, while (c and d) close to a three-phase contact line (upper left corner) created by a dewetting process in the molten state. Topography (a and c) and phase contrast (b and d) images are shown (image size: $2 \times 2\ \mu m^2$; height$_{max}$ (a and c): 100 and 150 nm, respectively). Cross sections from (a) and (b) (length: 2 μm; height: 100 nm and 40°, respectively, indicated by the full lines) are also shown. (Reprinted with permission from Ref. [174]. Copyright (1999) by the American Physical Society.)

increase of density inside the dispersed domains caused by higher crystallinity. The results indicate the possibility to control the dimensions of dispersed crystallizable microphases by means of the thermal protocol applied to the sample.

9.4
Block Copolymer Micelles

Whenever block copolymers are dissolved in a selective solvent which is a good solvent for one block and a precipitant for the other, the copolymer chains may associate to form micellar or vesicular aggregates. The block copolymer micelles obtained accordingly, thus, consist of a core formed by the insoluble blocks surrounded by coronal soluble blocks [35]. Such block copolymer micelles have been the focus of much interest during the last 30 years due to their possible application in a variety of fields including drug delivery [181–185]. Other interesting applications include use of block copolymer micelles as templates for nanoparticle synthesis or adaptative nanocontainers when stimuli-sensitive polymer blocks are included in the structure [186, 187].

The recent progresses achieved in controlled and/or living polymerization techniques as well as in macromolecular engineering have allowed the synthesis of a variety of original amphiphilic block copolymer structures, which have been further employed for block copolymer micelles formation. The aim of this section is not to provide a complete overview of the field, but rather to highlight some selected recent examples of block copolymer micelles. More complete information about block copolymer micelles can indeed be found in previous reviews including among others Price [188], Piirma [189], Tuzar and Kratochvil [190], Riess *et al.*, [191, 192], Webber *et al.*, [193], Alexandridis and Hatton [194], Nace [195], Hamley [35], Alexandridis and Lindman [196], Xie and Xie [197], Riess [198], Förster *et al.*, [199], Gohy [200], and Nakashima and Bahadur [201].

In this section, we would like to specifically address some recent advances in block copolymer micelles containing metal–ligand complexes and in multicompartment micelles made from ABC triblock terpolymers. A general introduction summarizing the main features of block copolymer micelles will first be presented.

9.4.1
General Concepts of Block Copolymer Micelles

Whenever amphiphilic block copolymer chains are dissolved, at a fixed temperature, in a selective solvent for one of the blocks, they self-associate through a closed association process to form micelles similar to low molecular weight surfactants [35]. The critical concentration at which the first micelle forms is called the *critical micelle concentration* (*CMC*). As the concentration of block copolymer chains increases in the solution, more micelles are formed while the concentration of nonassociated chains, called *unimers*, remains constant and is equal to the value of the CMC. This ideal situation corresponds to a system at the thermodynamic equilibrium. However, experimental investigations on the CMC have revealed that its value depends on the method used for its determination. Therefore, it seems more reasonable to define the CMC as the concentration at which a sufficient number of micelles is formed to be detected by a given method [202]. It has been shown that the CMC strongly depends on the hydrophobic block content in the copolymer; the more it is, the lowest the CMC [203–205].

The concept of CMC precludes that the copolymer chains could be directly dissolved in the selective solvent. This is, however, not the case for most block copolymer chains. A way to improve solubility then consists in ‘‘annealing’’ the solution by prolonged stirring, thermal or ultrasound treatments, although this can lead to nonequilibrium micelles, especially when the core-forming chains of are below T_g [206]. Another method is based on the dissolution of the block copolymer in a nonselective solvent resulting in the formation of molecularly dissolved chains. The properties of this solvent are further changed to trigger aggregation of the dissolved chains and hence, micelle formation. A selective solvent for one of the blocks and precipitant for the others is generally added to the molecularly dissolved chains and the initial nonselective solvent is eliminated by dialysis or evaporation [200, 206]. This method, however, generally results in nonequilibrium micelles. Other ways such as temperature or pH changes can be used to trigger micellization. In this case, the unimer-micelle equilibrium can be generally reversibly tuned by pH or temperature changes. These systems are then rather considered as stimuli-responsive micelles, which can be disassembled or assembled depending on the applied stimulus [5].

Most of block copolymer micelles have been studied in water as a selective solvent. However, it is possible to design block copolymer micelles in a variety of selective organic solvents [200] as well as peculiar media such as supercritical fluids [207] or ionic liquids [208, 209]. In this respect, self-association of block copolymers in ionic liquids has been recently pioneered by Lodge *et al.* [208]. These authors have demonstrated that the basic principles of block copolymer micellization defined in water or organic solvents could be translated to block copolymer micelles in ionic liquids. Moreover, those micelles could be easily transferred from an ionic liquid to an aqueous phase. By carefully playing with the thermosensitivity of one of the blocks, it was also possible to design block copolymer micelles specifically capable of delivering or encapsulating molecules of interest in either the ionic liquid or the aqueous phase [208, 209]. Such a system paves the way toward new interesting applications, e.g., in catalysis.

As described earlier, block copolymer micelles consist of a micellar core surrounded by a corona. Depending on the composition of the starting block copolymer, two limiting structures can be drawn: ‘‘starlike’’ micelles with a small core compared to the corona and ‘‘crew-cut’’ micelles with a large core and highly stretched coronal chains [200]. The process of micellization is characterized by the aggregation of a given number of block copolymer chains, defined as the aggregation number, Z. The core is characterized by its radius, R_c, while the overall radius of the micelle is measured either by its radius of gyration, R_g, or its hydrodynamic radius, R_h. Key parameters that control R_c, R_g, R_h, and Z are the DP of the polymer blocks and the degree on ionization in case of charged water-soluble block. The micelle will tend to adopt the structure corresponding to the minimal free energy, which is mainly determined by (i) the interfacial energy of the core/shell interface, (ii) the stretching energy of the block copolymer chains, (iii) the repulsion among coronal chains [210]. Several theoretical approaches have been developed to rationalize the characteristic features of block copolymer micelles [35, 199, 200]. These are based on either the scaling concepts derived from the Alexander–de Gennes theories or the mean field theories. In addition to theory, computer simulations have been extensively carried out on block copolymer micellar systems [211, 212]. Theories on block copolymer micelles have been previously reviewed by several authors including Tuzar [190], Hamley [35], Gast [213], Linse [214], and Riess [198] and will not be discussed further here.

The dynamics of micellar systems is a very important issue that is relevant at several levels. In this respect, the dynamics required for the establishment of the unimer-micelle equilibrium is one aspect [215–217]. The so-called problem of micelle hybridization that deals with the exchange rate of unimers between different micelles is closely related [218]. Finally, the chain dynamics of polymer blocks in either the core or the corona is another concern that can, however, be linked to some extent to the two concepts mentioned first [219]. Although they deserve a lot of attention, these different aspects have however, been scarcely studied. Techniques like stopped-flow light scattering can, however, be used to obtain information on the dynamics of micellization and has been demonstrated by Liu *et al.* [220].

In addition to the control of micellar size, the control of micellar morphology has early emerged has a key research field. For coil–coil diblock copolymers readily soluble in the selective solvent, one unifying rule accounting micellar morphology has been proposed by Discher and Eisenberg [221], that is based on the mass fraction of the hydrophilic block to total mass of the copolymer, $f_{\text{hydrophilic}}$. Indeed, spherical micelles are expected for $f_{\text{hydrophilic}} > 45\%$, rodlike micelles are observed for $f_{\text{hydrophilic}} < 50\%$, vesicles are formed for $f_{\text{hydrophilic}} \sim 35\%$, and finally inverted microstructures such as large compound micelles are observed for $f_{\text{hydrophilic}} < 25\%$. Sensitivity of these rules to the chemical composition and to the molecular weight of the copolymer chains has not yet been fully probed. According to previous experimental results, it seems that they can be applied for molecular weights ranging from 2700 to 20 000 g mol^{-1}.

Among those morphologies, vesicles obtained from amphiphilic block copolymers or polymersomes have attracted a lot of interest due to their structural resemblance to liposomes [221]. However, polymersomes exhibit enhanced mechanical stability and different permeability compared to liposomes, that greatly enhance the scope of their application. Moreover, polymersomes can be modified by inserting proteins with specific functions inside their wall. As a typical example, the bacterial water-channel protein

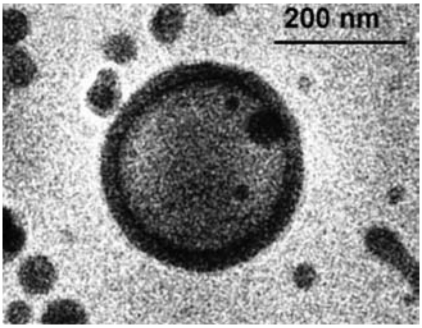


Figure 9.15 Cryo-TEM image of vesicles obtained from a poly(2-methyloxazoline)-*b*-poly(dimethylsiloxane)-*b*-poly-(2-methyloxazoline) triblock copolymer in which aquaporin proteins were further inserted. (Reprinted with permission from Ref. [222]. Copyright (2007) by the National Academy of Science, USA.)

Aquaporin (AqpZ) was inserted in the walls of vesicles made from poly(2-methyloxazoline)-*b*-poly(dimethylsiloxane)-*b*-poly-(2-methyloxazoline) triblock copolymers (Figure 9.15). The initial vesicles were shown to be highly water impermeable due to their poly(dimethylsiloxane) (PDMS) walls. However, a large enhancement in water permeability was observed when AqpZ was incorporated. This approach may lead to productive and sustainable water treatment membranes, whereas, the variable levels of permeability obtained with different concentrations of AqpZ may provide a key property for drug delivery applications [222].

Although polymersomes are quite interesting, they will not be extensively reviewed in this chapter due to lack of space. Comprehensive reviews on such systems can be found elsewhere [221, 223, 224].

It has been shown that the presence of a rodlike blocks in the block copolymer strongly affected the micellar morphology and triggered the formation of nonspherical morphology. Indeed it has been shown for rod–coil polymer that the aggregation of the rigid segment into (liquid–)crystalline domains competes with the phase separation between the blocks during the phase separation process. Moreover, the introduction of stiff segments results in an increase of the Flory–Huggins parameters in comparison with coil–coil copolymers [225]. The aggregation behavior of rod–coil block copolymers has been investigated on various systems by many groups. A variety of structures including vesicular, fibrillar, and helical micellar morphologies has been reported [226–235].

Block copolymer micelles in which the core-forming polymer blocks are able to crystallize are relatively similar to rod–coil copolymers. Typical examples are based on the crystallization of PEO blocks in the micellar core of non aqueous micelles [236–238]. These works demonstrated that lamellar microcrystals called *platelets* or *shish-kebab* structures were formed by chain-folding crystallization of the PEO blocks in the absence of water and resulted in nonspherical micellar cores. A typical picture of such platelets is shown in Figure 9.16. Another example of crystallized cores is found in micelles formed by polyferrocenylsilane (PFS)-based copolymers, as will be discussed later in this chapter [239].

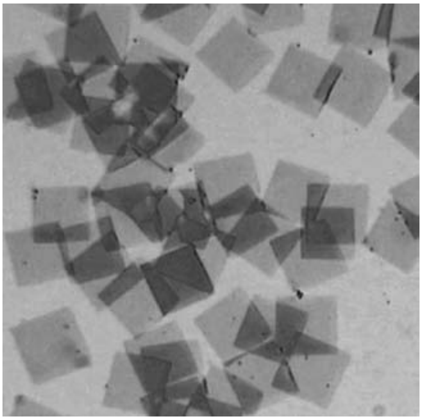


Figure 9.16 Transmission electron microscopy (TEM) micrograph of "platelets" micelles from a poly(styrene)-*b*-poly(ethylene oxide) diblock copolymer dissolved in methylcyclohexane. Total size of the picture 200 × 200 μm^2. (Reprinted with permission from Ref. [198]. Copyright (2003) with permission from Elsevier.)

After this short survey of the key characteristic features of block copolymer micelles, some specific recent advances in the field of block copolymer micelles will be discussed as highlighted in the introduction of this chapter.

9.4.2
Block Copolymer Micelles Containing Metal–Ligand Complexes

Block copolymers containing metal–ligand complexes can be defined as polymeric systems combining metal–ligand complexes to block copolymer structures [240, 241]. This should lead to systems combining the characteristic features of block copolymer micelles to the ones of metal–ligand complexes. Such micelles will be coined metallo-supramolecular block copolymer micelles in the following. The metal–ligand complexes could be localized in different areas of block copolymer micelles. In this respect, metal–ligand complexes could be located in the core, at the core–corona interface or in the corona of block copolymer micelles (Figure 9.17).

Metallo-supramolecular micelles with metal–ligand complexes in the core originate from either polycondensation-type supramolecular polymers or PFS-containing block copolymers. In polycondensation-type polymers, each monomer or macromonomer is linked by noncovalent interactions. This approach requires the use of monomers or macromonomers bearing at least two binding sites that could be further condensed through supramolecular interactions. This approach leads to polymers containing many supramolecular linkers along the main chain. Whenever, the polycondensation reaction is quenched by a polymer block bearing a single binding site, dissolving such a copolymer in a selective solvent for the quenching block results in micelles formed by a core containing the metal–ligand complexes.

This polycondensation approach has been first implemented for the polymerization of 1,16-bis(2, 2′ : 6′, 2″-terpyridin-4′-yloxy)hexadecane with

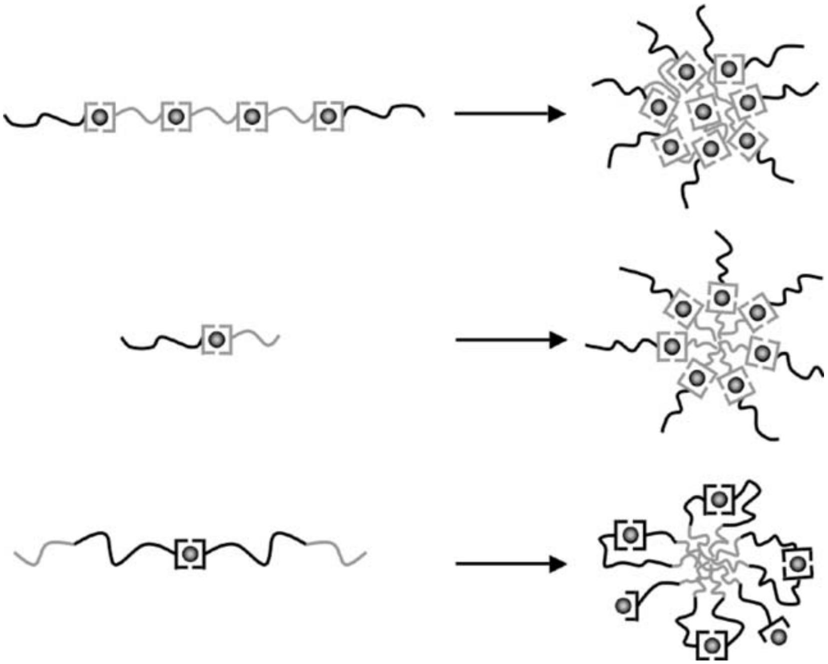


Figure 9.17 Schematic representation of the three different types of metallo-supramolecular block copolymers and of the accordingly formed micelles. The core and coronal blocks are represented in dark grey and black, respectively; the metal–ligand complexes are depicted as [●].

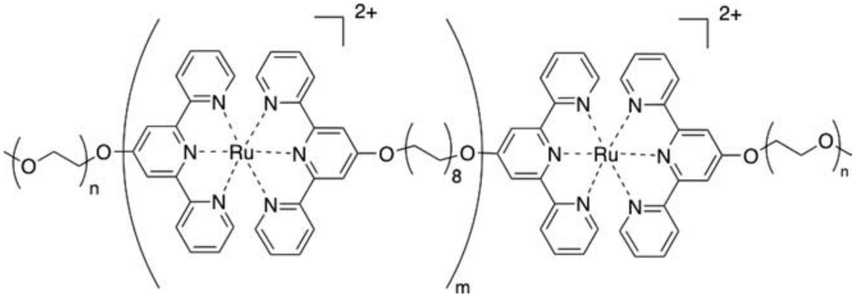


Figure 9.18 Chemical structure of polycondensation metallo-supramolecular block copolymers based on 1,16-bis(2,2′ : 6′, 2″-terpyridin-4′-yloxy)hexadecane–ruthenium complexes and α-terpyridine-ω-methyl-poly(ethylene oxide) as chain stopper. (Reprinted with permission from Ref. [242] Copyright (2006) by the American Chemical Society.)

$RuCl_3$ under reducing conditions [242]. This polymerization was further quenched by the addition of α-terpyridine-ω-methyl-poly(ethylene oxide) polymer blocks as chain stoppers (Figure 9.18). Spherical micelles with a supramolecular metal–ion complex containing a core and a PEO corona were obtained in water from this copolymer. The same polycondensation strategy was extended to prepare similar triblock copolymers using again, bis(2,2′ : 6′, 2″-terpyridin-4′-yloxy)hexadecane as the A unit in the core and a α-terpyridine-ω-methyl-poly(ethylene oxide) polymer as a chain stopper during the polymerization reaction. In contrast to the previous example, Ni(II), Co(II), and Fe(II) ions were used instead of ruthenium ions during the polymerization [243]. The influence of the different binding strengths of Ni(II), Fe(II), and Co(II) metal ions with terpyridine ligands on the metallo-polycondensation reaction was studied. Micelles were prepared from these copolymers in acetone/water (50/50) mixtures [243].

Beside polycondensation-type metallo-supramolecular block copolymers, another approach leading to micelles with metal–ligand complexes in the core is based on the use of block copolymers containing a PFS block The initial materials were block copolymers of poly(ferrocenyldimethylsilane) (PFDMS) blocks combined with PDMS or PS blocks [244]. Since the formation of these initial diblock copolymers, a variety of PFS-containing block copolymers has been reported. Dissolution of these block copolymers in a nonsolvent of the PFS blocks and a good solvent for the other blocks led to micelles containing a PFS core and a corona of the other blocks. Such micelles have been extensively studied by the groups of Manners and Winnik. Wormlike micelles (PFS/PDMS ratio 1:6) [245], or hollow tubes (PFS/PDMS ratio 1:13) [246, 247], with a PFS core and a PDMS corona, have been observed in hexane (Figure 9.19). The cylinders represent the thermodynamically preferred morphology in solution and this is controlled by the crystallization of the PFS segments. Indeed, when micelles are formed above the melting temperature of the PFS block, or when an amorphous PFS block is used, spherical micelles are formed [248]. The self-assembly of PFS-*b*-PMMA block copolymers was reported in acetone, a PMMA-selective solvent [249]. For a PFS/PMMA block ratio of 1:23, monomolecular or small spherical micelles were mainly formed, while only a fraction of the block copolymers associated into cylindrical micelles. As the PFS fraction increased, a larger proportion of copolymer chains aggregated into cylindrical micelles. At a block ratio of 1:6, well-defined cylindrical micelles were exclusively formed.

Aqueous micelles could also be obtained by combining PFS blocks with poly(dimethylaminoethylmethacrylate) (PDMAEMA) to lead to amphiphilic block copolymers [250]. In a further step, the PDMAEMA block was quaternized with methyl iodide. The micellization behavior of these two block copolymers was investigated in water.

Recently, Manners, Winnik, and coworkers reported on a unique behavior of these rodlike micelles with a crystallized PFS core [251]. They indeed demonstrated that the these micelles were capable of growing epitaxially through the addition of more polymer, producing extended micelles with a narrow size dispersity, in a process analogous to the growth of living polymer. By adding a different block copolymer, they could form co-micelles. They

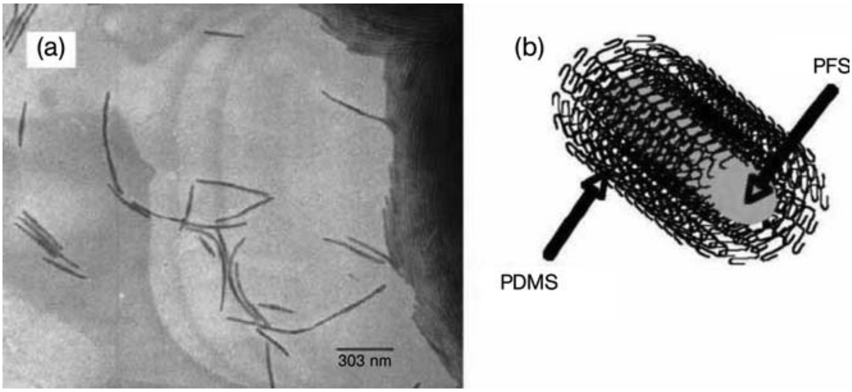


Figure 9.19 TEM image of rodlike micelles formed by a PFS_{50}–$PDMS_{300}$ (PFS/PDMS ratio 1:6, the numbers in subscript represent the average degree of polymerization of the corresponding block) block copolymer in hexane (a) and scheme for those rodlike micelles (b). (Adapted from Ref. [244] with permission.)

were also able to selectively functionalize different parts of these micelles. The authors initially prepared well-defined and stable cylindrical micelles from a PFS-*b*-PI (PFS-PI) diblock copolymer in hexane. However, when additional PFS-PI dissolved in a common good solvent such as tetrahydrofuran (THF) or toluene was added, the micelles appeared to become longer. Moreover, the authors noted that this growth process did not process via ‘‘self-micellization’’ of the free chains followed by addition to the ends of preexisting micelles (micelles fusion), but rather that the micelle growth happened via the addition of free chains on the preexisting micelle (Figure 9.20).

Furthermore, this growth process was monitored to proceed linearly with time, in agreement with the concept of a living polymerization process. The addition of another type of PFS-containing block copolymer (PFS-*b*-polymethylvinylsiloxane)–nonassociated chains to the initial PFS-PI micelles allowed the formation of co-micelles. The resulting rodlike micelles had ABA-like structures, as the growth process happened at both ends of the initial PFS-PI micelles. Finally, the authors demonstrated that the PI coronal part of these micelles could be stabilized by cross-linking leading to shell-cross-linked micelles [252]. Very recently, more complex structures have been obtained by using the same living polymerization driven by the epitaxial crystallization of a core-forming metallo block. In this example, the use of platelet micelles as initiators enabled the formation of scarf-like architectures in which cylindrical micelle tassels of controlled length are grown from specific crystal faces [253]. Living polymerizations driven by heteroepitaxial growth could also be performed leading to the formation of tri- and pentablock and scarf architectures with cylinder–cylinder and platelet–cylinder connections, respectively (Figure 9.21) [253].

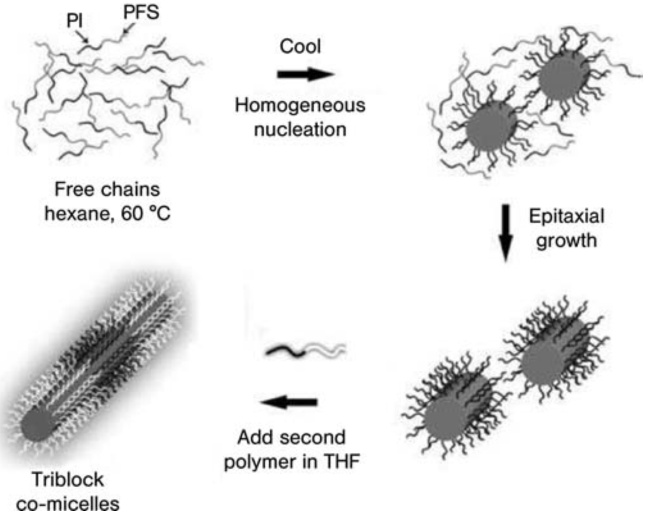


Figure 9.20 Schematic representation for the formation of co-micelles from PFS-containing block copolymers via epitaxial growth process. (Reprinted from [251] with permission from AAAS.)

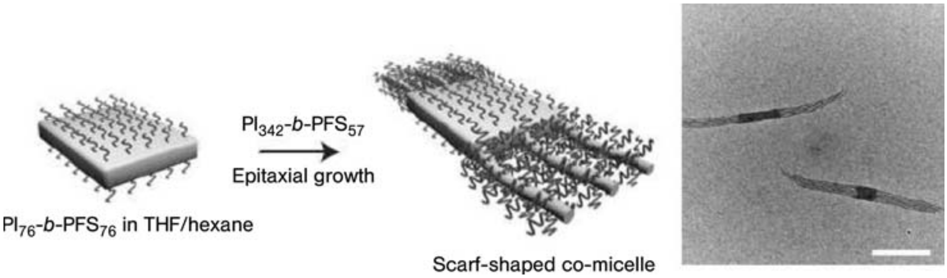


Figure 9.21 Schematic representation of scarf-shaped micelle obtained by growing PI_{342}-PFS_{57} unimers heteroepitaxially from a seed solution of PI_{76}-PFS_{76} crystals in xylene/decane (1:10 v/v). TEM micrograph of these scarf-shaped micelles (scale bar is 500 nm). (Reprinted from [253] with permission from Macmillan Publishers Ltd.)

Metal–ligand complexes have been also introduced at the core–corona interface in block copolymer micelles. With this aim, metallo-supramolecular diblock copolymers in which a metal–ligand complex is located between the two blocks have been designed [240, 241]. The synthesis of such block copolymers requires the formation of heteroleptic complexes and hence, the use of a two-step complexation process [254]. Such an approach could be used whenever bis-2,2′ : 6′, 2″-terpyridine–ruthenium complexes are used. Indeed, ruthenium(III) ions are known for forming a stable mono-complex with

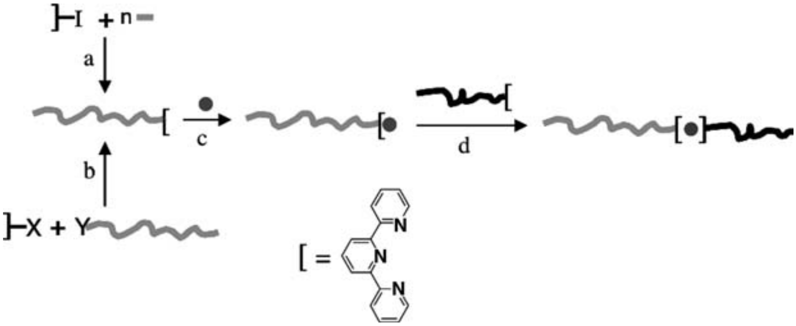


Figure 9.22 Schematic representation of the synthetic strategy to prepare metallo-supramolecular block copolymers with a metal–ligands complex at the block junction. The first step is the synthesis of the macroligands by using either a functionalized (supramolecular) initiator (a) or grafting a terpyridine on a reactive chain end (b). The second step is the preparation of a mono-complex with Ru(III) (c). Finally, the second block, bearing a free terpyridine unit, is added to form a terpyridine–ruthenium(II) bis-complex (d).

terpyridine, while ruthenium(II) ions do form a stable bis-complex with the same ligand [255]. Therefore, the synthesis of metallo-supramolecular block copolymers can be selectively achieved by first making a macromolecular ruthenium(III) mono-complex, which is further reacted under the appropriate reducing conditions and another terpyridine end-functionalized polymer block to form the desired diblock copolymer (Figure 9.22).

Poly(styrene)-[Ru]-poly(ethylene oxide) (PS-[Ru]-PEO) block copolymers were initially studied [254, 256]. Since the method for preparing metallo-supramolecular block copolymers relies on the coupling of two macroligands via a simple two-step synthesis, it is rather straightforward to prepare a library of block copolymers. This combinatorial approach is certainly an advantage of metallo-supramolecular block copolymers compared to classical covalent ones. Moreover, the high stability of the bis-2,2′ : 6′, 2″-terpyridine–ruthenium(II) complexes allows the integrity of the formed block copolymers to be kept in various environments, such as organic solvents or water, even under extreme pH and salt concentration [257]. A library of PS-[Ru]-PEO block copolymers was prepared and the micellization behavior in water was studied [258]. The core size of the accordingly obtained micelles did not scale linearly with the DP of the PS block as expected from the theory of classical covalent copolymers. This unusual behavior has been attributed to electrostatic repulsions between the charged terpyridine–ruthenium bis-complexes present at the junction of the two blocks, which strongly affect the self-assembly behavior. This has been demonstrated by preparing micelles in the presence of salt to screen out the repulsions. In this case, the metallo-supramolecular block copolymers behaved as their covalent counterparts. Besides the formation of libraries of copolymers, another advantage of metallo-supramolecular block copolymers is the reversibility of the bis-terpyridine complexes. This concept has been initially demonstrated on metallo-supramolecular micelles prepared from an amphiphilic poly(ethylene-*co*-butylene)-[Ru]-PEO (PEB-[Ru]-PEO) copolymer in water [259]. Although bis-2,2′ : 6′, 2″-terpyridine–ruthenium(II) complexes have proven to be extremely stable in various environments, experiments on PEB-[Ru]-PEO micelles have shown that the addition of a large excess of a competing ligand (hydroxyethyl ethylenediaminetriacetic acid (HEEDTA), trisodic salt) did allow the opening of those complexes. Very recently, the reversibility of bis-2,2′ : 6′, 2″-terpyridine–ruthenium(II) complexes has been employed by O'Reilly and coworkers to create nanocapsules from a PS-[Ru]-poly(acrylic acid) (PAA) diblock copolymer (Figure 9.23) [260]. In the first step, micelles with a PS core and a PAA corona were obtained in water from this copolymer. The PAA corona was then cross-linked by using 2,2′-(ethylenedioxy)-bis(ethylamine) in the presence of 1-[3′-(dimethylamino)propyl]-3-ethylcarbodiimide methiodide to create a cross-linked shell around the PS core.

The hollowing out of these nanoparticles was investigated using HEEDTA as a competitive ligand to open the bis-2,2′ : 6′, 2″-terpyridine–ruthenium(II) complexes. The shell-cross-linked micelles were then extensively dialyzed into a THF/water (2:1) mixture to remove the uncomplexed PS chains from the core. To confirm the hollow nature of the nanostructures, and thus complete removal of the hydrophobic PS core domain, sequestration studies were performed using a hydrophobic dye molecule. The response of the accordingly obtained nanocages to pH changes was also investigated. A reversible pH-dependent change in size was demonstrated. Indeed, the size of these nanocages could be readily cycled between about 90 and 240 nm by changing the pH between 5 and 9.

Interestingly enough, another approach toward similar hollow polymeric nanocages has been reported, again by O'Reilly *et al.* [261]. This strategy relies on both an SCS "pincer"-based nitroxy-mediated radical polymerization (NMP) initiator and a pyridine-functionalized NMP initiator, which were employed for the polymerization of styrene and *tert*-butyl acrylate, respectively. After deprotection of the *tert*-butyl group, the two polymers were connected to form a metallo-supramolecular amphiphilic block copolymer using relatively weak coordination of the pyridine to a palladium(II) metal center and strong noncovalent interaction with the SCS "pincer" ligand (Scheme 9.1). Shell-cross-linked micelles were then prepared by cross-linking of the PAA chains as described above. The hollowing of the micellar core was achieved at low pH by repeated dialysis. As a result, polymeric nanocages with well-defined interior chemical functionality were obtained. Besides micelles with spherical morphology, rodlike micelles were obtained from a PFS-[Ru]-PEO copolymer in water [262]. The micelles had a constant diameter but were rather polydisperse in length, and dynamic light scattering (DLS) indicated that they were rather flexible. Crystallization of the PFS in these micelles is thought to be responsible for the formation of these rodlike structures.

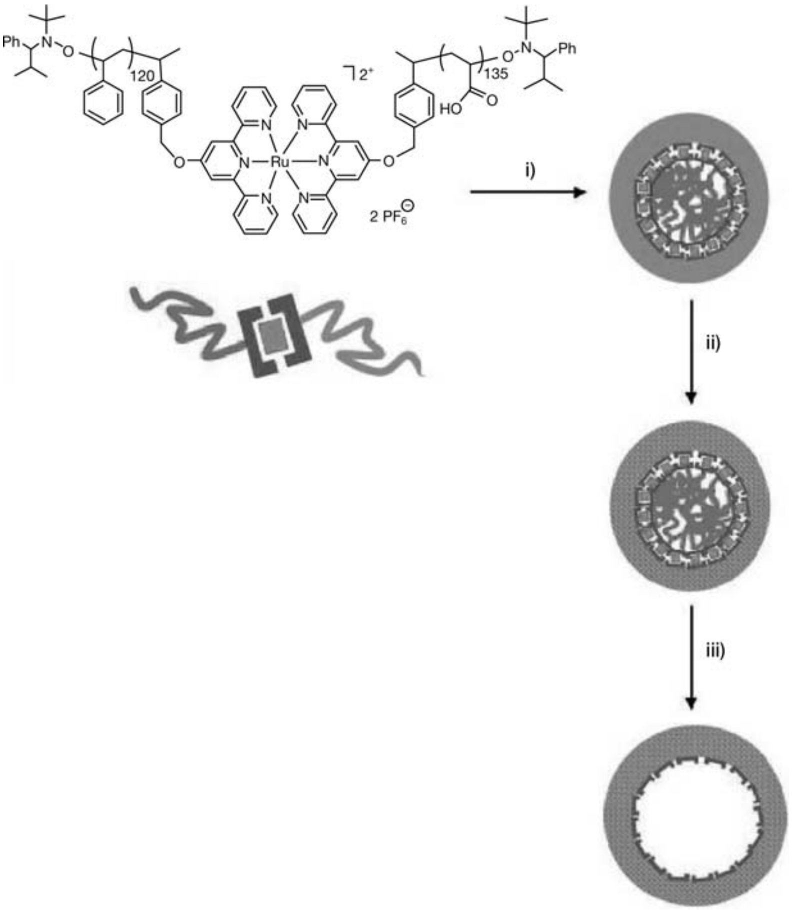
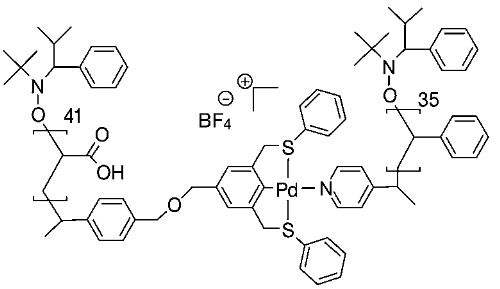


Figure 9.23 Formation of hollow nanocapsules from a PS-[Ru]-PAA metallo-supramolecular block copolymer (ruthenium(II) as a small square). The PS-[Ru]-PAA copolymer is self-assembled into micelles (i); the PAA shell is cross-linked (ii); the [Ru] complexes are opened by treatment with HEEDTA and the released PS blocks are removed by repeated dialysis in THF/water mixtures (iii). (Adapted with permission from Ref. [260]. Copyright (2008) by the American Chemical Society.)

Harruna *et al.* reported the synthesis of an amphiphilic PS-[Ru]-poly(*N*-isopropylacrylamide) (PNIPAM) using reversible addition fragmentation chain transfer (RAFT) polymerization with a terpyridine-functionalized chain transfer agent [263]. Such an approach is very interesting, since it allows the introduction of thermo-responsive PNIPAM with lower critical solution temperature (LCST) behavior in metallo-supramolecular block copolymer micelles. pH-responsive systems have been prepared by complexing a terpyridine-functionalized polystyrene-*b*-poly(2-vinylpyridine) (PS-P2VP) copolymer with a terpyridine-functionalized PEO to lead to a



Scheme 9.1 Structure of the SCS "pincer".

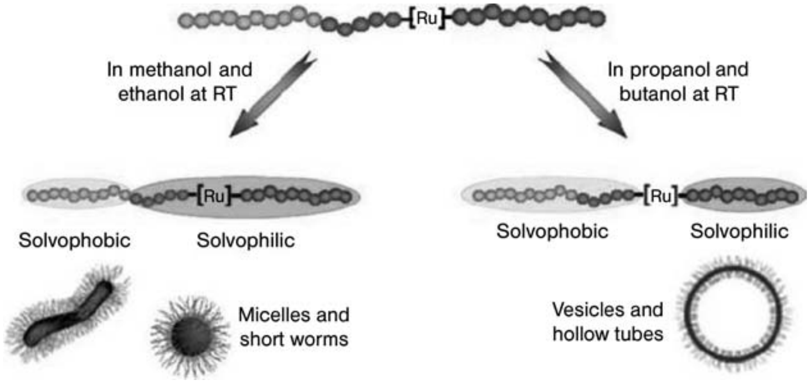


Figure 9.24 Schematic representation of the different structures formed by PS-PTFMS-[Ru]-PEO triblock terpolymers at room temperature. (Reproduced from Ref. [357] with permission of The Royal Society of Chemistry.)

PS-P2VP-[Ru]-PEO ABC triblock terpolymer [264]. This copolymer was further used to prepare core–shell–corona micelles consisting of a PS core, a P2VP shell, and a PEO corona. This kind of micelle has the capability to respond to pH via the protonation/deprotonation of the P2VP shell. The pH response of these micelles can be advantageously used for the encapsulation or release of active species reversibly trapped in the P2VP shell. Thermo-responsive systems were also very recently designed from polystyrene-*b*-poly(*para*-trifluoromethylstyrene)-[Ru]-poly(ethylene oxide) (PS-PTFMS-[Ru]-PEO) metallo-supramolecular triblock terpolymers [357]. Spherical micelles, wormlike micelles, vesicles, and hollow tubes were all accessed from this copolymer by varying the polarity of the solvent, which provokes a change in the hydrophilic to hydrophobic block length within the same macromolecule by dissolution or precipitation of the PTFMS-block (Figure 9.24). The self-assembled structures with both PS and PTFMS as insoluble blocks are presumed to be multicompartmentalized based on the incompatibility of these blocks. Furthermore, the thermo-responsive behavior of PTFMS allows reversible control over the micellar size and morphology [265]. The last two examples could be also discussed in the frame of Section 9.4, but have been included here due to the presence of a metal–ligand in their structure.

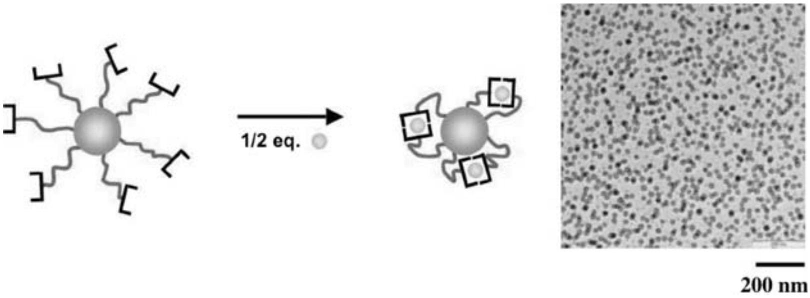


Figure 9.25 Schematic representation of the effect of added metal ions (metal ion/terpyridine molar ratio of 1/2) on metallo-supramolecular micelles prepared from a PS$_{47}$-*b*-P*t*BA$_{55}$-[copolymer in ethanol and TEM picture of the initial PS$_{47}$-*b*-P*t*BA$_{55}$-[micelles. (Adapted from Ref. [265]. Reproduced by permission of The Royal Society of Chemistry.)

Finally, metal–ligand complexes have been introduced in the corona of block copolymer micelles. More precisely, the terpyridine ligand has been introduced at the extremity of the coronal blocks [265]. In such systems, micellization of the terpyridine-functionalized block copolymer is realized prior to the addition of metal ions. Whenever sufficiently diluted solutions of micelles are considered, the addition of metal ions only resulted in intramicellar complexation. In sharp contrast, the addition of metal ions to more concentrated solutions of these micelles resulted in intermicellar complexation, which further allowed the formation of micellar gels. PS-*b*-poly(*tert*-butyl acrylate) (P*t*BA) diblock copolymers end-functionalized with a terpyridine moiety on the P*t*BA block have been considered in this approach. Micelles were prepared in ethanol, a selective solvent for the P*t*BA blocks that consist of a PS core and a P*t*BA corona with terpyridine ligands located at the extremity of the P*t*BA chains. The addition of metal ions (Zn^{2+}, Ni^{2+}, and Fe^{2+}) to the micelles resulted in a looping of the coronal chains inducing the formation of flowerlike micelles (Figure 9.25) [265]. The extent of this decrease depended on the metal ion used. The largest decrease was observed for Ni^{2+} ions and the smallest for Zn^{2+} ions. This decrease was attributed to a strong contraction of the P*t*BA coronal chains. To trigger the formation of mono-complexes instead of bis-complexes in the micellar corona, a large excess of metal ions was added. Under these conditions, the Ni^{2+} containing sample still formed flowerlike micelles, as no increase in the size of the micelle was observed. In sharp contrast, the Fe^{2+} and Zn^{2+}-containing sample showed an increased of R_h due to the disappearance of looped P*t*BA chains. These experimental observations have been indeed correlated with the corresponding stability constants of the complexes from terpyridine and Ni^{2+}, Fe^{2+}, and Zn^{2+}.

In addition to tuning the micellar size by changing the conformation of the coronal chains, this strategy could also be used to build more complex objects. This has been achieved by complexing a third terpyridine-functionalized polymer block on the PS-P*t*BA-[micelles decorated with metal ions. A terpyridine end-functionalized PEO, PEO-[, has been added to the PS-P*t*BA-[micelles previously loaded with 1 equivalent of Fe^{2+} ions. This should yield PS-P*t*BA-[Fe]-PEO micelles. To further prove that the additional PEO layer has been grafted to the initial micelles, the PS-P*t*BA-[Fe]-PEO micelles were transferred into water, a selective solvent for the PEO block. Stable micelles with a PS core, a P*t*BA shell, and a PEO corona were obtained, proving the success of the transfer in water and thereby, the efficiency of the grafting of the additional PEO layer through formation of Fe^{2+}–terpyridine complexes [265].

9.4.3
Multicompartment Micelles Made from ABC Triblock Terpolymers

ABC triblock terpolymers have attracted great interest due to the huge number of different morphologies that have been observed so far in the bulk [58]. The main motivation for studying ABC triblock terpolymer micelles is related to the presence of a third nano-sized compartment in the micellar structure. Depending on the investigated systems, this third compartment can be either soluble or insoluble in the considered solvent, leading to different types of micelles that will be discussed in the following text. In 2005, we published a review on triblock terpolymer micelles [266]. In the following, we will summarize the main developments that occurred recently. More complete information about previous works on triblock terpolymer micelles can be therefore obtained in the previous review [266].

9.4.3.1 Micelles with a Compartmentalized Core

These micelles are generally characterized by the so-called "onion," "three-layers," or "core–shell–corona" structures in which the first insoluble A block forms the micellar core, the second insoluble B block is wrapped around the core, and the third soluble C block extents into the solution to form the micellar corona. Most of the reported examples have used water as the selective solvent. Early examples include the works of Kriz *et al.* [267], Eisenberg *et al.* on crew-cut systems [268], Ishizone *et al.* [269], and Dumas *et al.* [270]. Core–shell–corona micelles have been also obtained by using a mixture of two diblock copolymers, AB and BC, in a selective solvent of block A or C instead of starting from an ABC triblock terpolymer as illustrated by the early work of Prochazka *et al.* [271]. Since these micelles are not produced from ABC triblock terpolymer, they will not be further discussed here.

Stimuli-responsive properties were also imparted to core–shell–corona micelles. In this case, one of the compartments of the core can become soluble upon application of a stimulus (pH, temperature, etc.). Such systems could be very interesting for the controlled release of active species encapsulated in the stimuli-responsive compartment. In this respect, Gohy *et al.* reported on pH-responsive micelles formed by polystyrene-*b*-poly(2-vinylpyridine)-*b*-poly(ethylene oxide) (PS-P2VP-PEO) triblock terpolymers in water and consisting of a PS core, a pH-sensitive P2VP shell, and a PEO corona [272, 273]. At pH values above 5, the P2VP blocks are hydrophobic and collapsed on the PS core, while at pH values below 5, they are protonated and adopt a stretched conformation because of the mutual electrostatic repulsions. These two micellar states have been characterized by DLS and visualized by TEM and atomic force microscopy (AFM). Moreover, the transition between the two types of micelles was entirely reversible and could be repeated many times [272]. Similar PS-P2VP-PEO micelles were also recently studied by Prochazka *et al.* [274, 275]. The pH-responsive P2VP shell was also used as template for the production of gold nanoparticles [272] or hollow silica nanoparticles [276], and can be complexed with low molecular weight anionic surfactants [277]. Interestingly enough, cylindrical micelles were prepared from the same PS-P2VP-PEO copolymers by using a mixture of toluene and dimethyl formade (DMF) as initial solvent before transfer to a pure water phase [278, 279]. These micelles had a core–shell–corona structure, but the P2VP chains in the tubular shell were found to be in a stretched conformation whatever the pH. Further swelling of the PS core of the PS-P2VP-PEO micelles resulted in segmented wormlike micelles and ultimately in vesicular structures (Figure 9.26) [280]. Giant segmented wormlike micelles were also prepared from PS-P2VP-PEO copolymers with larger PS and P2VP blocks. This study showed that these micelles comprised sequences of repeated elemental disks that further became connected through threads to form various giant segmented wormlike micelles [281].

pH-responsive micelles from PS-P2(4)VP-PMAA (PMAA = polymethacrylic acid) triblock terpolymers were prepared by Giebeler *et al.* [282]. These authors investigated the polyelectrolyte complex formation in these micelles by potentiometric, conductimetric, and turbidimetric titrations of acidic THF/water solutions. The formation of an inter-polyelectrolyte complex at the isoelectric point was evidenced, in which the hydrophobic PS cores are most likely embedded in a mixed corona of the two polyelectrolyte blocks. Very recently, pH-sensitive poly(2-vinyl pyridine)-*b*-poly(acrylic acid)-*b*-poly-(*n*-butyl methacrylate) (P2VP-PAA-P*n*BMA) was investigated in aqueous solution [283]. A unique diversity of structural organizations was observed, including thermosensitive centrosymmetric core–shell–corona micelles, compact spheres, polyelectrolyte flowerlike micelles, a charged pH-sensitive 3D network, toroidal nanostructures, and finite size clusters (microgels). The transition between different micelles and the hydrogel was induced via the regulation of electrostatic and hydrophobic interactions in the system [283].

Thermo-responsive ABC triblock micelles were investigated by Patrickios *et al.* using copolymers containing an insoluble poly(ethyl vinyl ether) block, a thermo-responsive poly(methyl vinyl ether) mid-block, and a water-soluble poly(methyl triethylene glycol vinyl ether) outer block [284]. While in aqueous solutions only unimers were found, addition of salt led to aggregates. Other examples of temperature-sensitive micelles are described in Refs [285] and

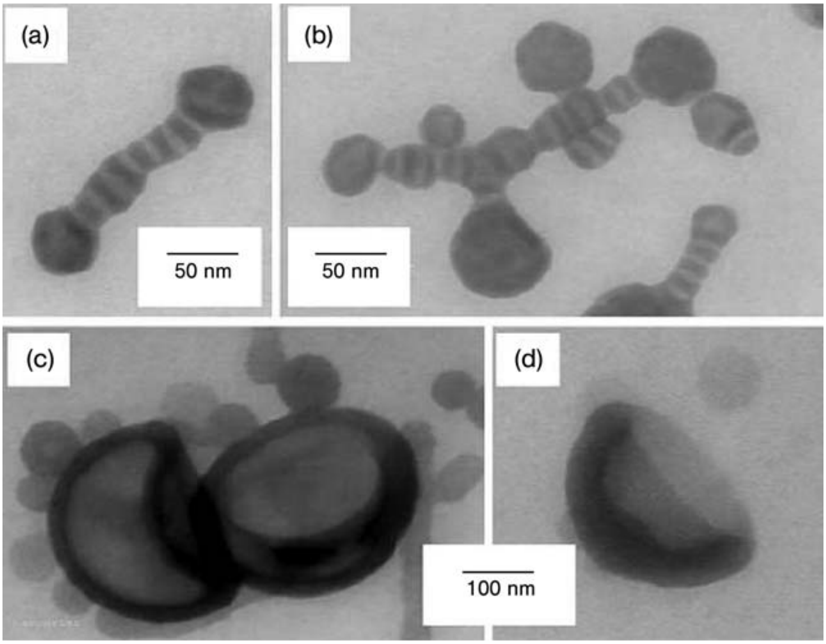


Figure 9.26 Segmented wormlike micelles (a and b) and vesicles (c and d) prepared from a PS-P2VP-PEO triblock terpolymer in toluene/water mixtures. (Reprinted from Ref. [280]. Copyright (2006) with permission from Elsevier.)

[286]. In addition to temperature, these micelles can also respond to pH changes. The temperature-dependent association of ABC triblock terpolymers composed of segments with different LCST was also recently investigated. Poly(2-ethoxyethyl vinyl ether)-*b*-poly(2-methoxyethyl vinyl ether)-*b*-poly(2-(2-ethoxy)ethoxyethyl vinyl ether), PEOVE-PMOVE-PEOEOVE, forms micelles in water when the temperature is increased above the LCST of the PEOVE block. The micelles then associate to form a physical gel above the LCST of the PEOEOVE block, and finally precipitate when the temperature is higher than the LCST of the PMOVE block [287]. Thermo-responsive core–shell–corona micelles have been prepared from polystyrene-*b*-poly(*N*-isopropylacrylamide)-*b*-poly(ethylene oxide) (PS-PNIPAM-PEO) triblock terpolymers [288]. These micelles can be seen as the thermo-responsive analogs of the previously discussed pH-responsive PS-P2VP-PEO system.

In all these examples, the two compartments found in the micellar core are expected to adopt a sphere-in-sphere morphology (core–shell model). Other morphologies could, however, be expected for multicompartment cores such as the spheres-on-spheres (raspberry) morphology.

Such a morphology was evidenced by Laschewsky and coworkers in micelles formed by a linear poly(4-methyl-4-(4-vinylbenzyl)morpholin-4-ium

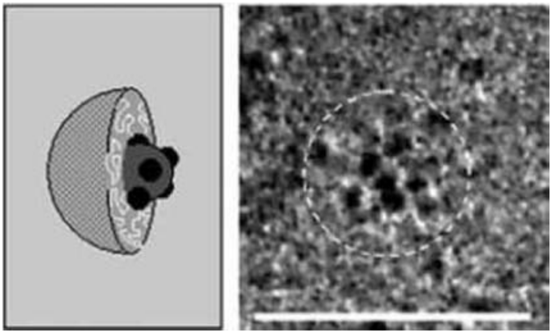


Figure 9.27 Cryo-TEM image and schematic representation of multicompartment micelles from the PVBM-PS-PVBFP triblock terpolymer in aqueous medium. The scale bars correspond to 50 nm. (Reprinted with permission from Ref. [289].)

chloride)-*b*-polystyrene-*b*-poly(pentafluorophenyl 4-vinylbenzyl ether) (PVBM-PS-PVBFP) triblock terpolymer in water [289]. The investigated copolymer consisted of a long cationic hydrophilic block, PVBM, a hydrophobic PS block, and a mixed hydrocarbon/fluorocarbon one (PVBFP). Hydrocarbon and fluorocarbon blocks were selected, since such segments tend to be strongly incompatible and should therefore favor the segregation into distinct domains. Cryo-TEM imaging showed that the core of the accordingly obtained micelles in water was segregated into nanometer-sized compartments in which many small, fluorocarbon-rich domains coexist with a continuous hydrocarbon-rich region (Figure 9.27) [289].

Multicompartment micelles in dilute aqueous solution were reported for miktoarm ABC triblock terpolymers containing PEO, hydrogenated 1,2-polybutadiene (polyethylethylene, PEE), and perfluorinated polyether blocks [290]. Because of the miktoarm architecture of the copolymers, the two incompatible hydrophobic blocks were forced to make contact with the PEO coronal chains. The resulting micellar structures were shown to depend on the relative lengths of the blocks and could be tuned from discrete multicompartment micelles to extended wormlike structures with segmented cores (Figure 9.28). The wormlike structures were shown to result from the uniaxial clustering of discrete micelles. In this peculiar morphology, the different cores are able to share their PEO coronas, thus protecting them from the highly unfavorable exposure to water [290]. The addition of THF (60 wt%) into these aqueous solutions induced an evolution from multicompartment micelles to mixed PEE + PEO corona micelles [291]. Cryogenic TEM suggested that, as the PEE block transitions from the core to the corona, the micelle morphologies evolve from disks to oblate ellipsoid micelles, with worms and spheres evident at intermediate compositions [291].

The micellization of $(ABC)_n$ multiarm star triblock terpolymers was also recently studied by Tsitsilianis and coworkers [292]. Four linear and four

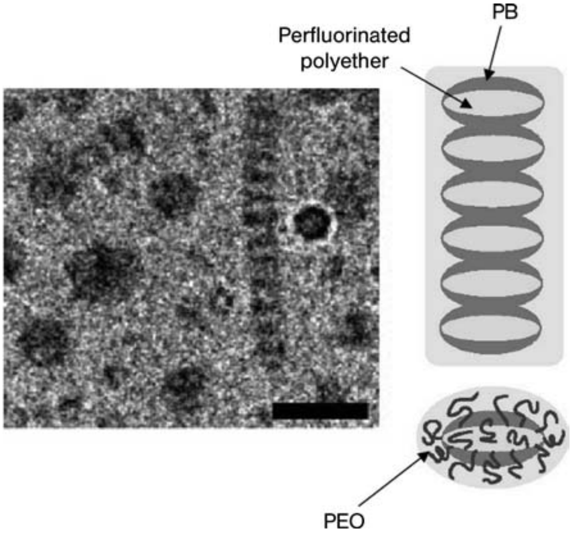


Figure 9.28 Cryo-TEM image of isolated micelles and segmented rods made from miktoarm ABC block copolymers containing PEO, PB, and perfluorinated polyether blocks. A schematic representation of the stacking of block copolymer chains in segmented worms is also shown. (Reprinted from Ref. [290] with permission from AAAS.)

star equimolar terpolymers based on hydrophilic methylhexa(ethylene glycol) methacrylate, 2-(dimethylamino)ethyl methacrylate, and methyl methacrylate were investigated in aqueous dilute solutions. It was found that the $(ABC)_n$ multiarm star terpolymers formed unimolecular micelles comprising three centrosymmetric compartments. The position of each compartment could be determined by the block sequence (ABC, ACB, or BAC) at will. On the other hand, the ABC linear counterparts formed loose associates with very low aggregation numbers [292].

For some applications, it is desirable to lock the micellar structure by cross-linking one of the micellar compartments. Cross-linked core–shell–corona micelles have been prepared and investigated by several groups as illustrated by the work of Wooley and coworkers [293] who reported the cross-linking of micelles made from poly(styrene)-*b*-poly(methyl acrylate)-*b*-poly(acrylic acid) (PS-PMA-PAA) triblocks in aqueous solution by amidation of the PAA shell. Wooley, Pochan, and coworkers prepared toroidal block copolymer micelles from similar PS-PMA-PAA copolymers dissolved in a mixture of water, THF and 2,2-(ethylenedioxy)diethylamine [294]. Under optimized conditions, the toroidal phase was the predominant structure of the amphiphilic triblock terpolymer. The collapse of the negatively charged cylindrical micelles into toroids was found to be driven by the divalent 2,2-(ethylenedioxy)diethylamine cation. The same group reported on various cross-linked micellar aggregates prepared by the same strategy [295, 296]. For example, nanoparticles with different

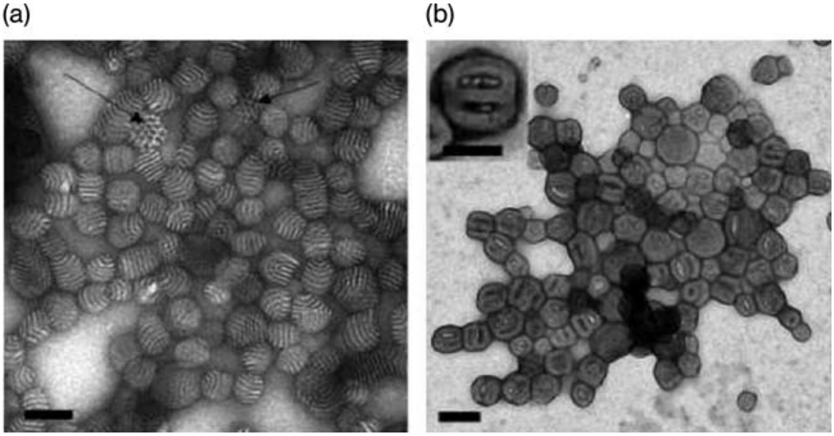


Figure 9.29 TEM image (a) showing nanoparticles formed via the self-assembly of the PS-PMA-PAA triblock terpolymer complexed with the 2,2-(ethylenedioxy) diethylamine (EDDA) counterion in 1:0.4, THF:water volume ratio (lamellar phase separated particles and a few with a hexagonal phase are observed) and TEM image (b) porous and channel-like particles formed by PS-PMA-PAA triblock terpolymer complexed with spermidine. Scale bars are 200 nm. (Reprinted with permission from Ref. [298]. Copyright (2008) by the American Chemical Society.)

internal structures (lamellar, bicontinuous-like, or porous) were formed by PS-PMA-PAA triblock terpolymers in THF/water mixed solvents in the presence of multivalent organic counterions [297, 298]. The internal lamellar spacing of the particles could be tuned by using triblock terpolymers with different block lengths. In addition, the internal symmetry of the nanoparticles was changed simply by changing the solvent composition (Figure 9.29). When spermidine was used as multiamine counterion, nanoparticles with pores or channels were produced by adjusting the water content (Figure 9.29). In these systems, the internal nanostructure is due to local phase separation of the block copolymers and can be tuned by varying the solvent composition, the relative block composition, and the valency of the organic counterion [297, 298].

Cross-linked micelles from triblock terpolymers were also reported by Armes *et al.*, who used a bifunctional alkyl iodide to cross-link amino-methacrylate groups [299]. In a very recent report, pH-responsive cross-linked micelles were reported from poly(ethylene oxide)-*b*-poly[*N*-(3-aminopropyl)methacrylamide]-*b*-poly[2-(diisopropylamino)ethyl methacrylate] (PEO-PAPMA-PDPAEMA) triblock terpolymers prepared by RAFT [300]. These triblock terpolymers molecularly dissolve in aqueous solution at low pH due to protonation of the PAPMA and PDPAEMA blocks. Above pH 6.0, the polymers self-assemble into micelles consisting of PDPAEMA cores, PAPMA shells, and PEO coronas. The carboxylic acid chain ends of a telechelic PNIPAM were converted to *N*-hydroxysuccinimidyl esters (NHS) through dicyclohexylcarbodiimide coupling, yielding an amine-reactive polymeric cross-linking agent, NHS-PNIPAM-NHS. The micelles formed by the PEO-PAPMA-PDPAEMA copolymer were then cross-linked via reaction of PAPMA (shell) amine functionality with NHS-functionalized PNIPAM. Other recent examples of shell-cross-linked micelles from triblock terpolymers can be found in Refs [301–305], thus demonstrating the interest in this approach.

Liu and coworkers have investigated the micellization of polyisoprene-*b*-poly(cinnamoethyl methacrylate)-*b*-poly(*tert*-butyl acrylate) (PI-PCEMA-P*t*BA) triblock terpolymers in mixtures of THF and methanol and have used these micelles to create various nano-objects. The shell-forming PCEMA block was then cross-linked by ultraviolet (UV) irradiation to lock the structure [306]. In a further step, hollow nanospheres were obtained by ozonolysis of the PI micellar core. If pure methanol is used as solvent, cylindrical micelles are formed, which can also be transformed into nanotubes by the same procedure [307]. The micellization of the same copolymer in mixtures of THF and hexane was also studied [308]. Under these conditions the corona is formed by the PI block, the shell by PCEMA, and the core by P*t*BA. After cross-linking the shell, the PI corona was hydroxylated to make the micelles dispersible in water, and the P*t*BA core was made compatible with inorganic species by cleaving the *tert*-butyl groups.

9.4.3.2 **Micelles with a Compartmentalized Corona**

Micelles of this type are formed by ABC triblock terpolymers containing one block insoluble in the considered solvent. The insoluble block can either be located in between the two soluble blocks (block B) or can be located at one extremity of the triblock (block A or C). Different situations have to be considered, depending on the extent of segregation observed between the two solvated coronal blocks. Indeed, the two coronal blocks can give rise to a homogeneously mixed corona or to segregated corona. If there is no segregation between the coronal chains, only two compartments are obtained, and micelles similar to usual AB diblock copolymers are formed. The factors controlling the extent of segregation among coronal chains have not yet been clearly established or experimentally investigated. They will be shortly discussed here in view of the few following examples.

Early examples of micelles containing two types of coronal chains homogeneously mixed were reported by Patrickios and coworkers who studied the formation of micelles from different topological "isomers" of PDMAEMA-PMMA-PMAA triblock terpolymers as a function of pH [309–311]. The isomer having the hydrophobic block in the center yielded micelles characterized by an AB-like structure with a PMMA core and a shell composed of a mixture of the PDMAEMA and PMAA blocks. The other two isomers yielded core–shell–corona micelles twice as big with a PMMA core, and a shell and corona formed by the chains of the two other blocks.

Biodegradable/biocompatible copolymers with potential application for drug delivery can also be used to prepare micelles. PEO-polyglycidol-poly(L,L-lactide)

(PLLA) triblock terpolymers were synthesized and it was shown that they form micelles in water if the PLLA block has a molecular weight above 5000 g mol^{-1} [312]. The application of triblock terpolymer micelles in biomedical applications is currently a topic of high interest as illustrated by the numerous recent publications in that field [313–316].

Micelles from PS-P2VP-PMMA triblock terpolymers dissolved in toluene were reported by Tsitsilianis and Sfika [317]. Spherical micelles with a dense P2VP core, surrounded by mixed PS and PMMA chains in the corona were observed. It was shown that the aggregation number Z and the micellar size were strongly influenced by the length of the P2VP middle block. A similar study was performed on PS-PI-PMMA terpolymers in nonsolvents of the PI block. In this case, Z is much larger in DMF than in dimethylacetamide, because the latter is a better solvent for the PS and PMMA blocks [318].

In all the examples previously discussed in this section, the coronal chains are expected to be statistically mixed in the corona. It is not clear whether partial or complete phase separation is occurring among coronal chains. A method to produce micelles with completely segregated coronal chains has been reported for the so-called ‘‘Janus’’ micelles. The strategy to create such Janus micelles is based on the transfer of a preformed bulk organization in solution directly leading to noncentrosymmetric objects. Janus micelles have been initially obtained by transferring in solution, the bulk morphology of a PS-PB-PMMA (PB, polybutadiene) triblock terpolymer in which the central PB minor block forms spheres at the interface between PS and PMMA lamellae. To preserve the PS and PMMA coronal hemispheres, the PB spheres had to be cross-linked in the bulk structure. Dissolution of the bulk material in THF, a good solvent for both the PS and PMMA chains, yielded Janus micelles with a PB core surrounded by PS and PMMA half coronas (Figure 9.30) [319]. These Janus micelles showed a strong tendency to form larger aggregates that can be regarded as supermicelles. Supermicelles coexist with single Janus micelles, as evidenced by various morphological observations realized both in THF solution and on silicon and water surfaces [319, 320].

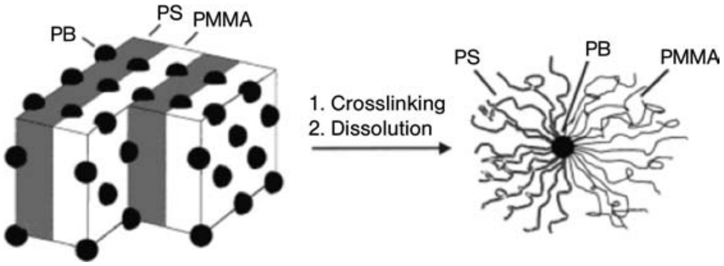


Figure 9.30 Schematic representation of the Janus micelle preparation. (Reprinted with permission from Ref. [319]. Copyright (2001) by the American Chemical Society.)

The hydrophobic/hydrophilic contrast in the Janus micelles can be strongly enhanced by the hydrolysis of the PMMA chains resulting in PMAA hydrophilic blocks [321]. The resulting micelles can then be gradually transferred in pure water starting from a 1,4-dioxane solution. However, the hydrophobic PS hemicorona collapses on the PB core and the whole insoluble part is then fully or partially surrounded by the PMAA chains. Aggregation into supermicelles and formation of aggregates of supermicelles was also evidenced in this investigation [321]. The influence of pH on PS-PB-PMAA Janus micelles was also investigated. At high pH, the hydrodynamic radius of the supermicelles is larger than under acidic conditions as a result of the ionization of the PMAA chains leading to their stretching [321]. Cylindrical micelles with an asymmetric corona, i.e., Janus cylinders, were also produced from PS-PB-PMMA triblock terpolymer. Those asymmetric nanocylinders were prepared by the same procedure as for spherical Janus micelles, but with a polymer composition forming another bulk morphology. In this case the PS-PB-PMMA terpolymer formed PB cylinders embedded at the interface between PS and PMMA lamellae [322]. Preliminary investigations on Janus spherical micelles with a cross-linked P2VP core and PS and poly(butyl methacrylate) (PBMA) coronal hemispheres have also been reported by Saito *et al.* [323].

Segregated coronal chains were also obtained by direct dissolution of triblock terpolymer chains without the need to stabilize a preexisting bulk organization as presented for Janus micelles. Indeed, the self-assembly of poly(*tert*-butyl acrylate)-*b*-poly(2-cinnamoyloxyethyl methacrylate)-*b*-poly(glyceryl monomethacrylate) (P*t*BA-PCEMA-PGMA) triblock terpolymers in pyridine/methanol mixtures yielded (partial) segregation of P*t*BA and PGMA blocks, as recently demonstrated by Liu *et al.* [324]. While pyridine is a good solvent for all of the three blocks, methanol is selective for P*t*BA and PGMA. For methanol fractions in the solvent mixture of 80 and 90 vol% and at 50 °C, spherical and cylindrical micelles with P*t*BA and PGMA coronal chains were observed. At methanol fraction of 95 vol%, vesicles were formed, whose outer surface mostly consisted of PGMA chains, while some P*t*BA chains formed circular patches. In pure methanol, tubular micelle-like aggregates coexisted with vesicles [324]. The same group also evidenced the formation of twisted cylinders with segregated A and C coronal chains from an ABC triblock terpolymer in a block-selective solvent for the A and C blocks [325]. Such cylinders consisted of left- and right-handed helical sections (3D twisting) connected by wriggling (2D twisting) sections after aspiration on a solid substrate. The copolymer used, was again a P*t*BA-*b*-PCEMA-*b*-PGMA triblock terpolymer, but a composition different form the one described in Ref. [324]. Twisted cylinders were prepared from the dialysis of an aqueous solution of the triblock terpolymer against methanol (Figure 9.31). In water, the copolymer formed core–shell–corona cylinders with a core of P*t*BA blocks surrounded by a shell of PCEMA blocks and a corona of PGMA blocks. The cylinders with PCEMA cores twisted in water/methanol with high methanol contents, e.g., >90 vol%, probably to create more space to accommodate the segregated

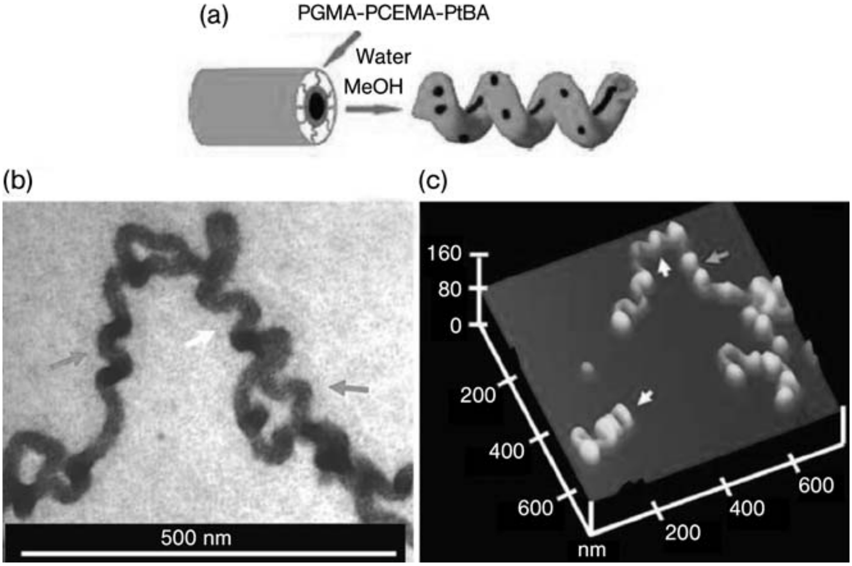


Figure 9.31 Schematic representation for the formation of twisted cylinders from P*t*BA-*b*-PCEMA-*b*-PGMA triblock terpolymer micelles in methanol. Typical TEM and AFM pictures are also shown. (Reprinted with permission from Ref. [325]. Copyright (2008) by the American Chemical Society.)

PGMA chains, which were longer, better solvated, and more crowded than the P*t*BA chains.

Segregated coronal chains were also recently evidenced in thermo-responsive wormlike micelles from a polystyrene-*b*-polyethylene-*b*-poly(methyl methacrylate) (PS-PE-PMMA) triblock terpolymer with a crystallizable PE middle block in organic solvent [326]. These micelles were composed of a core formed by crystalline PE domains and a patched corona formed by microphase-separated PS and PMMA chains. The formation of wormlike micelles is rather unexpected, because PE-containing diblock copolymers usually form platelet-like structures.

9.5
Applications

Block copolymers find applications as thermoplastic elastomers, as will be discussed in Chapter 10. Their potential as compatibilizers in immiscible polymer blends has been demonstrated convincingly [327]. Taking advantage of attractive interactions between the immiscible "matrix" polymers and individual blocks of a block copolymer, the latter one self-assembles at the interface of the matrix polymers and thus, stabilizes it [2, 328, 329]. Also, their potential as additives leading to shock resistance in a thermoset such a selective attractive interaction between one block and the matrix has been demonstrated [330, 331]. With the block copolymer domains having diameters up to a few tens of nanometers, glassy components of block copolymers often display a ductile behavior, while the corresponding homopolymers are brittle. Such a toughening effect was shown, for example, on a polystyrene-*b*-polybutadiene-*b*-poly(ε-caprolactone) triblock terpolymer with a PS matrix ($\sim$70%). This triblock terpolymer could be elongated up to the order of 1000% at room temperature, i.e., well below the glass transition temperature of the matrix [332].

In the field of thin films, block copolymers are used for nanotemplates and nanofabrication, nanolithography, filtration, and membranes for fuel cells. Many recent reviews deal with the applications of block copolymer thin films for nanolithography and nanofabrication [131, 136, 140]. The wide interest in nanolithography is mostly related to the potential of block copolymer thin films for microelectronics. In the area of nanotemplates and nanofabrication, one of the microdomains is either etched away or loaded with metal salts. Since the selected domain is usually a dispersed one, i.e., domain forming cylinders or spheres in a matrix, the technique is widely used for fabrication of nanorods and spherical nanoparticles [14, 142, 155, 156].

The self-assembly ability of block copolymers in thin films has been used for the fabrication of nanoporous materials and membranes. For example, the recognition-driven supramolecule formation focused on polymers with a comb-shaped architecture has been extensively studied by Ikkala *et al.* [333–336]. Other examples are the asymmetric membranes of block copolymers, either by the self-assembly of a thin film on a neutral substrate and further transfer onto the support layer [337], or by generation of an integral asymmetric membrane by dipping the cast film into a nonsolvent bath, i.e., the so-called phase inversion process [338].

It has been found that block copolymer isoporous membranes cause low percolation thresholds in gas permeation processes [338, 339]. Glassy polymer membranes such as sulfonyl-containing polyamides show high selectivity in pervaporation, while rubbery polymers generally show higher permeability because of their high free volume. Therefore, block copolymers with hard and soft segments have been investigated to achieve a high affinity to aromatics and simultaneously avoid excessive swelling of the membrane [340–342]. Block copolymers that exhibit proton conductivity are employed in membranes for fuel cell applications, where the membrane swelling can be controlled thanks to the microphase separation, and therefore, the methanol permeability is decreased [343–347].

Block copolymer micelles are generally considered for three main types of applications, i.e., biomedical applications, templating, and surface modifications. These features have been reviewed elsewhere [191] and will be briefly summarized in view of the two types of micelles discussed in this chapter, i.e., metallo-supramolecular micelles and micelles from ABC triblock terpolymers. The following few selected applications demonstrate that block copolymer micelles are quite interesting nano-objects for high added-values applications.

The application of block copolymer micelles for biomedical applications has become a major field of investigation as illustrated by several reviews on that topic [181–185, 348–350]. Block copolymer micelles are indeed of interest for controlled delivery of drugs, diagnostic agents, and gene transfection (also called *gene therapy*). For gene therapy applications, electrostatic complexes between positively charged diblock copolymers and negatively charged DNA or oligonucleotides have been essentially considered. Excellent reviews on this topic are available in the literature [348–350]. Loading of block copolymer micelles by complexation with contrast agents, e.g., with colloidal metals or heavy elements such as bromine or iodine, opens interesting application possibilities in medical diagnostic imaging [191]. The use of block copolymer micelles for such applications precludes that specific biological and medical aspects, such as drug efficiency or toxicity, specific interactions with cells, adequate particle size, biocompatibility, and biodegradability are taken into account. Moreover, since block copolymer micelles are generally characterized by a very low CMC, they are reported to survive dilution in the blood stream circulation.

Controlled delivery applications are essentially based on the solubilization capacity of block copolymer micelles. The most relevant feature of block copolymer micelles for this purpose is the formation of a well-defined core–shell architecture. A variety of hydrophilic polymers with a flexible nature, including PEO, can be selected as the shell-forming segments, which assemble into dense palisades of tethered chains to achieve effective steric stabilization propensities. The micellar core serves as a reservoir for a variety of drugs with diverse characteristics. These drugs could be either simply dispersed in the micellar core or covalently bound to the core-forming blocks. The latter bond should be, however, cleavable to release the active molecules. In a further step, the periphery of the micelles can be functionalized with pilot molecules allowing an increase in the uptake of micelles into the particular cells expressing targeted receptors. The release of the drug molecules can be achieved in several ways including simple diffusion from the micellar core, hydrolytic degradation of the core-forming blocks and stimuli-driven disassembly of the core-forming blocks. In this respect, pH-sensitive, temperature-sensitive, and light-sensitive polymer blocks have been introduced as core-forming blocks. Such micelles could liberate the drugs initially loaded in the micellar core upon application of the appropriate stimulus that results in the solubilization of the core-forming chains. The most commonly found polymer blocks in drug-loaded micelles are PEO for the water-soluble blocks and aliphatic polyesters such as poly(ε-caprolactone) or polylactide for the hydrophobic blocks, although many other polymer blocks, e.g., poly(amino acids) and poly(anhydrides) have been considered. As previously discussed in this chapter, triblock terpolymers have been considered for drug release

[313–315]. The increased complexity found in triblock terpolymer micelles compared to diblock copolymers could be interesting not only from a structural point of view, but also because it can bring additional functionality and/or stimuli-responsive properties.

Vesicles made from block copolymers are also extremely interesting for biomedical applications [221]. In this respect, Discher and coworkers have investigated the formation of micelles with various morphologies by directly dissolving poly(ethylene oxide)-*b*-poly(butadiene) and poly(ethylene oxide)-*b*-poly(polyethylethylene) copolymers in water [351–353]. These authors focused on the formation of large unilamellar vesicles which were referred to as *polymersomes* [221, 350]. Ten-micron giant vesicles were prepared from these copolymers by extrusion techniques, and were further characterized by single vesicle micromanipulation. This has allowed to get a deep insight into the typical physical properties of these vesicles including membrane viscosity, area elasticity measurements of the interfacial tension, as well as electromechanical stability [351–354]. Permeation of water through the polymersome membranes has been measured to be considerably reduced compared to phospholipid membranes [352]. Since those initial reports, polymersomes have become popular objects for bio-related applications.

Besides biomedical applications, block copolymer micelles have been also considered as an alternative to conventional lithographic techniques. In this respect, metallo-supramolecular block copolymer micelles and especially PFS-containing block copolymers have shown potential for these applications. More precisely, rodlike micelles made from PFS-PI and PFS-PDMS diblock copolymers were utilized as precursors of arrays of continuous ceramic nanolines with micrometer lengths and widths as small as 8 nm [355, 356]. The oriented deposition of those micelles was realized along prepatterned grooves on a resist film using capillary forces. This was followed by a treatment with either hydrogen or oxygen plasma, which resulted in the degradation of the organic polymer materials and in the chemical transformation of the PFS blocks into ceramic nanolines with high aspect ratio. This composition is particularly (Fe and Si) needed for the formation of the ceramic.

9.6
Summary and Outlook

Although the morphological behavior of tailor-made block copolymers has been a subject for quite a few decades already, new insights have still been gained during the last few years. Owing to the improvements in controlled synthesis, factors like the polydispersity and their influence on the morphology could be investigated in more detail. More complex architectures, as for example triblock terpolymers of various block sequences, could be studied; and more systematic descriptions of triblock terpolymers in terms of the relative segmental interactions between the three blocks became available. Blending of block copolymers of various architectures with homo- or other block copolymers has broadened the map of superstructures. The use of specific interactions between different blocks was also further developed to access more hierarchical superstructures. Future developments of morphological studies in the bulk state will be combined with the study of other properties, to establish or improve our insights into various structure–property relationships (i.e., mechanical, electrical, and optical properties). Also, the combination of the domain sizes in the nanometer range with the localized incorporation of so-called nanofillers will become an attractive field of research, and will open new areas of applications for block copolymer-based nanocomposites.

Some of these properties will be also very interesting in thin films of block copolymer or block copolymer nanocomposites. The common interest of controlling the structure formation in block copolymers is an important issue in thin film applications, since the natural restrictions associated with thin films enhance the possibilities for ordering the block copolymer domains over large scales. Therefore, techniques used on bulk systems, such as the application of external fields, can be successfully applied on thin films. Moreover, such approaches can be used in combination with parameters inherent to thin films, such as substrate interactions and film thickness, and a synergetic effect can be found for alignment of block copolymer domains. This phenomenon indicates that the successful implementation of block copolymers as thin films for industrial applications might become a reality in the near future.

Although block copolymer micelles is an already well-established and rather old field of research in polymer science, it is still an extremely active area of research. To illustrate this point of view, we selected two recent directions in the development of novel micellar systems: metal–ligand containing micelles and triblock terpolymer micelles with segregated domains in either the micellar core or corona.

As shown by the results already available in the literature, metallo-supramolecular block copolymers are ideal candidates for the assembly of new, stimuli-responsive, functional micellar systems. The metal–ligand complexes have been incorporated in the core, corona, and at the core–corona interface of block copolymer micelles.

Micelles formed by ABC triblock terpolymers in solution are extremely interesting and potentially very useful for a broad range of applications. Indeed, the control of size and shape of these compartments could be of high interest for templating applications. Another crucial point is the extent of segregation among coronal chains in the case of ABC terpolymers with two soluble blocks. Another attractive issue to be developed is the formation of novel superstructures from noncentrosymmetric nano-objects such as Janus micelles. Owing to their inherent asymmetry, these micelles have indeed the potential to build noncentrosymmetric aggregates with physical properties based on this symmetry.

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10
Industrial Applications

Dale L. Handlin, Jr., David R. Hansen, Kathryn J. Wright, and Scott R. Trenor

10.1
Introduction

The origins of styrenic block copolymers (SBCs) can be found in the US Government's Synthetic Rubber (GR-S) program which began during World War II. At that time, Germany was well advanced in the synthesis of rubber and the United States was concerned that the inability to secure a rubber supply would cripple the military effort. Between 1942 and 1945, this program spent $700 million to build 51 synthetic rubber plants in the United States, all run by different companies. This program was successful in developing a synthetic rubber called GR-S for government rubber – styrene, the first large-volume commercial elastomeric polymer produced in the United States. This rubber was generally a random or tapered copolymer of styrene and butadiene which we now refer to as *styrene-butadiene rubber* (SBR). In 1955, with the goals of the GR-S program complete, the program ended. The government-owned plants were sold to the various operating companies through a bidding process. Shell Chemical Company and Philips Chemical, both butadiene suppliers, bought the plants that they were operating. The Shell-owned plant in Torrance, California, was of particular importance because this plant combined styrene, butadiene, isoprene, and rubber, compounding which allowed the eventual synthesis and processing of block copolymers. Another key event in 1955 was the first public presentation by Stavely at Firestone of his work on high *cis*-1-4 polyisoprene using anionic chemistry. On the basis of Stavely's results, Lee Porter at Shell began lithium alkyl polymerization of polyisoprene. He developed a process to make 93% *cis*–polyisoprene, which was the closest thing to natural rubber yet developed. Shell started a rapid development to commercialize anionic homopolyisoprene that ''imitated nature'' with the intent to produce polyisoprene on large scale for tires. At about the same time, Michael Szwarc, Morris Levy, and Ralph Milkovich announced the synthesis of block copolymers using anionic initiators [9]. This single-page letter in which they reported the synthesis of styrene-butadiene diblocks and the ability to

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synthesize ABA and other types of block copolymers was published in the *American Chemical Society Journal*, 1956. After Milkovich finished his Ph.D. under Maurice Morton at the University of Akron, he was hired by Shell to help commercialize the first anionic polyisoprene in 1959. Commercial production of anionic polyisoprene rubber began in Torrance, California, and then expanded to a dedicated plant in Belpre, Ohio, in 1961.

Shell was the first, but not the only company, to commercialize synthetic polyisoprene. Firestone, who did much of the original work, also commercialized anionic polyisoprene as did Asahi. At the same time, Zellinski and others at Phillips developed and commercialized high *cis*-polybutadiene by anionic polymerization. Bob Zellinski described the period between 1955 and 1960 as being like Thanksgiving and Christmas all rolled into one (Personal communication between coauthor and Bob Zellinski). The ability to generate a wide variety of AB, $(AB)_{x'}$, ABA, and ABC polymers made this an exciting time for polymer chemistry. Most major chemical companies were exploring block copolymers in the late 1950s and early 1960s. Given the excitement about anionic polymerization in industry and academia, why did Shell Chemical Company develop SBCs? The answer is a simple one: the large market for synthetic rubber was automotive tires. Goodyear and B.F. Goodrich had found that they could use Ziegler–Natta catalysts to make very high (95–98%) *cis*-polyisoprene, which was closer to natural rubber than anionic polyisoprene, and it worked well in tires. Firestone and Philips commercialized anionic *cis*-polybutadiene, and Philips also commercialized tapered polystyrene-butadiene, both of which were useful in tires. Anionic polyisoprene, which is only 91–93% cis, did not have the green strength (needed to make good sheet), build tack (surface stickiness needed to keep the plies together during production before molding so that no bubbles are introduced), or hot tear strength (needed for performance under driving conditions) to succeed in tires. Facing the potential failure of a large chemical plant in 1961, N. R. Legge at Shell put together a group including R. Milkovich, G. Holden, and W. Hendricks to attack the problems plaguing the commercial polyisoprene. Although SBCs had been known since 1956 and even patented by Lee Porter in 1958 [10], the focus had been on new compositions while their potential as thermoplastic elastomers (TPEs) remained undiscovered. Milkovich, who was part of the original block polymer chemistry team and an expert in anionic synthesis, shared an office with Geoff Holden, a rheologist. Their initial objective was to develop a polymer that could be added to anionic polyisoprene to provide an infinite zero shear rate viscosity comparable to natural rubber. They made a series of styrene/isoprene diblocks, tapered polymers, and triblocks for rheological evaluation to create an additive to address the green strength problem of anionic polyisoprene. As shown in Figure 10.1, natural rubber is both very high in molecular weight and lightly cross-linked so that even at very low shear rates it does not flow, an attribute known as *green strength*. Anionic polyisoprene, however, behaves as a typical linear homopolymer with a Newtonian plateau at low shear rates.

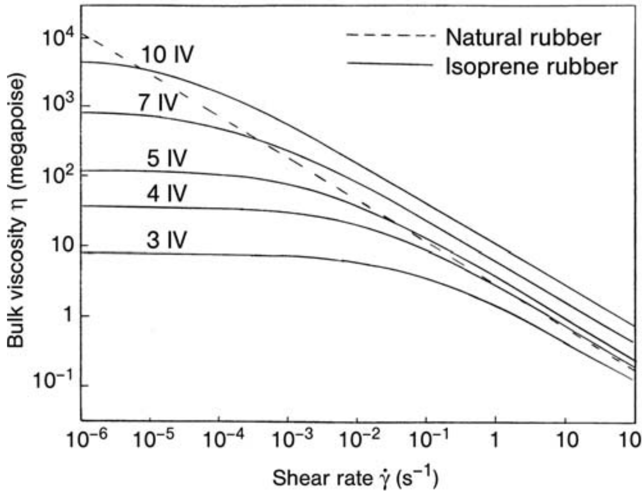


Figure 10.1 Bulk viscosities of isoprene and natural rubber at 100 °C.

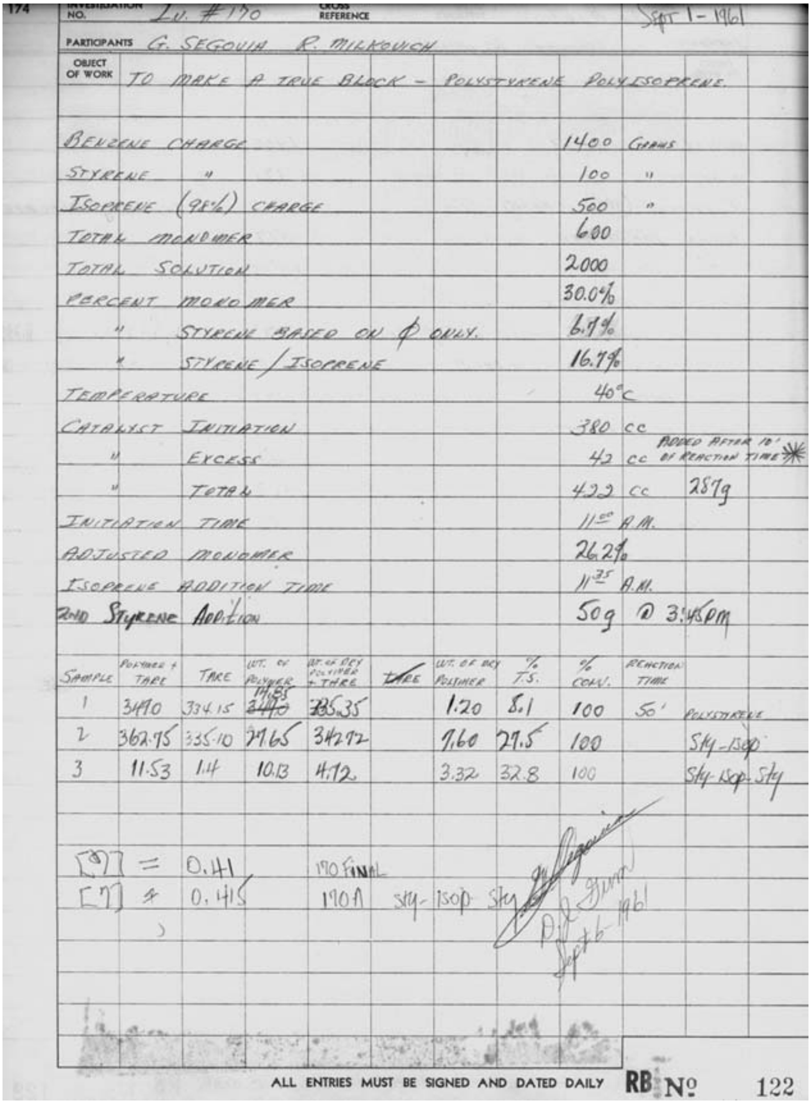
Therefore, even though the molecular weight was increased to match the viscosity of natural rubber at typical application shear rates, flow would still occur at low shear rates. According to G. Segovia's Shell laboratory notebook, the first styrene-isoprene-styrene (SIS) triblock copolymer with interesting mechanical properties was made on September 1, 1961 (Figure 10.2) [11].

However, initially only its rheological properties were measured. They confirmed that the addition of 25% SIS triblock copolymer to an anionic polyisoprene could allow it to mimic the flow curve of natural rubber over a wide range of shear rates (Figure 10.3).

Further the activation energy of flow measurements indicated that the flow mechanism was based on the phase separation of the polystyrene (PS) blocks from the polyisoprene blocks. On November 29, 1961, an SIS was made in the pilot plant with molecular weights 30 000–90 000–20 000 g mol^{-1} whose pure mechanical properties were measured by Bill Gergen, Bill Hendricks and Geoff Holden on December 6, 1961. This was the first polymer that was recognized as an exceptionally strong elastomer without vulcanization. Styrene-butadiene-styrene (SBS) and styrene-isoprene (SI) coupled star polymers were made and evaluated over the next few months. For the first time, the possibilities of these materials outside of the area of polyisoprene flow modification were realized.

Dale Meier, a polymer physicist who was a supervisor in the Emeryville lab with Shell, developed the confined chain model of block copolymer phase separation, which was later published in 1969 [12]. Dale Meier has reviewed the development of block copolymer theory in Ref. [4], Chapter 8.

Understanding how the SIS and SBS block copolymers behaved, and to some extent what they were useful for, allowed Milkovich and Holden to file



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INVESTIGATION NO. Lv. #170 CROSS REFERENCE Sept 1 - 1961

PARTICIPANTS G. SEGOVIA R. MILKOVICH

OBJECT OF WORK TO MAKE A TRUE BLOCK - POLYSTYRENE POLYISOPRENE.

BENZENE CHARGE	1400 GRAMS
STYRENE "	100 "
ISOPRENE (98%) CHARGE	500 "
TOTAL MONOMER	600
TOTAL SOLUTION	2000
PERCENT MONOMER	30.0%
" STYRENE BASED ON ϕ ONLY.	6.7%
" STYRENE / ISOPRENE	16.7%
TEMPERATURE	40°C
CATALYST INITIATION	380 cc
" EXCESS	42 cc ADDED AFTER 10' OF REACTION TIME ✳
" TOTAL	422 cc 287g
INITIATION TIME	11⁰⁰ A.M.
ADJUSTED MONOMER	26.2%
ISOPRENE ADDITION TIME	11³⁵ A.M.
2ND Styrene Addition	50g @ 3:45PM

SAMPLE	POLYMER + TARE	TARE	WT. OF POLYMER	WT. OF DRY POLYMER + TARE	~~TARE~~	WT. OF DRY POLYMER	% T.S.	% CONV.	REACTION TIME	
1	349.0	334.15	~~349.0~~ 14.85	335.35		1.20	8.1	100	50'	POLYSTYRENE
2	362.75	335.10	27.65	342.72		7.60	27.5	100		Sty-Isop
3	11.53	1.4	10.13	4.72		3.32	32.8	100		Sty-Isop-Sty

[η] = 0.41 170 FINAL

[η] ≠ 0.415 170A Sty-Isop-Sty

G. Segovia

Sept 6-1961

ALL ENTRIES MUST BE SIGNED AND DATED DAILY RB Nº 122

Figure 10.2 Page 122 of G. Segovia's laboratory notebook from Shell Chemical Company showing the synthesis of the first SIS triblock with commercial potential.

for a US patent in 1962 [13]. This was the first process and composition patent for commercially interesting ABA block copolymers.

While the addition of SIS block copolymers to anionic polyisoprene did improve the green strength and build tack, they did not improve the hot tear properties. Thus the block copolymer effort to produce a large volume synthetic tire rubber, as conceived, was a failure. The group at Shell had created polymers

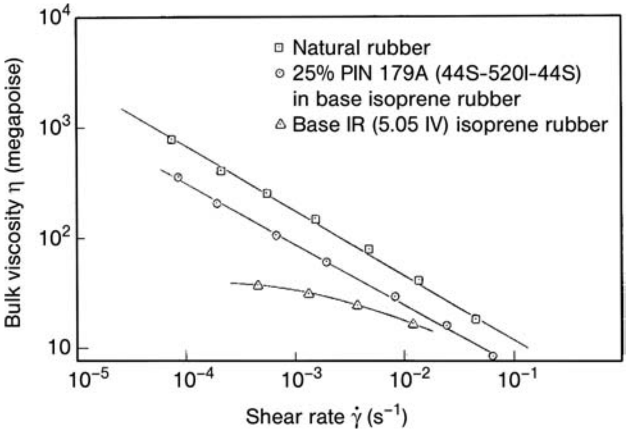


Figure 10.3 Bulk viscosity of isoprene rubber at 100 °C blended with block copolymer.

with outstanding properties, but not ones suited for the target application. This was a pivotal point in polymer development. Two events helped launch block copolymers in a commercial direction: first, Shell was in the footwear business with SBR compounds and, therefore, knew the application requirements; second, a German company, Desma, introduced a new direct injection machine for footwear called the Desma 10. It had a single extruder for the injection of natural rubber into molds held on a rotating table. Bill Hendricks and Dick Danforth at Shell realized that if the injected compounds were TPEs, the table could rotate more rapidly because no cure time would be required. The reduced cycle time offered by TPEs became a reality in the foot wear market. The first trials were done in 1964, and in 1965 Scotty Shoes in Massachusetts bought the first truckload of an SBC compound. The 10 000 pounds of compound was made 30 pounds at a time on a Banbury mixer at the original government-sponsored Torrance plant. This footwear application led to the announcement of the first commercial block copolymers at an American Chemical Society (ACS) symposium on May 3, 1965 in Miami Beach [14].

With the advent of earth shoes with their large TPE soles, volumes of SBS block copolymers soared, driving the construction of the first dedicated block copolymer plant by Shell Chemical in Belpre, Ohio, in 1971 next to the anionic polyisoprene plant. Although Phillips had been working on block copolymer since the early 1960s, it was the burgeoning footwear market that encouraged their first commercial polymers in 1973 [5]. Phillips circumvented the Shell patent, which only claimed linear SBCs, by making four-arm block copolymers. Further discussion of the footwear application can be found in Section 10.7.

While footwear applications accelerated, adhesives, asphalt modification, and compound applications were slow to take hold. In the 1960s, adhesives were primarily solvent-based. Although SIS polymers offered good tack and excellent strength without curing, their application from solvent offered little advantage over natural rubber as long as solvents were cheap and there were limited emission regulations. As described in Section 10.2, it was not until the early 1980s with the advent of hot-melt coating, a process that, similar to direct footwear injection, offered significant efficiencies, that the adhesives market began to emerge as a large commercial application.

The history of block copolymer application in the road and roofing markets was a similar story. Although the first trials were in 1967, sales were limited. In the 1980s, however, European commercial roofing began to shift from concrete to metal, which required a more flexible roofing felt thereby encouraging the use of SBS-modified bitumen for better elasticity, particularly at low temperatures. In the United States, the Strategic Highway Research Program (SHRP) in the early 1990s helped to standardize requirements for paving bitumen, which led to dramatic increases in SBS-modified bitumen in the United States, especially in climates with large temperature swings. More details about Bitumen modification can be found in Section 10.7.

Footwear also played a prominent role in the development of hydrogenated block copolymers. One of the prominent features of SBS footwear was good wet traction. Therefore, SBS-soled shoes were frequently used for boating and other outdoor applications. In the late 1960s, it was found that the foxing, that is the upper edges of the soles, cracked when extensively exposed to sunlight and ozone. At that same time fundamental research into hydrogenation chemistry at Shell's Emeryville laboratory was producing fully hydrogenated SIS polymers, referred to as *poly(cyclohexane-ethylene propylene-cyclohexane)* or *CEPC polymers*. These polymers were undergoing trials by the National Institute of Health as materials for artificial hearts [15]. They had the high strength, good elasticity, and low thrombogenicity required to make a good heart wall. These polymers were put to trial in footwear, but could not be compounded with oils normally used to adjust the hardness of the sole. The development of selective hydrogenation, in which only the rubber block of the polymer was hydrogenated, gave rise to so-called SEPS (styrene-ethylene/propylene-styrene) and SEBS (styrene-ethylene/butylene-styrene) polymer (described in Section 10.10.3) that are widely used today [16].

While these selectively hydrogenated polymers had good properties in compounds, they did not succeed in footwear because it proved too difficult to glue the saturated polymer sole to the uppers. However, they found an immediate place in automotive compounds. SBS compounds had already been put to trial in a number of automotive applications with at least one spectacular failure. In 1965, black hornpads were made for new Fords. When the cars were placed in the sun, the pads cracked and the horns went off leading to their quick replacement. With the development of hydrogenated block copolymers, however, ultraviolet (UV) and thermally stable compounds were now readily formulated. From 1967 to 1970, a series of compounds were developed using oil and polypropylene (PP) with SEBS polymers. The oil and PP reduced cost and allowed adjustment of flow and harness over a wide range. The PP also provided high-temperature stiffness. Market place demand was provided in 1972 when the 5 mph bumper law was passed. This led to the first successful commercial automotive application of hydrogenated block copolymers as a fascia (flexible panel between the bumper and body of the car) for the 1974 AMC Matador. In 1975, the Jeep CJ fenders were made from block copolymer compounds and sound dampening panels, and air ducts and other applications followed as described in Section 10.4.

Despite these high-profile applications, a lesser known application, i.e., viscosity index improvers (VIIs) for motor oil modification (discussed in Section 10.9) actually drove the commercialization of hydrogenated block copolymers. This was a purely internal application to Shell Chemical. In 1969, a group began to screen a wide variety of block copolymers for the modification of motor oils. Dave St. Clair found that styrene-ethylene/propylene (SEP) diblocks were very effective as VIIs which allowed the generation of the first 10W/50 motor oil. While it was not clear why 10W/50 motor oil was needed, it was a great marketing tool. This application drove the conversion of the first dedicated synthetic polyisoprene plant built in 1961 to a hydrogenated block copolymer plant in 1974. Shell exited the polyisoprene business altogether in the United States but continued to make medical-grade polyisoprene in Europe.

On February 28, 2001, Kraton Polymers became an independent corporate entity from Shell Chemical Company. At that time, all the technology developed by Shell Chemical Company related to SBCs was assigned to Kraton Polymers LLC. Since then, Kraton Polymers continues to manufacture and develop new SBCs.

10.2
Synthesis of Anionic Styrenic Block Copolymers

SBCs owe their success to a unique block structure. The key to the structure is the living anionic synthesis chemistry (as described in Chapter 1) used in the manufacturing process. Typically, the polymerization begins by adding a very pure styrene monomer to an alkyl lithium initiator in an appropriate solvent. This initiator is so reactive that initiation is much more rapid than propagation, resulting in chains of uniform length. In addition, the reactive chain end does not die or undergo side reactions. The chain end remains ‘‘living’’ at the end of the polymer chain as long as water and other chain terminating agents are excluded from the reactor. The reaction continues until all of the styrene monomer is consumed. Thus linear polymer chains of polystyrene (PS) are formed, which have a narrow molecular weight distribution that can be measured and controlled very precisely. The next sequence of the reaction starts by adding a new monomer such as isoprene (I) or butadiene (B). The diene monomer units are polymerized onto the ends of the chain in a uniform manner, thus forming identical styrene-diene diblock molecules. The microstructure of the polybutadiene block (1,2 polybutadiene/1,4 polybutadiene) or the polyisoprene block (1,4 polyisoprene/3,4 polyisoprene) can be carefully controlled over a wide range with special additives. In addition, mixed monomer systems, such as isoprene/butadiene or butadiene/styrene, can be copolymerized in the rubber block. The styrene block typically will have a molecular weight of 4000–100 000, and the diene midblock will have a molecular weight of 20 000–200 000. At this point, one of three reactions can be carried out (Figure 10.4). The reaction can be terminated or capped with a functional group such as an alcohol forming a diblock copolymer. A second option is to add more styrene monomer to make a third block of PS. The third option is to add a coupling agent. If a difunctional coupling agent is added to the reactive diblocks, a triblock copolymer is formed (SB-*x*-BS or SBS). With multifunctional coupling agents, multiarm polymers can be formed with 3–20+ arms.

The diene midblocks, such as polyisoprene and polybutadiene, are elastomeric and still contain unsaturated double bonds. The SIS and SBS polymers can then be subjected to a further chemical reaction that selectively hydrogenates the double bonds in the diene elastomer and leaves the PS endblocks unchanged. Thus SEBS and SEPS polymers can be formed which have outstanding UV and thermal stability. The SEBS or SEPS polymers can be reacted further by grafting monomers such as maleic anhydride onto the rubber block of the molecule.

Certain portions of diene blocks can be selectively hydrogenated to create partially hydrogenated blocks which can be selectively functionalized (by reactions such as epoxidation) to create functionalized blocks in the

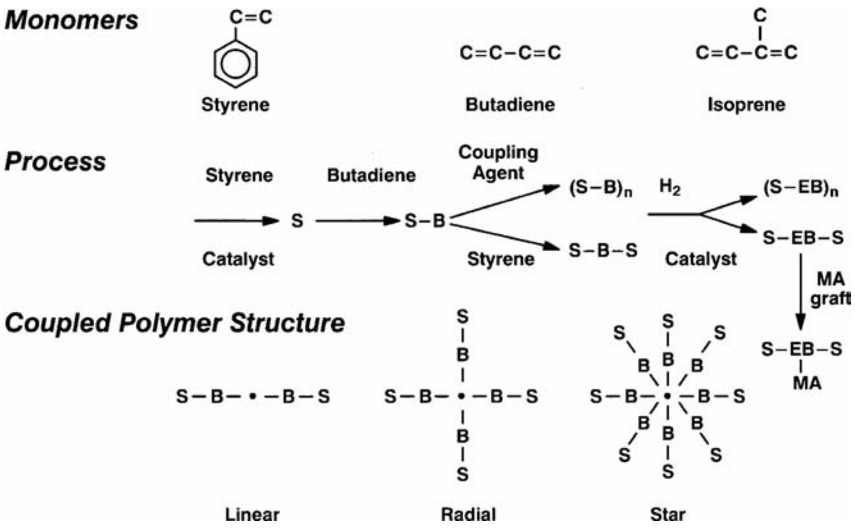


Figure 10.4 Synthesis route to making different block copolymer structures.

polymer [17]. Alternatively, the unhydrogenated segments can be used for cross-linking in selected regions. There are new anionically polymerized block copolymers recently introduced, in which special aromatic blocks can be selectively sulfonated only in certain blocks to make unique, strong, ion and water transporting membranes as described in Section 10.10.3 [18, 19].

The most common and widely used monomers are styrene, butadiene, and isoprene because of their availability and price, but other monomers (styrene derivatives and other vinyl containing monomers) can be anionically polymerized.

The block structure creates the unique properties of these polymers as described in Chapter 9. The PS blocks are incompatible with the elastomeric diene segments and, therefore, they phase-separate on a nanoscale. The styrene domains are glassy and form ‘‘physical’’ cross-links that hold the molecules together in a strong elastic network. The tensile strength of the block copolymers can be as high as 20–35 MPa (3000–5000 psi) because the styrene domains also act like reinforcing fillers. This strength is greater than that of most chemically cross-linked elastomers. For many applications, this means the block copolymers can be very highly extended with fillers, oils, tackifying resins, or other polymers and still have adequate strength for an application. Since the size of the styrene domains is roughly 30 nm, they do not scatter light and thus the block copolymers are transparent.

The phase separation of the styrene blocks from the diene blocks is typically strong at room temperature, but is weak enough that an order–disorder temperature can be reached above which the blocks mix. At this point, the domain softens and the copolymer can flow like any thermoplastic polymer. When the block copolymer is cooled, the blocks phase-separate again to re-form their strong physical network (Figure 10.5). The re-forming process is so quick that hot-melt adhesive coating lines can be run in excess of 300 m min^{-1} (1000 ft min^{-1}). Processing can also be achieved by dissolving the block copolymer in a solvent, which will solvate both phases. Since many SBCs are

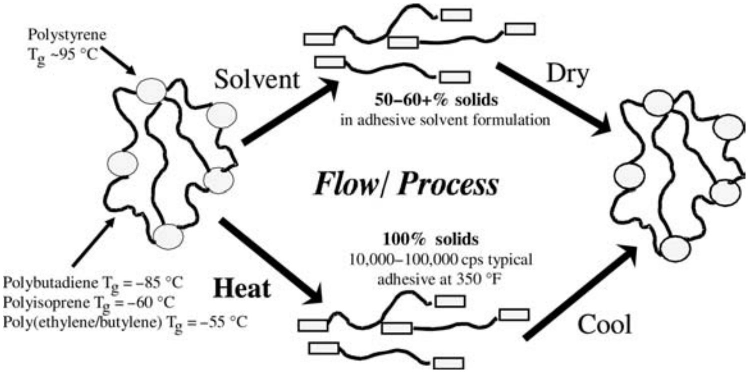


Figure 10.5 Nanophase-separated structure and processing options.

only about 100 000 g mol^{-1} in molecular weight, the solution viscosity of most block copolymers is low compared to other elastomers such as natural rubber (1 000 000 g mol^{-1}). Adhesive formulations with high solids levels (50%+) can easily be achieved. By comparison, natural rubber adhesive solutions are typically limited to 25–35% solids. In addition, the block copolymers will regain their strength once the solvent is evaporated. No time-consuming and complicated chemical cross-linking steps are required as is commonly practiced with most elastomers.

Because the molecular control and the wide range of structures possible, anionically polymerized block copolymers can be very precisely tailored to a wide variety of applications with truly unique properties. Very few other polymer systems have such a wide variety of structures and molecular control. Anionically polymerized block copolymers are a good example of ''nano'' technology in commercial practice.

10.3
Adhesives and Sealants

The use of SBCs in adhesives and sealants was first developed by researchers at the Shell Chemical Company in the 1960s and continues to be among the most important applications today. Pressure-sensitive adhesives (PSAs) represent a major class of the adhesive market. A typical PSA must possess the following five material properties [20]:

- should be aggressively and permanently tacky;
- should adhere without the need of more than finger or hand pressure;
- should require no activation by water, heat, or solvent;
- should exert a strong holding force;
- should have sufficient cohesiveness and elasticity that it can be removed from smooth surfaces without leaving a residue.

These five requirements seem simple enough to achieve, although in practice they require a material to possess contradictory properties. For example, for a PSA to adhere by applying only a small amount of pressure it must possess a low enough modulus and viscosity (liquid-like) to wet out the surface over the timescale of the application [20–25]. However,to exert a strong holding force, there must be sufficient resistance to flow (entanglements and/or cross-links) to provide the desired mechanical strength.

There are three predominant classes of PSAs available today: solvent-based (typically natural rubber or acrylics), emulsions (aqueous based), and hot-melt adhesives (typically SIS and SBS). Of these three classes, hot-melt adhesives and emulsions have experienced the largest growth [20, 21, 26–34]. Hot-melt adhesives and emulsions each have their advantages. Emulsion systems can experience increased water absorption due to the surfactants incorporated during polymerization and have lower shear holding power than SBC hot melts, due to the lack of a reinforcing, heterogeneous network morphology [35, 36]. Production speeds of the emulsion acrylic PSA tapes and labels are slower because of the drying step to remove water. Acrylic copolymers are currently the primary competitors for SBCs in the PSA market. While acrylics have better specific adhesion to polar materials, better weatherability, and better die cuttability in labels, adhesive manufacturers cannot easily formulate them for varied adhesion applications such as nonpolar polyolefin substrates. Ease of formulation combined with strength, the desired reduction in the use of solvents, and fast production line speeds contributes to the popularity of hot melt-adhesives based on SBCs. In addition, the inherent purity required for anionic synthesis of SBCs has allowed the Food and Drug Administration (FDA) clearance of most SBCs that permit their use in sensitive applications such as diaper and personal-care adhesives.

SBC hot-melt adhesives are also quite attractive owing to their ease of use, high production speeds, and, again, the lack of solvents (if desired, SBC adhesives can also be applied from solvent using essentially the same formulations). Since tackifiers and plasticizers are necessary to make the SBC hot melts usable as PSAs, a single hot-melt based polymer can be formulated to provide an extremely wide range of properties. For these reasons, hot-melt PSAs constitute a very significant PSA market [20]. That said, traditional hot melts do have a few drawbacks. For example, unless the isoprene or butadiene blocks are hydrogenated, residual unsaturation in the polymer backbone is susceptible to oxidation, which can lead to discoloration and loss of properties. Since the styrene domains soften around 95 °C, the service temperature of the SBC adhesives are limited close to this ceiling [26, 28, 37]. Unsaturated SBCs can be cross-linked to increase the high-temperature shear, but the cross-linking typically decreases the tack [27, 38–40].

SBC adhesives typically do not have any strong specific interactions with substrates such as polar or acid/base interactions. The van der Waals forces of these nonpolar SBC polymers provide only moderate molecular-level adhesion. The principal characteristic of SBCs that makes them useful as adhesives is their ability to conform to the surface and to dissipate energy uniformly throughout the bulk of the adhesive layer during peel deformation. The ability of a material to conform (adhesive creep compliance) quickly to a surface is generally referred to as *tack* and is inversely proportional to its modulus. Dahlquist first studied the adhesive creep compliance necessary for adhesive bond formation in the late 1960s [22, 35, 41]. He determined that a 1-s creep compliance greater than 10^{-5} Pa^{-1} (at the use temperature) was necessary for an adhesive to conform to the substrate. As the compliance increases above that value, the adhesive is too stiff and cannot properly wet or conform to the substrate. On the other hand, if the compressive modulus is too low, the adhesive will have very poor strength.

The most common SBC used in adhesives are SIS polymers with molecular weights between 100 000 and 200 000 g mol^{-1} and 10–20 wt% PS. Isoprene is the preferred midblock since it has a higher molecular weight between entanglements compared to polybutadiene or the hydrogenated midblocks. The higher molecular weight between entanglements translates to fewer entanglements and the lowest rubber modulus of the commercial SBCs. The low styrene content is desired to ensure that the styrene domains will be predominantly spherical, which minimizes the hard phase contribution to the adhesive's modulus. The low styrene block molecular weight also provides a lower order–disorder transition (ODT) temperature, which can be further reduced with diluents during the adhesive formulation to allow for practical melt processing temperatures of 150–170 °C.

As previously mentioned, SBCs are typically diluted with oil, diblock copolymers, and tackifying resins to improve the adhesion at the desired use temperature range. Although this may seem counterintuitive, recall that the strength of the adhesive bond is strongly related to its ability to dissipate the energy exerted during debonding than the bulk strength of the adhesive. Figure 10.6 shows the elastic modulus and tan δ of a SBC polymer with and without tackifying resin (solid and dashed lines, respectively) as a function of temperature. Note that the tan δ peak is shifted to higher temperatures with the addition of tackifying resins. Most PSAs are thus formulated to a T_g near −10 °C from −60 °C by blending with tackifying resins (polyisoprene soluble oligomers) that have glass transitions above room temperature. Tackifying resins are rigid oligomers such as oligomerized piperylenes or rosin esters that serve several functions: to increase the T_g of the midblock; to perhaps add polarity to increase adhesion either to the backing or the substrate; and to reduce the melt viscosity, strength, and cost of the adhesive formulation. By changing the tackifiers and oils, an SBC adhesive formulation can easily be formulated for a lower use temperature.

The type of adhesive formulated can be predicted using the "viscoelastic windows" concept first described by Chang and coworkers [23–25]. The combinations of the values of the dynamic loss (G') and shear (G'') moduli, as measured from the rheological master curves of the PSA, are divided into four regions plus a general-purpose region each describing the PSA properties [23]. For example, an adhesive with G' between 8×10^4 and 1×10^6 Pa and G'' between 7×10^3 and 1×10^6 Pa (at the use temperature) is classified as a general-purpose PSA because the viscoelastic properties of the adhesive place it in the transition flow region (possessing medium modulus and

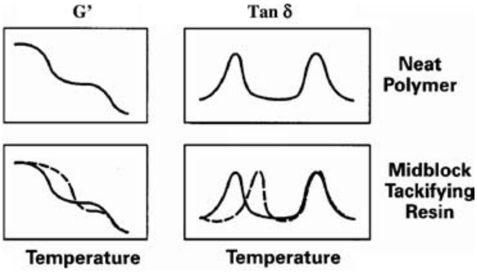


Figure 10.6 Effect of tackifying resin on shear modulus and tan δ.

medium energy dissipation during peel). If the G' and G'' are shifted to lower temperatures, the adhesive then can be used as a cold temperature PSA. A properly balanced adhesive will have enough strength to uniformly distribute the stress from the surface throughout the adhesive so that it will exhibit maximum viscous dissipation at a stress just less than the stress necessary to debond the adhesive from the surface.

A wide variety of other additives have been developed to precisely tailor the modulus, strength, and T_g of the soft and hard phases. These additives fall into three general categories: plasticizers, midblock resins (previously described), and endblock resins. Plasticizers are generally diblock copolymers and oils chosen to match the solubility parameter of the rubber block. Diblocks are typically used in combination with, or in the place of, oils because they will not migrate to the surface and form a weak boundary layer. The plasticizers reduce the modulus of the rubber phase, the viscosity of the formulation during melt processing, the strength of the bulk adhesive, and the cost of the adhesive. A typical general use PSA formulation includes 40% SIS, 55% tackifying resin, and 5% paraffinic/naphthenic oil.

The endblocks of block copolymer-based PSAs can also be modified with aromatic resins to reinforce and strengthen the styrene domains, to lower hot-melt viscosities, and in some cases to increase service temperature. For example, adding low molecular weight poly(phenylene ether) (PPE) (often referred to as *polyphenylene oxide*) increases the T_g of the styrene endblocks, which increases the ultimate service temperature of the adhesive formulation. Further details about specific formulations for adhesive tapes were reviewed by Ewins *et al.* [42].

SBS polymers or star SIS polymers are often used as cross-linkable adhesives when higher service temperatures are desired. The polybutadiene midblock is much more readily cross-linked by peroxides, UV light (with the addition of photoinitiators), and electron beam radiation than the polyisoprene midblock. The vinyl content of the butadiene block (1,2-butadiene content) is often modified from 8% (standard vinyl content from anionic polymerization) up to nearly 50% to increase its reactivity. Radial and branched architectures are also used to reduce the number of cross-linking reactions necessary to form a continuous network.

A new family of block copolymers with mixed butadiene and isoprene midblocks has recently been commercialized for adhesive applications [43]. The new polymers combine the advantages of both butadiene and isoprene monomers in one material. While adhesive formulations based on the mixed midblock polymer require a slightly more aromatic midblock resin than the traditional SIS polymers, they can be more easily formulated for use at lower temperatures due to an approximately 12 °C lower T_g. The mixed midblock polymers are also more melt-stable in a hot melt because of the competing degradation reactions at elevated temperatures. Polybutadiene tends to cross-link whereas polyisoprene tends to chain scission, thus stabilizing the hot-melt viscosity.

For adhesives that require long-term stability in the melt or that will be exposed to UV light, ozone, or other oxidative environments, the hydrogenated versions of SBS and SIS (SEBS or SEPS, respectively) are used. While the saturated rubber blocks are inherently more stable than their unsaturated precursors, they are also more expensive and have a higher modulus (more difficult to formulate into a pressure sensitive), thus reducing their use in commercial tape formulations. However, the hydrogenated SBCs are preferred for sanitary napkin adhesive applications because of the good hot-melt stability (particular color) and lower tack so it is easy to remove from clothing.

SBCs can also be formulated into non-pressure-sensitive applications. One very large application is the hot-melt glue used to assemble disposable diapers on high-speed production lines. The SBC adhesive formulations are preferred for this application because they spray well, form very good bonds to polyolefin surfaces, set up very quickly for high-speed production, and have good strength for demanding applications like gluing elastic structures into the diaper.

Solvent-based sealants and construction adhesives benefit from the strength, flexibility, high extendability, and adhesion to a wide variety of substrates including concrete and wet lumber. The hydrogenated block copolymer can be formulated into durable clear sealants that are clear in the tube as well as being clear after application. SBS-based construction adhesives formulated with high levels of filler, tackifying resin, and endblock resins are the preferred calking tube-dispensed construction adhesive for gluing plywood flooring to the floor beams on the second story of homes to eliminate floor creaking and nails pulling out.

10.4
Compounding Applications

Compounding applications represent a wide range of end uses from footwear to automotive, and medical to toys. Regardless of the application, raw material selection and processing conditions are critical to achieving a consistent compound that meets the performance requirements. This section addresses both material selection and processing conditions for SBC compounds.

10.4.1
Raw Material Selection

Very few applications utilize “neat” block copolymers without any other formulating ingredients. Compounding is often necessary to achieve optimal processability within a desired performance window. SBC compounds are based on either hydrogenated block copolymers (SEBS, SEPS, or styrene-ethylene/ethylene-propylene-styrene (S-E/EP-S)) or unsaturated block copolymers (SBS or SIS). The ethylene/ethylene-propylene (E/EP) is hydrogenated butadiene/isoprene mixed monomer block or E/EP. For the purposes of this discussion, hydrogenated SBCs will only be referred to as SEBS unless otherwise noted. They are the most common hydrogenated block copolymer used in compounds. Hydrogenated SBCs are preferred for most high-performance technical compounds owing to superior weatherability and mechanical performance. In addition, high molecular weight SEBS copolymers are intractable and cannot be processed using standard thermal techniques without the aid of other compounding ingredients to enhance flow. Additional compounding ingredients are chosen to provide desired performance attributes including hardness, tensile strength and elongation, tear strength, compression set, weatherability, cost, surface appearance, and color. Typical compounding ingredients include oil, one or more polyolefins, fillers, endblock resins, and other additives such as stabilizers and pigments. Proper selection of raw materials is important to ensure performance and proper processability.

Oils improve processability while decreasing hardness and cost of the compound. Paraffinic white oils are most compatible with SEBS-based compounds, while naphthenic oils are more compatible with SBS- or SIS-based formulations. It is also important to consider color, stability, availability, and FDA and United States Pharmacopeia (USP) compliance when selecting an oil. Volatility should also be considered with respect to the processing conditions. Some SEBS-based compounds are processed in excess of 230 °C, which require oils of higher flash point to ensure manufacturing safety as well as to minimize smoke generation. Oil viscosity should also be considered to maximize cycle time while minimizing the oil bleed out (OBO) potential. Lower viscosity oils are typically easier to incorporate but, due to higher volatility, have an increased tendency to bleed out of the finished part. Higher viscosity oils typically take longer to absorb and incorporate homogeneously but exhibit a lower tendency to bleed out of the formulation after molding. Low molecular weight hydrogenated tackifying resins can be used in SEBS compound formulations as midblock plasticizers. Raw materials such as these promote flow and allow the formulator to remove some oil from a formulation in oil-sensitive applications.

Both PP and polyethylene (PE) can be used to promote flow and generate high-strength compounds. Polyolefins increase hardness, modulus, tensile strength, and tear strength but decrease elongation, resiliency, and other rubbery characteristics. Owing to its higher melting point, PP is typically the polyolefin of choice for SEBS formulations, although high density polyethylene (HDPE), low density polyethylene (LDPE), and metallocenes can also be used although uniform mixing is slightly more difficult to achieve with HDPE. If compounded incorrectly, HDPE formulations have an increased tendency to form skins resulting in delamination. Ethylene vinyl acetate (EVA) can be used, but special attention to processing temperatures and to odor is needed.

Mixing is best accomplished when the viscosities of the SEBS/oil blend and polyolefin are matched appropriately at the mixing temperature to achieve isoviscous mixing resulting in a macroscopic interpenetrating network (IPN). The formation of an IPN for SEBS compounds has been described elsewhere in detail [44, 45]. In a mechanically stabilized IPN, a co-continuous morphology exists where each phase has three-dimensional connectivity; therefore, both phases contribute their respective physical characteristics to the overall blend performance.

Endblock resins and endblock plasticizers are compatible with the PS endblocks and are occasionally used in SEBS formulations to achieve desired properties. An endblock resin serves to reinforce the endblocks typically by increasing the endblock T_g. Endblock plasticizers serve to improve flow of a formulation and typically decrease the endblock T_g. The effects of endblock resins and plasticizers on shear storage modulus (G') and tan δ are illustrated in Figure 10.7. The solid lines represent the response of a neat block copolymer, and the dashed lines represent the response of a modified block copolymer.

As previously mentioned, PPE is miscible with the PS domains and serves as an interesting endblock resin when compounded efficiently. Even though the use of PPE has significant disadvantages such as yellow color, odor, poor UV stability, and difficult processability, it can still be utilized effectively to increase the T_g of the PS endblocks, which allows for improved upper service temperature. Table 10.1 demonstrates the level of improvement in compression set (ASTM D395 method B) at elevated temperature that an addition of 30 phr (parts per hundred rubber) of PPE offers in an SEBS formulation while maintaining hardness. The formulation is based on Kraton G1651 (Kraton is a registered trademark of Kraton Polymers US LLC).

The use of endblock resins could also increase compound stiffness, so a lower amount of polyolefin should be used to maintain hardness and stiffness requirements.

Many different types of fillers are currently available. There is really no limitation on the type of fillers used in SBS or SEBS compound formulations. Fillers serve to reduce cost, adjust surface appearance and feel, and enhance oil absorption. The addition of too much filler leads to property deterioration. Filler levels <200 phr are usually desirable for technical SEBS-based formulations, while filler levels <500 phr can be used for nontechnical SBS compositions.

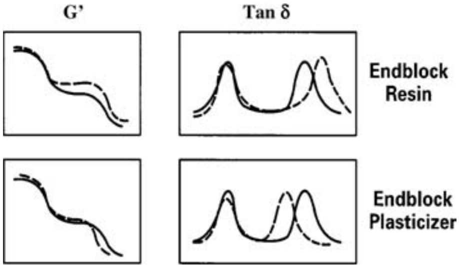


Figure 10.7 Illustration of dynamic mechanical data for an unmodified block copolymer (solid lines) relative to that modified with an endblock resin and endblock plasticizer (dashed lines).

Table 10.1 Data illustrating effectiveness of PPE addition to an SEBS/oil/PP compound in terms of compression set (CS) improvement.

Formulation	1	2
SEBS (Kraton G 1651)	100	100
Oil	150	150
PP	40	40
Filler	60	60
PPE	0	30
Stabilizers	1	1
Hardness	52	52
CS 70 °C, 72 h	42	33
CS 100 °C, 24 h	63	47
CS 125 °C, 24 h	75	67

Calcium carbonate ($CaCO_3$) is a very common filler. However, the formulator should be cautioned that ''sharp'' grades like ground calcite can damage the polymer matrix and lead to property erosion. $CaCO_3$ in the range of 5–10 μm is recommended for good dispersion. Talc and silica are also commonly used to adjust surface appearance and feel of the final part. Clays can also be used but typically give rise to greater machine wear. In general, mineral fillers offer little reinforcing effects in SEBS or SBS-based compounds. Filler addition reduces tensile strength and elongation, while hardness and stiffness increase only moderately upon addition of 100–200 phr filler.

A wide range of other additives are commonly used in SBC compounds. These can include antioxidants, UV absorbers, antiozonants, fire retardants, pigments, dispersants, and color concentrates. There are a variety of antioxidant types: primary, secondary, or carbon centered radical scavenging agents. Figure 10.8 shows the degradation pathway of elastomers and the role

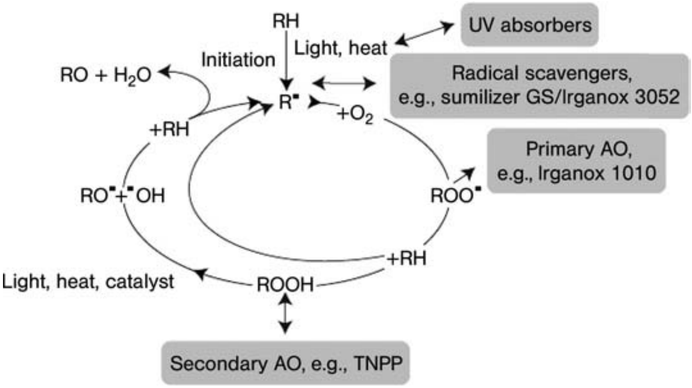


Figure 10.8 Degradation pathway of elastomers.

of various antioxidant types. A combination of these is often used because of synergistic effects. The choice of the antioxidant package will depend on the nature of the compound (natural or black), the intended application (outdoor or indoor), and the aging requirements (UV, Florida test, etc.).

A common and robust antioxidant package often consists of a hindered phenolic antioxidant in conjunction with a secondary synergist (e.g., IRGANOX® 1010 and IRGAFOS® 168, respectively) in a ratio of 1 : 2. Carbon black at levels above 2 phr tends to deactivate phenolic antioxidants. As such, it is often recommended that amine-type or sulfur bridge antioxidants be used in formulations containing carbon black. Carbon-centered radical scavengers such as SUMILIZER® GS are occasionally used as process aids primarily in SBS compounds where gel formation is of prime concern. Filler loadings of 50 phr or more can deactivate antioxidants because of absorption of the antioxidant on the surface of the filler. Epoxy resins preferentially coat the filler surface and thus are often used to prevent this antioxidant absorption and deactivation. For enhancing UV stability, UV absorbers such as TINUVIN® 327 or 329 are often used. To improve weathering stability, a combined package of TiO_2 and TINUVIN can be used. TiO_2 reduces light transmission by reflectance, while the TINUVIN agent absorbs it. Adding 1% of TiO_2 reduces light transmission by more than 60%. Very good retention of mechanical properties can be obtained by adding such stabilizer packages in addition to the primary and secondary antioxidants. Hindered amine light stabilizers (HALS) like TINUVIN 770 can also be used for better aging resistance. Gas fading or pinking can be a major obstacle when selecting the optimal stabilizer package for color-matched parts. While phenolic antioxidants are very effective stabilizers for long-term heat aging, they are prone to gas fading (primarily due to nitroxide emissions). Gas fading can be minimized by eliminating the use of a basic HALS in conjunction with a phenolic antioxidant. Many suppliers currently have nonbasic HALS systems to choose from.

Contour diagrams can be generated using statistical design of experiments and are extremely useful to the formulator in terms of determining the optimum formulating range to achieve the desired property set. Contour diagrams are often based on 100 phr of SBC, with lines representing formulations of equal performance. As an example, the contour diagram in Figure 10.9 represents Shore A hardness for the formulating range of 25–125 phr homopolypropylene, 0–160 phr paraffinic oil, and 100 phr high molecular weight SEBS with 33% polystyrene content (PSC). Lines represent formulations with equal hardness. Care should be taken when interpreting data at the extremes of the formulating window especially near 0 phr oil, as data near the outer edges are often extrapolated in these regions. The utility of contour diagrams is realized when trying to determine a starting point formulation to fulfill a complicated property specification. A single formulation must often meet multiple requirements (e.g., hardness, tensile strength, tear strength, elongation, abrasion resistance, etc.). Contour diagrams can be generated for each property and overlayed to determine whether a formulation even exists

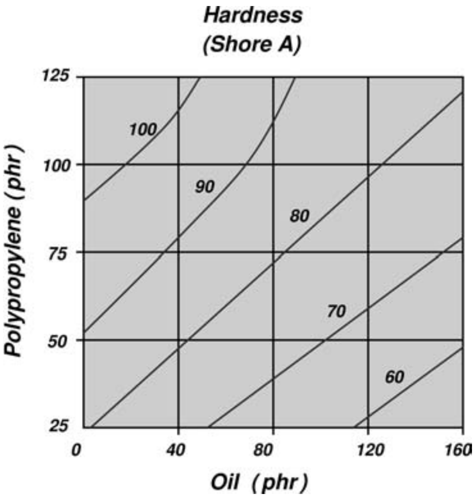


Figure 10.9 Hardness contour diagram for SEBS/oil/PP formulation based on 100 phr high molecular weight SEBS.

that meets all requirements. If so, the formulator can glean some insight into the flexibility of the applicable formulating space and the cost/performance trade-offs.

SBCs are attractive from a material selection view point because of their versatility and the wide range of properties that can be achieved using various formulating techniques. SEBS-based compounds can be formulated to achieve hardnesses ranging from 50 Shore 00 to 60 Shore D. Tensile strengths up to 17 MPa (2500 psi), elongations up to 750%, and tear strengths up to 97 kN m^{-1} (500 pli) can also be achieved depending on hardness. SEBS-based formulations can easily have temperature ranges of −50 to 100 °C, while SBS-based formulations can extend down to −70 °C.

10.4.2
Processing and Forming

The use of proper blending and processing techniques is critical to generating the desired compound properties and maintaining good reproducibility and quality control. Processing aspects related to compounding that need consideration are oil incorporation via dry blending or direct injection, metering and blending of dry components, screw and equipment design, process conditions, pelletization/finishing, dust application, and packaging. Each of these areas will be discussed separately below with an emphasis on compounding with hydrogenated SBCs; however, differences for unhydrogenated SBC compounding will be noted when necessary.

To achieve a homogeneous compound, formulating ingredients should be dry-blended prior to thermal mixing. Various dry blenders can be utilized effectively such as ribbon blenders, high-speed mixers, or tumbler blenders.

Most hydrogenated SBCs are supplied in crumb or powder form, which has inherent internal porosity through which oil is absorbed and diffuses into the crumb interior. It is important to incorporate oil into the crumb in the most uniform way possible. This is best accomplished by slowly adding oil to deblocked crumb in a dry blender or high-speed mixer. If slow, continuous oil addition is not feasible because of preexisting equipment, the oil should be incorporated in multiple (2–3) aliquots of equal size. If crumb is added to a pool of oil, or all of the oil is added to the crumb at one time, the oil will not be distributed evenly through out the crumb. This can often lead to the appearance of ‘‘gel-like'' particles in the final part. If the formulation is highly extended (>200–300 phr oil), a portion of the oil should be carried in with the polymer via dry blending and a portion of the oil should be directly injected into the melt. It is not necessary to apply external heat to the dry blender, as frictional heat will be generated during mixing. Once the oil is incorporated into the crumb, other dry ingredients can be directly added to the dry blender for incorporation.

SBCs form phase-separated structures in the melt below their characteristic ODT temperature [45–47]. At temperatures above the ODT, the block copolymer becomes homogenous and behaves like a homopolymer melt. However, because of the strong thermodynamic driving force for phase separation, the characteristic ODT for high molecular weight SEBS polymers is often far above the SBC decomposition temperature and thus normal processing temperatures. While the addition of oil to an SEBS polymer serves to depress the ODT, most high molecular weight SEBS compound formulations are processed at temperatures below the ODT of the oiled SEBS polymer. As such, these polymers are very shear sensitive as demonstrated by the shear viscosity curves (Figure 10.10) and will not flow without the presence of shear.

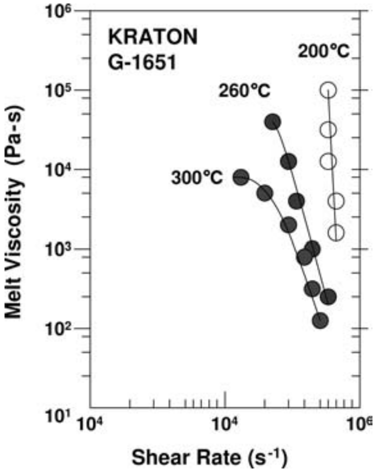


Figure 10.10 Shear viscosity data of SEBS Kraton G-1651.

In fact, infinite viscosity at zero shear is what contributes to successful IPN formation. The IPN morphology is formed in high shear zones during mixing, and phase growth is prevented after removal of the shear stress by the infinite viscosity of the SEBS phase [48].

Owing to this shear sensitivity, it is necessary to use the appropriate processing equipment and screw designs to achieve the optimal compound morphology. While Banbury Mixers and Farrel Continuous Mixers can be utilized to adequately compound many SBC formulations, the twin screw extruder is the most preferred processing technique because of its versatility. Corotating intermeshing screws with an L/D (length to diameter ratio) of at least 40 and a compression ratio >2 is optimal for SEBS compounding. At least two mixing zones with reversing elements are necessary to adequately compound SEBS-based formulations, while a single mixing zone can be utilized for SBS or SIS formulations. Some SBS or SIS formulations can even be processed on a single-screw extruder equipped with a mixing head. If oil is directly injected into the melt, it is important to do so prior to the first or second mixing element while pulling vacuum on the melt in the metering zones. While the specific formulation will determine the optimal processing temperatures, SEBS-based formulations are typically processed $<230\,^{\circ}\mathrm{C}$, while $200\,^{\circ}\mathrm{C}$ is often the maximum temperature for SBS and SIS formulations because of degradation tendencies. As more oil is added to the formulation, temperature profiles must be lowered because of lower compound viscosity and to ensure proper feeding by preventing excess lubrication at the feed throat. Compounding SEBS formulations with PPE is an exception to these temperature guidelines. To adequately incorporate high molecular weight PPE into the SEBS endblocks, a masterbatching approach is often necessary with temperatures in the first pass approaching $250\,^{\circ}\mathrm{C}$.

Once properly mixed, finishing can be achieved either by strand-cutting or dicing of harder formulations, or under-water pelletization for softer formulations. Soft formulations will require dusting to prevent pellet blocking during shipping and storage. Common mineral dusts include silica, talc, and magnesium carbonate. PE wax and antioxidants are ideal for transparent compounds if explosion-proof equipment is available for organic dust handling.

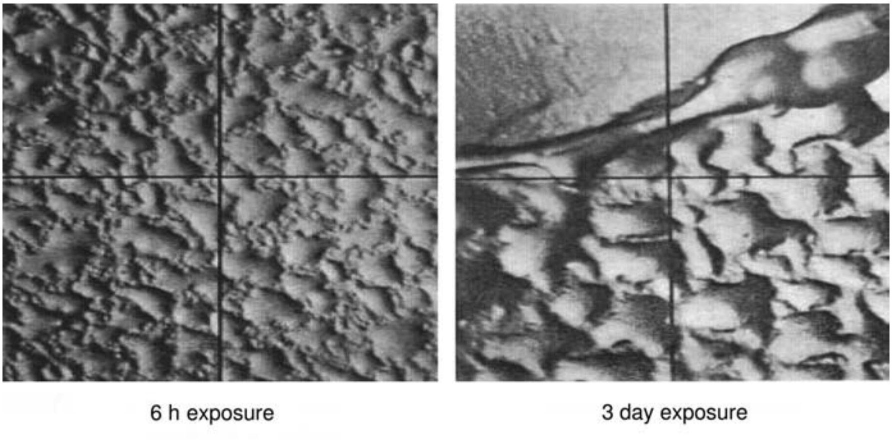
These fundamental formulating and processing techniques can be utilized to make a wide range of formulations applicable to many market segments. Some of these will be briefly highlighted below.

10.4.3
Automotive

It was not until the 5 mph bumper law of 1972 that hydrogenated SBC formulations “took off” in the automotive market. Bumpers that could withstand the new requirements of the bumper law could be made out of SEBS/PP/oil/filler formulations. Since then, SEBS-based formulations have found utility as fenders, sound dampening panels, air ducts, dampers, shift boot covers, cup holders, air bag door covers, and more recently automotive weather stripping. SEBS-based formulations are typically not applicable in "under-the-hood" applications, as they cannot withstand the high temperature and oil resistance requirements. Product specification requirements that are of prime importance to most automotive applications include hardness, tensile strength, compression set, tear strength, scratch/abrasion resistance, UV stability, surface appearance, and creep performance. Most automotive formulations are based on high molecular weight SEBS polymers to meet these often stringent requirements. As cost is a major concern, it is often desired to extend the SEBS with as much oil and PP and other formulating ingredients as possible while still meeting the minimum performance requirements.

As automotive parts are often in direct sunlight for many years, UV-induced OBO tendencies are also of prime concern. UV induced OBO is a phenomenon in which the surface of a molded part becomes oily and sticky upon exposure to UV light, as illustrated by Figure 10.11, after high intensity/accelerated UV exposure for 6 h and three days, respectively. It should be noted that the unexposed material has a visually smooth surface when viewed through a microscope.

If exposed to UV long enough, the oil will seemingly disappear from the surface and the part will appear "normal" again. This phenomenon has been studied in great detail and found to be a function of the surface residual stresses, formulation, and stabilizer packages [49, 50].


6 h exposure

3 day exposure

Figure 10.11 Optical microscopy images of SEBS/PP/oil compound surface after 6 h and 3 days UV exposure.

UV-induced OBO can be mitigated by elimination of residual stress. This can be done by mold design or improving compound flow through the use of endblock plasticizers, high melt flow polyolefins, or partial substitution of the high molecular weight SEBS with a lower molecular weight version. Adjusting the formulation by removing some oil and PP can also help mitigate UV-induced OBO. In addition, the use of talc as opposed to $CaCO_3$ tends to significantly reduce this tendency, as talc has an oleophilic surface that reduces the solution activity of the oil. Choosing the optimal stabilizer package is essential for mitigating this phenomenon as well. The combination of a phenolic antioxidant, a UV absorber, and an antiozonant appears to be the most effective at mitigating UV-induced OBO. The formulator is cautioned that the use of dilaurylthiodipropionate seems to promote UV-induced OBO.

SIS polymers that have very high levels of 3,4-isoprene in the midblock as well as the hydrogenated version of the same polymer exhibit very good vibration and sound dampening at room temperature. The glass transition temperature of the rubber phase is relatively close to room temperature and the glass transition is very broad, which results in good vibration dampening characteristics by itself or in formulations with other polymers such as PP. Such bends are useful for automotive and general molded applications. The hydrogenated versions of these polymers make very fine dispersions and clear blends with PP, so the blends can be used as a flexible poly(vinyl chloride) (f-PVC) substitute.

10.4.4
Wire and Cable

Flame-retardant SEBS compounds were developed in the 1970s for electrical wire and cable sheathing. Cold-temperature flexibility was the main advantage that SEBS formulations brought to the market place over incumbent thermoplastic materials, such as poly(vinyl chloride) (PVC). These formulations are often based on high molecular weight SEBS polymers to achieve the abrasion, flex crack, and tensile requirements. In addition, high molecular weight SEBS polymers have enough extendibility to incorporate the large amounts of flame retardant necessary to achieve the V-0 flammability requirements. Traditional flame retardants include halogenated resins in conjunction with antimony oxide. Legislative and environmental pressures are pushing the industry toward nonhalogenated flame retardants, some of which include magnesium hydroxide, phosphite esters, graphite, and nitrogen-phosphite types. Owing to the high levels of flame retardant needed to achieve V-0 ratings, it is difficult to make soft formulations (<80 Shore A). In addition, the wire and cable industry is cost competitive, and other types of polymeric materials are gaining market share.

10.4.5
Medical

SBS and SEBS-based compounds for medical applications were first introduced to the market around 1980. Most medical compounds are based on SEBS/PP/oil, SBS/oil, or SBS/oil/PS depending on the application requirements. The most important requirement for material selection in the United States is US Pharmacopoeia approval, and most end users also desire direct food contact FDA approval. Most medical applications require long qualification lead times, which make raw material changes extremely difficult. Physical properties of most concern to the formulator include sterilization requirements, resiliency, tensile strength, tear strength, transparency, and colorability. Most SEBS/PP/oil compounds are sterilizable by γ-radiation, β-radiation, ethylene oxide, or steam. Radiation or ethylene oxide is best for SBS-based formulations, as warpage can occur when using steam sterilization techniques. It is best if parts can be individually wrapped prior to sterilization as opposed to adjacent parts touching each other, which can sometimes lead to part sticking and warpage. Medical applications for molded and extruded goods based on SBC technologies include clear flexible tubing, surgical draping, port caps, syringe bulbs, syringe tips, nipples, and physical therapy equipment.

In addition to general molded and extruded goods, SBCs are also used as a layer in coextruded films for blood bags, removable protective coatings, heat-sealable films, and reclosable packaging constructions. The SBC layer usually consists of a neat or formulated SEBS or SIS. When formulating the SBC, it is important to match the rheology of the layers while balancing functionality. For example, it is sometimes necessary to blend an SEBS with a maleated SEBS to tailor the rheology and to optimize the maleic anhydride level. Maleated SEBS and blends with other polymers can be used as a tie layer between polyolefins, polycarbonate (PC), polyesters, nylons, and polyethylene vinyl alcohol (EVOH).

SEBSs with high butylene content in the midblock are unique in forming clear, flexible blends with PP because of their improved compatibility with PP and the submicron dispersion of the SBC in PP that does not scatter light. These blends have the autoclavability of PP but the strength and flexibility of the SBC and are thus good replacements for clear, plasticized f-PVC in medical applications where there are plasticizer and disposal problems.

10.4.6
Soft-Touch Overmolding

Soft-touch overmolding has become a value-added market trend only in the early 1990s, and involves molding a soft skin layer on top of a rigid, hard engineering thermoplastic. Soft-touch overmolds serve to provide highly frictional and waterproof surface, vibration damping, impact resistance, insulation from heat and electricity, and cushioning for improved ergonomics [51]. Consumers often perceive a rubbery look and feel to be of higher value than a "cold" hard plastic feel. Soft-touch overmolding can be achieved either by insert molding or two-component (two-shot) molding. Two-component molding utilizes equipment containing two independent injection units each shooting a different material. This type of setup involves two independent runner systems with a rotating mold and is preferred because of faster cycle times when compared to insert molding.

There are many types of TPEs for a fabricator to choose from when selecting a soft-touch overmold material. SBC formulations are of the most widely used in the marketplace. This is largely due to the wide hardness range, ease of colorability, excellent adhesion to polyolefins such as PP, and good UV stability as well as low polarity which minimizes the need for drying prior to use. Low polarity also makes SBC solutions less prone to staining [51]. However, this lower polarity often makes it difficult for SBC formulations to adhere to polar substrates like polyamide. When this is required, it is often necessary to incorporate a maleic anhydride-functionalized SEBS into the formulation [52]. For some applications, SBCs are limited by oil resistance and upper service temperature performance. When developing a soft-touch overmolding formulation, many requirements have to be considered including adhesion, ergonomics, physical performance, colorability, and processability.

10.4.7
Ultrasoft Compounds

At the turn of the twenty-first century, ultrasoft compounding began gaining popularity. These types of materials are often in the Shore 00 hardness range and are on the verge of being considered stiff "oil gels" (Section 10.9.2). These types of formulations often contain 300–500 phr oil relative to 100 phr SEBS polymer. As such, low processing temperatures must be employed because of very low viscosities. Formulating parameters to be considered include low tack, low-to-no OBO, clarity, and colorability. Molding is often challenging, as cycle times are long, and demolding can be difficult. Applications include adult novelty items, cushions, squeezables, mattresses, and toys [53].

10.4.8
Elastic Films and Fibers

Lower viscosity SBCs can be formulated with a minimum of other formulating ingredients, such as polyolefins and midblock compatible additives, to make strong but easily processed formulations. Such formulations can be extruded or coextruded into strong elastic films and fibers with good stress relaxation, good hysteresis, and good strength properties. These elastic films and fibers are useful in products such as disposable diapers, which require elasticity and form-fitting characteristics.

10.5
Polymer Modification

SBCs are frequently used as impact modifiers of thermoplastic polymers. Most plastics are susceptible to brittle failure due to an inherent lack of energy-absorbing processes throughout the bulk of the material. To increase toughness, energy-dissipating mechanisms must occur over a large volume of the plastic. These energy-dissipating mechanisms must limit void growth and crack propagation to prevent catastrophic failure. This can be achieved by dispersing high-strength rubber polymer particles with a low glass transition temperature in the thermoplastic matrix. Good adhesion of the rubber particle to the thermoplastic matrix is usually also required. These particles act as stress concentrators that initiate localized energy-absorbing mechanisms. Optimum energy dissipation is a function of rubber loading, particle size, and uniform dispersion. To achieve optimal particle size and dispersion, it is necessary to have the right degree of compatibility between the rubber and the plastic. Incompatibility can lead to large rubber particles with poor toughening results, while high levels of compatibility can lead to rubber particles that are too small and essentially ‘‘invisible’’ to the crack tip, also resulting in poor toughening. The incorporation of a small amount of and SEBS or SBS polymer into a thermoplastic can serve as a very efficient toughener because of their high strength and low glass transition temperature. In addition, SEBS and SBS polymers provide the right balance of compatibility and adhesion with a variety of thermoplastic substrates to achieve optimal particle sizes for enhanced toughening [54].

Traditional SBS and SEBS polymers with small styrene endblocks that have molecular weights of 10 000–30 000 g mol^{-1} serve as good tougheners for crystal clear PS (often called *crystal polystyrene*), high impact PS resins, and polyphenylene ether polymers. However, there is a significant loss of clarity because the rubber particles are on the order of a micron in size and large enough to scatter light. Special dissimilar-arm SBS polymers with 75% PSC serve to maintain clarity in blends with clear PS resins while enhancing ductility. These 75% PS dissimilar-arm S-B-s or $(\text{S-B})_x\text{-Z-}(\text{B-s})_y$ polymers where Z is a coupling agent, have at least one large styrene block (S) that is large enough (on the order of 100 000 g mol^{-1}) to compatibilize with the high molecular weight clear PS to form submicron mixtures with the PS which will not scatter light. It is also important to have small styrene blocks (s) so that the viscosity is manageable. The rubber block B can be pure polybutadiene or a copolymer of butadiene/styrene. These types of formulations can be used to make water-clear, disposable packaging, thermoformed containers or plates, film, and molded parts.

The addition of small amounts of SBS (<10%) to LDPE can improve both impact resistance and stress-crack resistance. Addition of SBS to HDPE provides improvements in impact strength, flexibility, as well as film tear and impact strengths [54].

Blending SEBS or SBS polymers with PP can significantly increase the impact strength particularly at low temperatures. Low molecular weight SBS or SEBS polymers tend to give the best results because of their ability to form a fine dispersion [54]. New grades of SEBS polymers have recently been introduced to the market that improve toughness of PP, even at low temperatures while maintaining good clarity [55]. SEBS polymers can also be used to improve the ductility of PC in thick sections ($\geq 1/4''$). High molecular weight SEBS polymers are unique modifiers for PC, as they form blends highly resistant to delamination particularly at SEBS concentrations <10% [54]. Addition of a small amount of high molecular weight SEBS also serves to improve environmental stress-crack resistance and retards the PC embrittlement process when parts are annealed at elevated temperatures. Unfortunately, the PC/SEBS blends are not clear.

Maleic anhydride functionalized SEBS polymers can be effective modifiers for polar engineering thermoplastics such as polyamides and polyesters. Nylon 6,6 can be efficiently toughened ($30 + \mathrm{kgf\,cm^{-1}}$ ($15 + \text{ft-lbs in.}^{-1}$) notched izod at 24 °C) with approximately 20% of an SEBS polymer with 1.7% maleation. Nylon 6 requires a lower level of functionality, which can be achieved by using a cutback blend consisting of 60–75% of a conventional SEBS in addition to a SEBS with 1.7% maleation. The saturated midblock of maleated SEBS polymers allows them to stand up to severe processing conditions, heat, and UV-aging tests necessary for polyesters like poly(butylene terephthalate) (PBT). Notched izod impact strength is significantly increased by the addition of 20 and 30% of a maleated SEBS polymer to poly(ethylene terephthalate) (PET) and PBT, respectively [54].

SB diblocks can be used in the polymerization of acrylonitrile/butadiene/styrene (ABS) polymers to help control the rubber particle size during polymerization to achieve the optimum impact. SBS, SB, and tapered SB with the appropriate level of styrene in the block copolymer to achieve the proper index of refraction can be added during the polymerization of styrene/methyl methacrylate (SMMA) polymers to make clear, tough SMMA polymers.

A rather unusual application for styrenic polymers is in polyester sheet molding compounds (SMCs) as a shrink control agent during cure. SMC is composed of unsaturated polyester, styrene monomer, peroxide curing agent, and high levels of calcium carbonate filler and glass fiber. Unmodified SMC, when cured in a high-temperature mold, will shrink, resulting in an uneven surface which is not aesthetically appealing, especially in automotive panel applications that require a smooth, mirror-like appearance. Levels of only 3.6% block copolymer in the SMC are required to achieve zero shrinkage, smooth surfaces, and precision molding. The key is forming fine, stable dispersions of the block copolymers in the SMC formulation which act as styrene monomer reservoirs and points for microvoid formation during cure. The microvoids are small enough that they do not interfere with the color of pigmented part unlike what will happen with other commonly used SMC shrink control agents such as vinyl acetates. The best block copolymer shrink control agent contains a combination of SBS and SEP diblock [56].

10.6
Cross-Linked Systems

10.6.1
SBC-Based Dynamic Vulcanizates

Dynamic vulcanization refers to the process of blending a rubber into a thermoplastic matrix wherein the rubber is cross-linked during the mixing process [57]. This process was first realized in the late 1970s and has since led to the introduction of many new commercial products into the TPE market place. Dynamic vulcanizates are often referred to as *thermoplastic vulcanizates* (TPVs) and are traditionally based on cross-linked poly(ethylene-propylene-diene monomer) (EPDM) blended with processing oil in a thermoplastic PP matrix. Traditional TPVs provide improved upper service temperature performance and solvent resistance as compared to traditional SEBS/PP/oil compounds; however, they are often more difficult to process, have undesirable odor tendencies, and until recently have been more difficult to color-match. As such, many new TPV systems have recently been developed and introduced into the market. These new materials have been referred to as super-TPVs and utilize differentiated elastomeric phases [58].

The use of traditional SBCs as the cross-linked elastomer phase in TPVs has recently been explored. TPVs based on cross-linked SEBS and/or SBS using standard peroxide technology in conjunction with processing oil, PP, and/or PE have recently been described [59, 60]. The purpose of these compositions is to make soft, rubbery materials that have improved oil resistance, scratch resistance, and upper temperature performance with less stickiness than traditional SEBS-based compound while providing improved processability over traditional EPDM-based TPVs. A typical 60 Shore A formulation contains approximately 25% high molecular weight hydrogenated SBC, 2% SBS, 40% paraffinic oil, 10% PP, 20% $CaCO_3$, and 1–1.5% each of an organic peroxide and a coagent [60]. While initial compression set values of these materials are worse than traditional TPVs, they exhibit superior long-term compression set performance. Tests have also been conducted to evaluate the effect of different types of oils (paraffinic, ASTM oil #3, automobile grease, and petroleum) on the oil resistance behavior of SEPS-based TPVs [61, 62]. The dynamic viscoelastic properties of SBC-based TPVs have also been studied recently [63].

Super-TPVs have also been developed with new SBCs that have cross-linkable hard domains [60, 64]. The soft domains are cross-linkable via traditional routes, while a modified hard block structure enables cross-linking of the hard domains via dynamic vulcanization. The use of these new SBCs can result in products with improved heat and oil resistance when compared to traditional SBC compounds, making them suitable for many segments of the automotive market as competition against traditional EPDM-based TPVs. TPVs based on this technology have been claimed to have compression set performance that meets or exceeds that of traditional EPDM- and SBC-based TPVs while maintaining good oil resistance [60]. A possible explanation for the significant property improvements is a dual rubber phase network morphology with micro- and nanoscale cross-linked phases that serve to increase the cross-link density and elasticity of the elastomer phase [65].

In addition to using an SBC as the cross-linked elastomer phase to make TPVs, others in the industry have created hybrid blends of traditional EPDM-based TPVs with SBCs. In these hybrid systems, the SBC is not cross-linked. Benefits of these hybrid materials include excellent moldability as well as low hardness and mechanical strength like an SBC compound while maintaining good permanent set and high-temperature performance similar to a traditional EPDM-based TPV [66]. It is generally difficult to manufacture an EPDM-based TPV of low hardness (<50 Shore A). By modifying the TPV with oiled SEBS material, the hardness can be reduced while improving flexibility and workability without significant loss of the inherent TPV properties, thus expanding the hardness range of traditional TPVs [67].

10.6.2
Flexographic Printing Plates

Flexographic printing is utilized to print on a variety of difficult-to-print substrates, which vary from rough cardboard to thin plastic films or thin foils. Common examples of articles printed via flexography include newspapers and grocery bags; other substrates include corrugated cardboard, continuous webs of plastic films, foils, and laminates [68–71]. Printing plates must be soft and flexible so that they can be wrapped around printing cylinders via either a PSA or vacuum suction. The substrate to be printed is then contacted with an inked printing plate on the printing roll, producing the desired image. A typical plate is a multilayer construction of a polyester backing film, one or more flexible photoreactive polymer layers, a UV-impermeable protective layer, and a cover sheet [72]. The 1–7-mm-thick photoreactive polymer layer is made of an extruded mixture of approximately

- 80% SBS, SIS, isoprene, and butadiene mixed midblock polymer or a combination thereof;
- 10% reactive diluents such as hexanediol diacrylate or other mixtures of mono- and di(meth)acrylates;
- 10% oil;

- 1–2% photoinitiator chosen based on desired wavelength;
- 1% antioxidant.

Varying the combination of SBC (SIS, SBS, and mixed midblock polymers) and the reactive diluents allows the manufacturer to tailor the hardness of the final cross-linked printing plate.

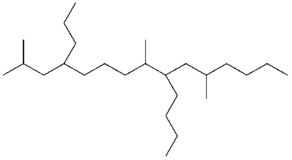
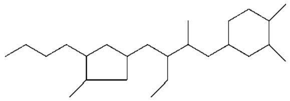
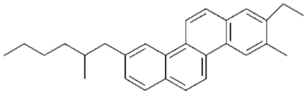
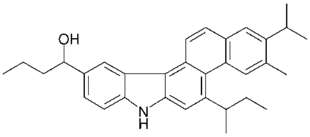
Once the plate arrives at the printer, the bottom of the plate is usually lightly cured to create a strong cured elastic base, and the protective layer is then removed from the top of the plate. In traditional printing plate preparation, a UV mask with the desired image is placed on top of the plate and the plate is exposed to UV irradiation. Sections of the plate that are exposed to the UV light cure, forming the desired image. The plates are then developed by removing the unreacted polymer via either washing with solvents, or application of heat and blotting [68]. Newer technologies include laser-engraving with a UV or infrared laser [69]. Formulated SBCs are unique in this application because they are clear for good image definition, hold their form and dimensions very precisely until it is cross-linked, are curable, and lastly the uncross-linked material can be removed by solvent or heat. Formulating and creating a SBC polymer with the correct balance of properties is challenging because of demanding precision required.

10.7
Bitumen Modification

10.7.1
Paving

The modification of bitumen with SBC is the second largest market for SBCs in the United States and the largest market for SBCs in Europe. The bitumen modification market is typically split into two segments: roofing and paving. Bitumen (often called *asphalt* in the United States) is a byproduct of crude oil refining. It is complex and varies with the crude oil source, age of the oil well, and processing conditions. Thus, unlike modifiers in adhesive formulations, manufacturers have less control over its composition. Its primary components are asphaltenes and maltenes, which in practice are differentiated by solubility in *n*-heptanes [73]. Asphaltenes, insoluble in *n*-heptanes, are poly-condensed aromatic molecules with molecular weights from 1000 to 100 000 g mol^{-1} and hydrogen to carbon ratios of 1.1–1.2. Their physical structure consists of mostly aromatic sheets with paraffinic side chains. They possess some polarity in the form of ketones, alcohols, ethers, and carboxylic acids. The asphaltenes are not soluble in either the styrene or butadiene blocks. Maltenes, soluble in

Table 10.2 Description of bitumen components [73].

Compound	Example structure	MW Range	H:C
Saturates (Paraffins)		300 – 2,000	1.9 – 2.0
Saturates (Napthenes)		300 – 2,000	1.9 – 2.0
Aromatics		300 – 2,000	1.5
Resins	 	500 – 5,000	1.3 – 1.4

n-heptanes, consist of three basic types of molecules: saturates, aromatics, and resins (Table 10.2) [73]. Saturates are typically soluble in the butadiene block, whereas the aromatics are partially soluble in the styrene blocks as well at ambient temperatures. They become increasingly soluble in the styrene block at processing temperatures. The asphaltenes are not soluble in either phase of the SBCs and compete with the SBCs for the maltenes which can cause some compatibility problems. In general, bitumen with high asphaltene contents (>10%) are undesirable for mixing with the SBCs. Conventional bitumens are often "blown" (air is bubbled through the bitumen at high temperature with a catalyst) to increase the upper service temperature. This increases the molecular weight of the bitumen, forms more asphaltenes, and deteriorates the low-temperature properties of the bitumen which is very undesirable for an SBC-modified bitumen systems. Thus "unblown" bitumens with low asphaltene contents are preferred for blending with SBCs. Adding SBCs to an "unblown" bitumen, so that a three-dimensional network of swollen thermoplastic rubber is formed in the bitumen, improves the high-temperature properties and the strength of the bitumen significantly without deteriorating the low-temperature properties. Oftentimes, the low-temperature properties are even improved. SBC-modified bitumen thus has a much wider service temperature range and better physical properties than conventional bitumens (Figure 10.12).

The saturate/aromatic balance is particularly important in formulating high-quality paving and/or roofing materials. If too little aromatic fraction is present, the strong phase separation of the SBC will prevent it from dissolving in the bitumen at processing temperatures of 160–190 °C. Too much aromatic

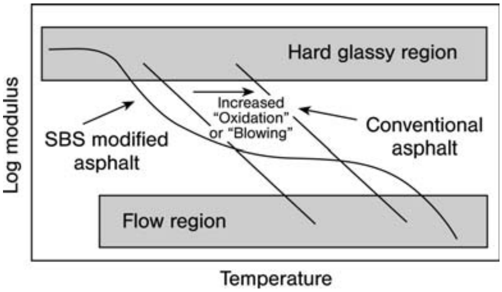


Figure 10.12 Comparison of the service temperature properties of conventional "blown" bitumens and SBC rubber-modified bitumens.

fraction will reduce the strength of the styrene phase association at ambient temperatures, thereby reducing the upper service temperature of the modified bitumen. During melt mixing, a wide range of grafting, chain scission, and coupling reactions can occur, which aid in the compatibilization of the SBS and bitumen mixture.

Other than special applications, SBS block copolymers are preferred over SIS or SEBS in bitumen modification because of the lower cost of the base polymers. In addition, the SIS polymers tend to chain-scission and lose their properties during high-temperature processing of the modified bitumen. The optimal SBS polymers usually contain 30% styrene and are generally of high molecular weight, typically 100 000–300 000 g mol^{-1}, with two to four arms [45]. The high styrene content and high molecular weight help to create a continuous swollen rubber network at low polymer levels. Once properly blended, the butadiene phase is able to absorb up to 10 times its weight in maltenes. At concentrations of 3% polymers, a continuous network swollen by the soluble bitumen components begins to form (Figure 10.13). By increasing the polymer concentration to 5% or greater, the SBS polymers forms a continuous polymer network. Typical concentrations of SBS polymers in roads are 2–6% based on bitumen (where the bitumen concentration in roads is approximately 5 wt% with the rest being graded stone aggregate), so the total percentage in a road is actually very small. However, the benefits of using an SBS- modified bitumen in a road are significant and include the following:

- reduces permanent deformation (rutting) at elevated temperatures and high traffic loading;
- reduces fatigue and low-temperature cracking by increasing the ductility and strength of the bitumen binder at low temperatures;
- reduces aggregate loss by increasing the binder toughness over wide temperature ranges [73].

SBS-modified bitumen is ideal for hot-melt-applied road crack sealants at a loading of roughly 6–10% in the sealant. It provides good low-temperature properties as well as good elevated service temperature, good elongation and recovery properties over repeated stress cycles, and good adhesion to the

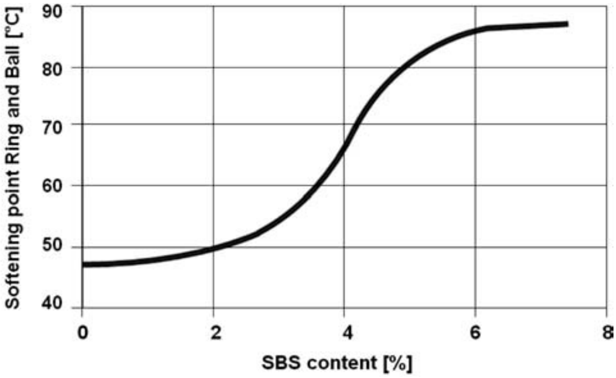


Figure 10.13 Indication of the onset of a three-dimensional swollen rubber network in the bitumen as exhibited by the ring and ball softening point and the concentration of the SBC in a suitable bitumen.

cracked road surface. Conventional bitumen road crack sealants will usually fail and crack in the first winter, so they often do not even last a single season. Preventing water intrusion into the road base structure is critical for the life of a road, so having good road crack sealants, such as the SBS-modified bitumen sealants, that last multiple years is very cost effective. The best balance of sealant properties is usually achieved with SBSs that have high levels of SB diblock.

A relatively new advance in bitumen modification is the use of high-vinyl SBS molecules. The higher vinyl content (higher 1,2-butadiene content) has two main advantages over standard SBS molecules. The first is a lower bitumen blend viscosity due to the shorter polymer backbone chain length of the high-vinyl SBS. A second advantage is evident if oxidation of the SBS molecules occurs during processing. Oxidation occurring on a backbone double bond (more prevalent in the standard vinyl molecule) results in chain scission, whereas if oxidation occurs on the side arm vinyl double bond, the backbone of the molecule is largely unaffected. However, care must still be taken in the processing of the high-vinyl polymers, as the have a higher propensity for gelation if they are handled improperly. Where high processing temperatures or harsh climates such as deserts require better long-term stability, SEBS polymers are sometimes used.

10.7.2
Road Marking

A small but growing market segment is the modification of hot-melt road marking paints with SBCs. Conventional hot melt applied thermoplastic road markings are a mixture of glass beads, pigment, and filler, held together by a binder. Historically, binders of the thermoplastic road markings consist of low molecular weight petroleum-based resins or rosin derivatives, which can be mixed with plasticizers to reduce the T_g of the binder and thus toughen the road marking. The addition of SEBS polymers to the road markings improves the mechanical properties of the binder, which leads to an improvement in the erosion resistance and thus the lifetime of the road marking. Including as little as 2 wt% of an SEBS polymer to the road marking paint increases the lifetime of the paint from 1 500 000 to over 4 000 000 wheel passages [74]. The retention of the glass beads is also improved with the inclusion of the SEBS polymer.

10.7.3
Roofing

Roofing membranes and waterproofing coatings require higher elasticity than paving bitumen; therefore, they typically contain from 8 to 20% SBS [45, 48, 50, 75]. At this SBS level, the membranes perform more like swollen elastomers than bitumen. Some of the benefits of replacing unmodified roofing materials with SBS modified roofing materials include

- increased resistance to flow at elevated surface temperatures, which helps prevent the membrane from flowing on highly sloped roofs;
- increased puncture resistance via increased toughness;
- increased low-temperature flexibility;
- increased resistance to damage by expansion and contraction of the roof during daily heating cycles.

In flat rolled roofing applications, strong nonwoven glass fiber or polyester felts are coated and impregnated with the SBS-modified bitumen and then covered with roofing granules to protect the membrane from sunlight. These modified membranes are typically adhered to the roof using conventional hot-mopped bitumen. It can also be adhered to the roof using a propane torch to melt the modified bitumen on the bottom side of the membrane as the membrane is unrolled on the roof. Roll roofing products may also be adhered with solvent-based adhesives or they may be formulated so they are self-adhering.

With the proper bitumen and formulation, SBS-modified bitumens can be made pressure sensitive. Rolls of a modified bitumen water proofing membranes are made by forming multilayered structures that are composed of PE film, a thick layer of the pressure-sensitive modified bitumen, and a removable release paper. Sometimes a metal foil is also included between the PE and modified bitumen layers. These membranes are typically applied to underground concrete structures during construction to provide effective water proofing even if the concrete cracks. These pressure-sensitive membranes can also be used on flat roofing to eliminate the hazards of hot mopping.

In special cases such as bridge decks, SBS-modified bitumens can be applied by hot mopping to provide special waterproofing. Solvent-applied SBS-modified asphalts are sometime used to waterproof walls and vertical surfaces.

In shingle applications, SBCs can be used to modify the bitumen-based sealing tab adhesive to give better wind uplift resistance, particularly at low temperatures. This reduces shingle cracking and shingle loss. SBCs are also used to modify the laminating adhesives used in multilayer architectural shingles. Shingles can also be made with SBC-modified bitumen as a major part of the shingle to provide significantly improved hail impact resistance.

10.8
Footwear

Footwear became the first commercial application for SBCs with the advent the direct injection molder for shoe soles in the 1960s [45, 48, 73, 75]. Although the molder was originally designed for natural rubber soles, the use of SBCs greatly reduced the cycle time and allowed for increased production. SBC footwear is also often preferred over PVC because of the better wet grip, low-temperature grip, and lighter weight. On a worldwide basis, footwear is the largest application for SBCs today, with most of the business centered in Asia, followed by South America and Europe. Because shoe soles require relatively stiff and cheap elastomers, the compounds used for making the soles are typically highly filled compounds containing linear or radial SBS copolymers with styrene contents between 30 and 50%. A typical foot wear compound consists of mixtures of 30% SBS polymers with 30% oil, 15% PS, and up to 25% talc and/or calcium carbonate. Occasionally, 5–10 phr poly(ethylene vinylacetate) is added to increase the UV, ozone, and casual solvent resistance of the shoe sole. SBS-based footwear has excellent skid resistance, low-temperature flexibility, and fatigue life. The SBC shoe soles are not suitable for high-performance athletic shoes, such as basketball shoes, which require high-temperature abrasion resistance, but they work very well for walking shoes, boat shoes, canvasware, sandals, thick sole shoes, and other casual footwear.

A market drive for lighter and more comfortable shoes has led to innovations in foaming SBS shoe soles [73]. With the inclusion of either chemical blowing agents (azodicarbonamides) or physical blowing agents (Expancel), the density of the sole can be reduced by as much as 30–40%. By varying the concentration of either blowing agent through the thickness of the sole, a manufacturer can vary the density and the energy absorption to the sole.

10.9
Viscosity Modification and Other Highly Diluted SBC Applications

10.9.1
Viscosity Index Improvers

Low levels of a hydrogenated SBC can also play a significant role in motor oils by changing a single-weight oil into a multigrade 10W/50 motor oil (Figure 10.14) [76]. Engine oil manufacturers utilize SEP diblocks or star ethylene-propylene $(EP)_x$ polymers (hydrogenated star polyisoprenes) to modify the viscosity of motor oils. Hydrogenated polyisoprene polymers are usually preferred over hydrogenated polybutadiene block copolymers because the EP polymers degrade by chain scission in the engine which avoids the formation of varnish and they do not crystallize with the oil at low temperatures. Even small amounts of crystallinity are very detrimental to the low-temperature properties of the motor oil. To be a good viscosity index improver, the polymer should increase the high-temperature viscosity as much as possible to create better lubrication and less wear in the bearings. However, the polymer should affect the low-temperature viscosity as little as possible so that the motor oil can still be efficiently pumped to the bearings and lubricating surfaces during engine startup on cold days. The anionic block polymers are unique as VIIs because of their precise optimized molecular weight, narrow molecular weight distribution, good shear stability, and low treat rate so there is less varnish buildup on the sides of pistons. In other words, there are no low molecular weight species that are inefficient in increasing the high-temperature viscosity and there are no very high molecular weight molecules that are sheared apart in the high-shear section of the engine reducing the viscosity of the oil with use.

The concentration of the hydrogenated SBCs used as modifiers varies between 0.4 and 4 wt%. This weight range typically puts the polymer

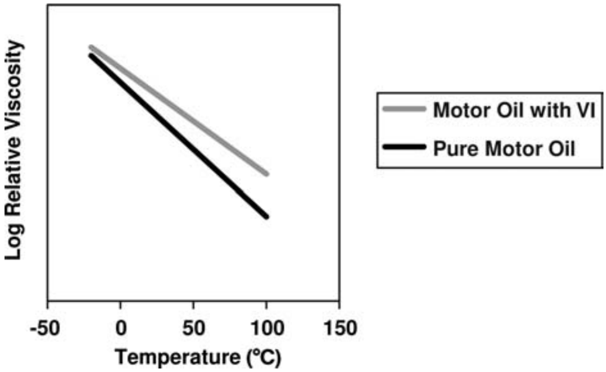


Figure 10.14 Viscosity of motor oil with and without a viscosity improver.

concentration very near the overlap concentration between the semi-dilute and dilute region of the polymer in the oil (C^*). Polymer loading much above or below C^* can lead to either inefficient viscosity modification or experience excessive degradation in the engine. At concentrations much below C^*, little viscosity modification occurs because of the lack of entanglements in solution. Conversely, concentrations higher than C^* contain too many entanglements, leading to excessive shear degradation in the engine. In addition to motor oils, SBCs, including hydrogenated polybutadiene containing polymers, are quite efficient thickeners for personal hygiene baby and moisturizing oils.

10.9.2
Oil Gels

Further increasing the concentration of hydrogenated SBCs above 6 wt% to as high as 15 wt% in various mineral oils can lead to the formation of tough gels or thick greases for a number of uses including cable-filling compounds, clear candles, and shock-absorbing gels in sporting equipment. Formulations based on triblocks are typically gels, whereas the use of diblocks leads to greases. The use of hydrogenated SBCs in cable filling, the largest of the above markets, was first discovered by Bell laboratories in the late 1970s [77, 78]. Typical cable-filling formulation include as little as 6% hydrogenated SBC and 4% PE with the remainder being mineral oil and a small amount of additional stabilizer. The filling compound is pumped into cables during fabrication so there are no air spaces in the final cable. The oil gel prevents water from penetrating the cables and wicking long distances in the inner bundle of wires ruining long stretches of the cable. Compared to other water-proofing systems in cables, like greasy petrolatum, the strong SBCs oil gels provide easy cable repairing (the repairman can grab the oil gel and easily strip it off the inner bundle of wires) and provide excellent low-temperature flexibility when the cable is installed on cold days.

10.10
Emerging Technology in Block Copolymers

10.10.1
Recycling Compatibilization

Recycling of polymeric waste and regrind streams as well as after market parts is becoming the norm in many industries including packaging and automotive. Even with intensive melt mixing in an extruder, many multicomponent blends of recycle material have poor mechanical properties because of compatibility problems and poor adhesion between the different phases. Low-level addition of SBCs to such recycle streams can serve to compatibilize the blend, resulting in useful mechanical and physical characteristics. Only 5% of a SBS or SEBS can sufficiently upgrade and toughen recycle streams, such as PS/polyolefin, while the addition of 5–10% of a maleated SEBS can upgrade polyolefin/polyester, polyolefin/polyamide, and ABS/polyolefin recycle streams [79].

10.10.2
PVC and Silicone Replacement

Replacement of silicone and f-PVC has become an increasing trend in the TPE market segment within the past five years. Silicone and f-PVC are both used in the personal-care and medical industries where clarity is required. In addition, silicone offers high-temperature performance and chemical resistance. f-PVC has a unique physical property set in terms of kink resistance and low tack. However, silicone is very expensive, and f-PVC has emerging health and environmental concerns. As such, SBC-based compounds are being developed to replace both silicone and f-PVC in the medical and personal-care market segments [80]. Compound formulations are often based on PP using low molecular weight SEBS copolymers. In addition, newly developed SEBS polymers with modified midblock structures can generate compounds with exceptional transparency [55]. In developing these types of compounds, the formulator must pay special attention to compound rheology relative to the desired processing technique to achieve a smooth surface to mitigate light reflection due to surface imperfections. Processing aids or special die coatings can also be utilized to enhance surface smoothness. Specific applications for these types of SBC compounds include baby-bottle nipples, IV bags, and medical tubing [80].

10.10.3
Sulfonated Block Copolymers

Sulfonated SBCs have been studied for some time for various applications centered around enhanced strength at high temperatures [81–84]. Recently, new applications for the technology in fields such as protective clothing, fuel-cell membranes, and water desalination have emerged [18, 19, 45, 55, 85–88]. The use of sulfonated block copolymers as semipermeable layers in protective clothing applications for chemical warfare has been studied in academic and military labs. The sulfonated blocks allow for water to permeate through the membrane while potentially reducing the flow of chemical warfare agents [85, 86, 89]. Similar to other applications, the use of block copolymers allows one to control the morphology of the membranes by controlling the casting conditions. For example, sulfonated styrene-isobutylene-styrene (S*i*BS, described later in this chapter) block copolymer can be cast into spherical, cylindrical, and lamellar morphologies. However, once the highly sulfonated membranes came into contact with water, the sulfonated blocks swelled to such an extent that the cast membrane morphology was destroyed. Partially cross-linking the sulfonated domains can partly remedy this effect while reducing the overall swelling [89]. The addition of calcium and cesium cations has been shown to reduce swelling in water and the permeation of water and dimethylmethylphosphonate, a mimic for S-[2-(diisopropylamino)ethyl]-O-ethyl methyl phosphonothionate (VX) gas, in sulfonated block copolymer membrane systems.

These applications, as well as those in fuel cells and water treatment, take advantage of the self-assembly of the sulfonated block copolymers. The excessive swelling issue can be partially overcome with proper molecular design. Given the ability to precisely control molecular structure (Chapter 7), one can design a molecule that has a reduced propensity to swell. Kraton Polymers has designed such a molecule by placing the sulfonated block in the center of a multiblock copolymer anchored by nonsulfonated *t*-butyl styrene blocks [19, 45, 90]. For example, the previously mentioned sulfonated S*i*BS at an ion exchange capacity of 2 mmol of acid per gram of polymer swells over 300 wt% when placed in deionized water [85]. Conversely, a molecule of the same ion exchange capacity with *t*-butyl styrene endblocks and a sulfonated midblock swells as little as 25% depending on casting conditions [87].

Figure 10.15 shows transmission electron micrographs of a sulfonated block copolymer with a sulfonated center block and *t*-butyl styrene endblocks [19, 45, 87, 90]. The top micrograph shows the styrenic (various shades of gray) phases of the polymer as it was stained with RuO_4. The middle micrograph is of the same polymer but stained with lead acetate. Lead acetate stains only the sulfonated phase of the block copolymer. In this example, the sulfonated phase is lamellar, approximately 25 nm wide, and continuous in the size scale of the micrograph. By changing the polarity of the casting solvent, one can change the morphology of the cast membrane as shown in the bottom micrograph in Figure 10.15. This sample, again stained with lead acetate, shows a disordered cylindrical morphology in the sulfonated phase with the cylinders having a diameter of approximately 25 nm. Changing the phase structure has been shown to change the transport properties of the sulfonated polymer membranes for protons and the rejection of salts in desalination applications [85–87].

10.10.4
Methacrylate and Acrylate Block Copolymers by Anionic Polymerization

Modified versions of anionic polymerization are predicted to produce commercial volumes of new materials in the near future. A pilot plant was recently built to produce styrene-*b*-butadiene-*b*-methyl methacrylate and styrene-*b*-butadiene-*b*-(methyl methacrylate-*r*-*t*-butyl methacrylate) triblock copolymers. They have focused their internal and sponsored research on the

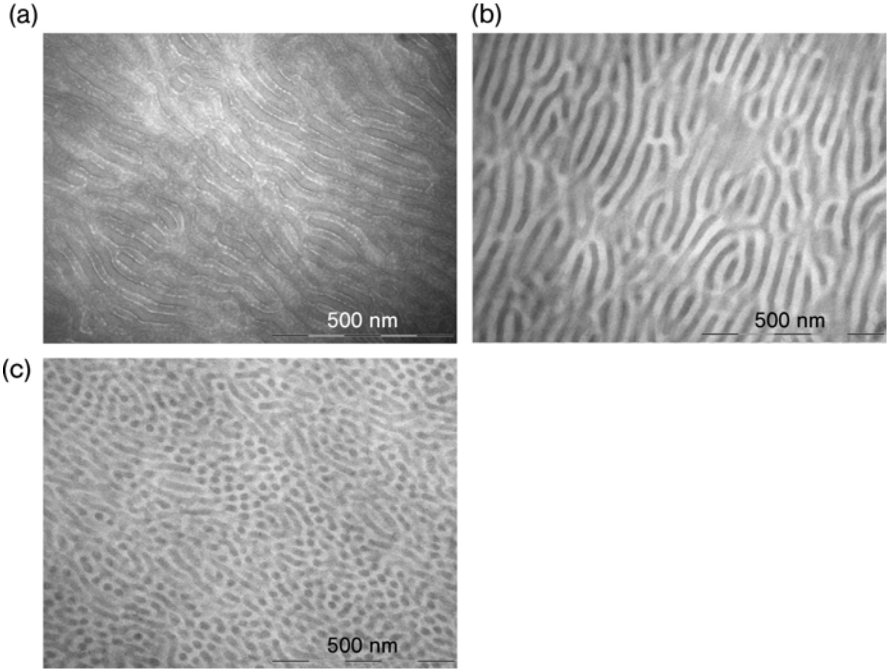


Figure 10.15 TEM micrographs of sulfonated block copolymers synthesized as described in Ref. [19]. (a) RuO_4 stained, (b) same polymer stained with lead acetate, and (c) lead acetate stained polymer cast from a more polar solution. The entire scale bar is 500 nm, black line is 100 nm [18, 87, 88, 91].

use of the triblocks as tougheners for both thermoplastic and thermosetting systems [92–97]. Examples include the toughening of PPE, an application that currently uses traditional SBC, and the toughening of poly(vinylidene fluoride) (PVDF) and PVC which are not efficiently toughened with traditional SBCs. The polar block of the S-B-MMA provides increased compatibility with PVC and PVDF. An interesting possibility of the S-B-MMA-modified PVDF polymers is the ability to fabricate toughened electrically conductive polymers with the addition of electrically conductive materials such as graphite, carbon black, carbon nanotubes, or carbon fibers [94].

The S-B-MMA, S-B-MMA/*t*BMA, and the hydrolyzed version of S-B-MMA/*t*BMA (S-B-MMA/methacrylic acid) triblocks have also been studied as tougheners for epoxy systems. The triblocks have been shown to effectively toughen epoxy systems based on the diglycidyl ether of bisphenol-A and various amine hardeners. While typical SBCs phase-separate out from the epoxies during curing (a phenomena that can be reduced with the use of anhydride functionalized SBCs), methacrylic acid dispersed in the methyl methacrylate (MMA) block of the polymers react quickly with the oxirane rings in the epoxies [93, 95–97]. Similar telechelic polyacrylates are being developed for various advanced applications via atom transfer radical polymerization (ATRP) methodologies (Chapter 3) [98].

Another pilot plant has been recently built to produce methacrylate and acrylate block copolymers using lithium aluminum alkyls to modify anionic polymerization to produce MMA-*n*BA-MMA triblock copolymers where *n*BA is *n*-butyl acrylate block [99–101]. Since the entanglement molecular weight of the *n*BA block is much higher than that of either polyisoprene or polybutadiene, the MMA-*n*BA-MMA block copolymers are softer and have lower tensile strengths than their analogous SIS and SBS (Figures 10.16 and 10.17) [102–104]. While the methacrylate-acrylate block copolymers may be weaker than their SBC counterparts, there is considerable interest in these polymers as PSAs, where the higher tensile strengths of SIS and SBS are not necessarily needed [100, 105]. There are a few other advantages to the methacrylate-acrylate block

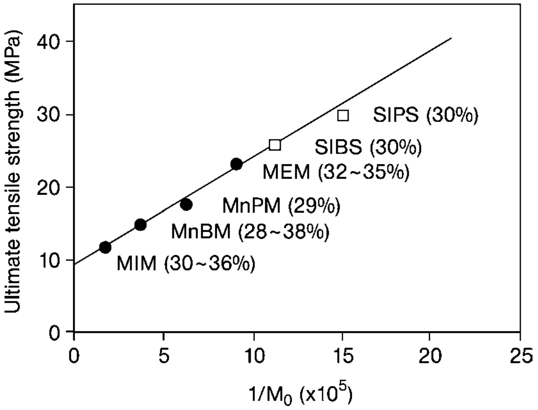


Figure 10.16 Effect of ultimate tensile strength as a function the molecular weight between entanglements, M_e [103].

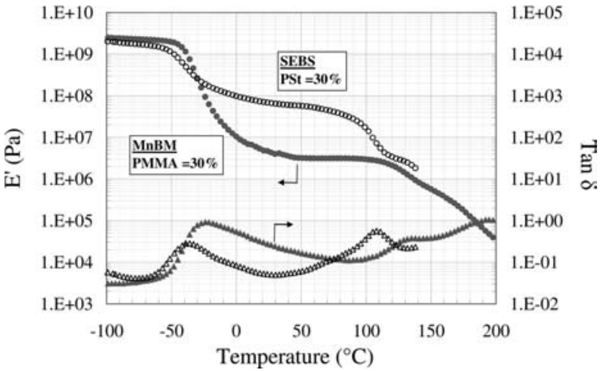


Figure 10.17 Dynamic Mechanical Analysis (DMA) of SEBS and MMA-*n*BA-MMA block copolymers [100].

copolymers including a slightly higher use temperature range due to the higher T_g of MMA vs. styrene (Figure 10.17). Also, unlike SBS and SIS, the MMA-nBA-MMA block copolymers are completely saturated and are thus more resistant to UV and oxidative degradation.

10.10.5
Styrene-Isobutylene-Styrene (SiBS) via Cationic Polymerization

While traditional SBCs are suitable for some packaging and sealant applications, they are often overlooked or found unsuitable for applications requiring low gas permeability. This is largely due to the inherent high diffusivity of gaseous molecules through the midblock which is only exacerbated upon addition of oil. SBCs with a midblock based on isobutylene rubber were developed at the turn of the twenty-first century [106]. These saturated S*i*BS block copolymers are unconventional, as they are polymerized via living cationic polymerization as described in Chapter 2. The synthetic strategy involves a living cationic polymerization initiated with a difunctional initiator making the polyisobutylene center block, followed by a PS end-capping reaction [107]. Performance of S*i*BS compounds have been compared to those based on the more traditional SEBS and SEPS copolymers. S*i*BS compounds typically exhibit lower hardness, lower gas permeability, and improved vibration damping performance and are expected to be suitable for gaskets, seals, and vibration-attenuating applications. In addition, they offer the formulator an opportunity to use no oil or significantly less oil than traditional SEBS polymers to reach the same compound hardness because of the inherent softness of the isobutylene midblock [107]. S*i*BS copolymers have also been evaluated in blends with Thermoplastic Urethans (TPU) to provide enhanced barrier properties and vibration-dampening characteristics for overmolding applications [108].

10.10.6
Commercial Uses of Other Controlled Polymerized Polymers

With the growing complexity of advanced technology, the demand for specifically tailored polymers for individual applications has dramatically increased. Traditionally, anionic polymerization methodologies offer the ability to accurately control the monomer composition and the resulting polymer architecture [109–111]. However, the reactive nature of the anionic propagating species renders it incompatible with many monomer families including most methacrylates or acrylates. This incompatibility necessitates specialty initiators or additives for polymerization. Controlled free-radical, carbocationic, ring-opening of heterocycles, coordination of olefins, and ring-opening metathesis polymerization methodologies, all described in Chapters 2–6 of this work, have all recently emerged in academic and industrial research as complementary methodologies to anionic polymerization [112–125]. Specialized applications such as the use of block copolymer as lithographic templates have greatly benefited from a combination of these techniques [126–130]. Although they newer controlled polymerization methodologies provide a vast array of possibilities, they have been slow to find wide-ranging commercial applications partially because of restrictive manufacturing hurdles such as the need for high monomer concentration, relatively slow reaction rates, removal of residual monomer or initiator, and initiator costs, all of which can lead to high production costs.

An ATRP (Chapter 3) process to produce block and comb copolymers, which are used as dispersants for pigments, has recently been commercialized [131–134]. Researchers found that the addition of salt-forming components, such as mono-, bi-, or tricyclic sulphonic, carboxylic, and phosphonic acids, to polymers containing amino groups as repeat units in a hydrophilic polymer block produces pigment dispersions having improved properties. Additional applications are emerging in the fields of lubrication additives (similar to the use of SEP block copolymers) and weather-resistant coatings [135].

Initiators and macroinitiators for nitroxide-mediated polymerization have also recently entered the market under the trade name BlocBuilder, which was first commercialized in 2005 [136, 137]. The alkoxyamine utilized in the BlocBuilder technology (3,7-dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2,2-dimethyl-, 6-oxide) cleaves as low as 35 °C in solution, which provides the possibility to initiate polymerization from 45 to 125 °C. Along with the initiating unit, a macroinitiator capped with the alkoxyamine for use in the synthesis of block copolymers.

It is important to note that, from the introduction in 1965 of SBCs, it took 20 years to reach 100 million kg (220 million lbs) per year. This is common for the development of a complex technology that creates significant change. As one is evaluating the emerging technologies in this work, it is helpful to remember that while many have existed for some time, their applications are still developing much as SIS and SBS were developing in the 1960s.

List of Abbreviations

ABS	acrylonitrile butadiene styrene copolymer
ATRP	atom transfer radical polymerization
C^*	overlap concentration between the semidilute and dilute region of the polymer in the oil
CEPC	cyclohexane-ethylene propylene-cyclohexane block copolymer
EP	ethylene-propylene polymer from hydrogenated polyisoprene
EPDM	poly(ethylene-propylene-diene monomer)
EVA	poly(ethylene vinyl acetate)

G'	dynamic loss modulus
G''	shear storage modulus
GR-S	US government's synthetic rubber
HALS	hindered amine light stabilizers
HDPE	high-density polyethylene
IPN	interpenetrating network
L/D	screw length to diameter ratio
LDPE	low-density polyethylene
MMA-*n*BA-MMA	methyl methacrylate-*n*-butyl acrylate- methyl methacrylate block copolymer
OBO	oil bleed out
ODT	order–disorder-transition temperature
PC	polycarbonate
PBT	poly(butylene terephthalate)
PE	polyethylene
PET	poly(ethylene terephthalate)
phr	parts per hundred rubber
PP	polypropylene
PPE	poly(phenylene ether) often referred to as *poly(phenylene oxide)*
PSA	pressure-sensitive adhesive
PSC	polystyrene content
PVC	poly(vinyl chloride)
PVDF	poly(vinylidene fluoride)
SBC	styrenic block copolymer
S-B-MMA	styrene-butadiene-methyl methacrylate block copolymer
S-B-MMA/*t*BMA	styrene-butadiene-methyl methacrylate/*t*-butyl methacrylate block copolymer
S-B-*t*BMA	styrene-butadiene-*t*-butyl methacrylate block copolymer
SBR	styrene-butadiene rubber
SBS	styrene-butadiene-styrene block copolymer
SEBS	styrene-ethylene/butylene-styrene block copolymer
SE/EPS	styrene-ethylene/ethylene-propylene-styrene block copolymer
SEP	styrene-ethylene/propylene block copolymer
SEPS	styrene-ethylene/propylene-styrene block copolymer
S*i*BS	styrene-isobutylene-styrene
SIS	styrene-isoprene-styrene block copolymer
SMC	polyester sheet molding compound
SMMA	styrene/methyl methacrylate copolymer
T_g	glass transition temperature
TPEs	thermoplastic elastomers
TPVs	thermoplastic vulcanizates
VII	viscosity index improver

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Controlled and Living Polymerizations. Edited by Axel H.E. Müller and Krzysztof Matyjaszewski

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Written by a highly prestigious and knowledgeable team of top scientists in the field, this book provides an overview of the current status of controlled/living polymerization, combining the synthetic, mechanistic and application-oriented aspects.

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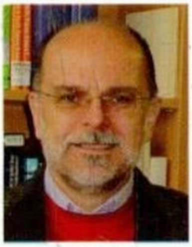

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