



Université catholique de Louvain
Faculté des Sciences
Département de Chimie

Metallo-Supramolecular Block Copolymers: From Synthesis to Smart Nanomaterials

Pierre Guillet

Promoteur: Professeur J.-F. Gohy

Dissertation présentée en vue de l'obtention
du grade de Docteur en Sciences

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Membres du jury:

Prof. J.-F. Gohy, promoteur
Prof. O. Riant
Prof. S. Demoustier-Champagne
Prof. U.S. Schubert
Prof. S. Lecommandoux
Prof. J. Marchand-Brynaert, présidente

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A mes parents,

ACKNOWLEDGMENTS

Quand vient l'heure des remerciements, il convient de faire le vide autour de soi. Contrairement à l'idée d'un roman où l'auteur s'isole pour imaginer ou raconter une histoire, la thèse est un recueil de résultats obtenus au sein d'une équipe. Et même si le jour de la soutenance, il est de tradition de féliciter le lauréat, il ne faut pas oublier pour autant l'ensemble des personnes qui ont permis à ce dernier de se tenir là devant eux.

Ainsi, il est de mon devoir de souligner à juste titre ma reconnaissance envers toutes ceux qui m'ont accompagné de près ou de loin à l'accomplissement de ce travail. En premier lieu, naturellement, celui qui est à la genèse de ce projet, le Professeur J.-F. Gohy: il a été le premier à me faire confiance en me proposant ce sujet de thèse. Toujours disponible et attentif, il m'a parfaitement encadré tout au long de ces quatre dernières années. Mais l'attention et la disponibilité ne faisant pas tout, il m'a aussi parfaitement intégré dans sa nouvelle équipe, me confiant rapidement le soin d'encadrer des stagiaires et de faire un stage à l'étranger pour développer mes connaissances en synthèse organique. Il m'a offert l'opportunité de présenter mes travaux de recherches au sein de différents congrès en Belgique mais aussi à l'étranger (Suisse, Autriche, USA) et de participer à différentes collaborations scientifiques. Et quand la science et le chercheur venaient à montrer leurs limites, il était toujours là pour m'insuffler de nouvelles et brillantes idées. Enfin, je terminerai ces quelques lignes d'admiration et de gratitude à mon cher Professeur en le remerciant pour m'avoir si bien transmis sa passion pour la recherche scientifique; grâce à lui, je me sens prêt aujourd'hui à relever un tel défi.

La deuxième personne que je tiens à remercier aussi chaleureusement est le Professeur C.-A. Fustin. En effet, bien que son nom ne figure pas sur la première page de ce manuscrit, il s'est pleinement impliqué dans ces travaux de recherches. Sa rigueur, son écoute, sa disponibilité, sa très grande connaissance scientifique m'ont été indispensables tout au long de ces quatre dernières années. Sa très grande complémentarité avec le Professeur J.-F. Gohy a été décisive quant à la réussite de mon projet scientifique. Travailler à ses côtés a été une véritable chance et je ne tarirai jamais suffisamment de reconnaissance

à son égard.

Pour terminer cette première salve de remerciements, je tiens aussi à exprimer toute ma gratitude au Professeur J. Marchand-Brynaert qui a accepté de nouveau avec enthousiasme d'être présidente de mon jury. Elle est, et restera toujours, la présidente de cœur de tous les chimistes de l'UCL. Je remercie également le Professeur O. Riant, qui, au-delà de sa mission de juger ce travail et le candidat, a toujours su se montrer disponible pour répondre et résoudre les subtilités de la synthèse organique que j'ai pu rencontrer. Enfin, j'exprime toute ma reconnaissance au Professeur S. Demoustier-Champagne qui a aussi apporté sa contribution à l'amélioration de ce manuscrit par ses remarques déterminantes et son sourire omniprésent.

At last but not least, I would like to acknowledge Professor U.S. Schubert and Professor S. Lecommandoux for reading this thesis as members of the commission. Furthermore, I especially thank Prof. U.S. Schubert for welcoming me in his research group during one month to learn with Dr. B.G.G. Lohmeijer the basis of metallo-supramolecular chemistry and for the several fruitful collaborations resulting in joined publications.

Moreover, I would like to stress the importance of people who participated directly or indirectly to the building of this thesis. The first, Dr. B.G.G. Lohmeijer for leaving me with a promising but quite tricky task: the synthesis of metallo-supramolecular heteroleptic copolymers. I would like also to thank Dr. D. Wouters and Dr. S. Hoepfner for helping me with cryo-TEM measurements. I would also express my gratitude to C. Ott and Dr. M. Meier for fruitful discussions and collaborations. Furthermore, I would like to offer my most sincere thanks to Professor P. Du Prez for giving me the opportunity to perform some preparative GPC in his laboratory with the kindly help of B. Dervaux and Dr. W. Van Camp. During the last year of this PhD-thesis, I was also delighted to collaborate with Professor C. Bailly and Dr. F. Stadler for the rheological characterizations of the supramolecular gels. Finally, I would like to shed lights on the nice collaboration with Dr. G. Heunen and D. Rousseaux which has offered me the possibility to study the diffraction at small angles at the synchrotron radiation facility in Grenoble.

Après ce petit interlude en anglais, je reviens à cette chère langue de Molière pour saluer l'ensemble des personnes qui ont participé à l'aboutissement de ce projet. Je commencerai ces quelques lignes avec les différents membres du laboratoire que j'ai eu la chance de côtoyer. Et par ordre chronologique (pour qu'il n'y ait pas de jaloux), le Dr. M. Filali et le Dr. Z. Hu, premiers stagiaires post-doctorat, qui m'ont assisté dans mes débuts au laboratoire. Sont arrivés ensuite très rapidement, les premiers mémorants, N. Lefèvre et C. Colard. J'ai eu l'occasion d'assister cette dernière dans la réalisation de son stage, et je la remercie de m'avoir supporté pendant un an. C'est ensuite avec brio que N. Lefèvre a réussi l'examen du FRIA et qu'elle liait sa destinée à celle du laboratoire pour les quatre prochaines années. Je n'étais plus le seul doctorant et c'est avec plaisir que j'accueillais une touche de féminité dans le bureau. J'oubliais

en effet de vous mentionner les visites ponctuelles d'un certain doctorant Moldave, A. Vlad: pauses "clopes" à répétition, café, bières, click-click...bref une ambiance, dans laquelle il était bien souvent difficile de se concentrer! Heureusement, cela ne masquait en rien ses nombreuses qualités, que je ne décrirai pas ici par souci de concision.

Ensuite, le bureau s'est agrandi pour accueillir un troisième doctorant, qui venait à son tour de réussir brillamment au FRIA, J.M. Schumers. Quand un vilain chimiste organicien décide de rejoindre le monde fabuleux des polymères, la transition peut paraître brutale, mais c'était sans compter mon humour un peu spécial. Grâce à un très fort charisme, il a su rapidement surmonter les quelques embûches que je lui glissais pernicieusement, et aujourd'hui je souhaite le remercier pour ne m'en avoir pas trop tenu rigueur. Sa présence m'a transcendé, m'obligeant à dépasser mes limites, à travailler plus (pour gagner plus...), pour, un jour peut-être, pouvoir enfin lui ressembler (sauf à la piscine...).

Je remercie également H. Chihi et K. Khayari, deux stagiaires de l'Institut Paul Lambin que j'ai eu le plaisir d'encadrer et qui m'ont bien aidé au laboratoire. C'est avec plaisir, que j'ajoute à cette énumération non exhaustive C. D'Haese-Bomal pour son aide ponctuelle mais toujours décisive. Ce sont les petits détails qui font la différence et je remercie Cécile d'avoir su se montrer toujours disponible. Pour m'avoir aidé à résoudre les subtilités administratives qui se dressent, par exemple, devant le vilain petit Français en territoire Belge, je remercie vivement C. Dubois, J. Boniver et C. Delaet.

Enfin, dans les personnes qui ont compté dans l'aboutissement de ce travail, je tiens à souligner l'importance du dernier arrivé au laboratoire, C. Mugemana. Venu comme mémorant pour son stage de fin d'études, j'ai vécu le grand privilège de pouvoir travailler à ses côtés. Son sourire, sa nonchalance et sa détermination ont été autant d'atouts pour mieux m'aider à surmonter le stress de la dernière année. Aujourd'hui, il est doctorant et je n'aurais pas su espérer une plus belle relève.

Les dernières lignes sont réservées traditionnellement à la famille en général pour son soutien, ses encouragements et toutes ces petites choses qui font que l'on écrit un jour ces lignes...sans oublier évidemment le cercle très privé avec Urco des Plots, Doudoune, le(s) poisson(s) et Nathalie.

Merci.

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ABBREVIATIONS

AFM	atomic force microscopy
ATRP	atom transfer radical polymerization
BCC	body cubic centered
CGC	critical gel concentration
CMC	critical micellar concentration
CMT	critical micellar temperature
DLS	dynamic light scattering
DMA	<i>N,N</i> -dimethylacetamide
DMAEA	2-(dimethylamino)ethyl acrylate
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
DP	degree of polymerization
DSC	differential scanning calorimetry
EtOx	2-ethyl-2-oxazoline
FCC	face cubic centered
GPC	gel permeation chromatography
HEEDTA	hydroxyethyl ethylene-diaminetriacetic acid sodium salt
HEX	hexagonally packed cylinders
ISL	intermediate segregation limit
LAM	lamellae
LCST	lower critical solution temperature
MLAM	modulated lamellae
MLC	metal ligand complexes
MLCT	metal to ligand charge transfer
NMP	nitroxide mediated polymerization
NMR	nuclear magnetic resonance
ODT	order-disorder transition

P2VP	poly(2-vinylpyridine)
P4VP	poly(4-vinylpyridine)
PCL	poly(ϵ -caprolactone)
PDI	poly(dispersity) index
PDMAEA	poly(2-(dimethylamino)ethyl acrylate)
PEB	poly(ethylene-butene)
PEG	poly(ethylene glycol)
PEO	poly(ethylene oxide)
PFS	poly(ferrocenyldimethyl-silane)
PhOx	2-phenyl-2-oxazoline
PI	poly(isoprene)
PLA	poly(lactide)
PLAM	perforated lamellae
PMMA	poly(methyl methacrylate)
PNIPAM	poly(<i>N</i> -isopropyl acrylamide)
PS	poly(styrene)
PSS	poly(styrene sulfonate)
PtBA	poly(<i>tert</i> -butylacrylate)
RAFT	reversible addition fragmentation chain transfer
ROP	ring opening polymerization
SANS	small angle neutron scattering
SAXS	small angle X-ray scattering
SCE	saturated calomel electrode
SFM	scanning force microscopy
SLS	static light scattering
SN	nucleophilic substitution
SS	styrene sulfonate
SSL	strong segregation limit
TEM	transmission electronic microscopy
THF	tetrahydrofuran
TLC	thin layer chromatography
UnOx	2-undecyl-2-oxazoline
WAXS	wide angle X-ray scattering
WSL	weak segregation limit
XPS	X-ray photoelectron spectroscopy

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INTRODUCTION

Abstract

Block copolymers form a large number of structures with characteristic dimensions in the range of a few nanometers up to several micrometers by self-organization. They can be used to produce in a controlled way a wide range of nano and microstructured materials such as nanoparticles, nanoporous materials and drug carriers. On the other hand, supramolecular copolymers have become of increasing interest in recent years for the search of new materials with tunable properties. In particular, metallo-supramolecular block copolymers have seen important progresses, allowing better control over the synthetic strategies for various architectures, and providing a better understanding of the parameters governing their self-assembly properties. This introduction is devoted to recent developments on the synthesis and self-assembly of such materials.

1.1 A few words about block copolymers

This thesis deals with polymers (especially block copolymers) and micelles. A polymer is a long molecule consisting of tenths to thousands of repeating units, called monomers. A homopolymer has only one type of repeating unit, a copolymer several. Block copolymers can have several architectures or topologies, e.g., linear, grafted, branched, or star-shaped (see Fig 1.1).

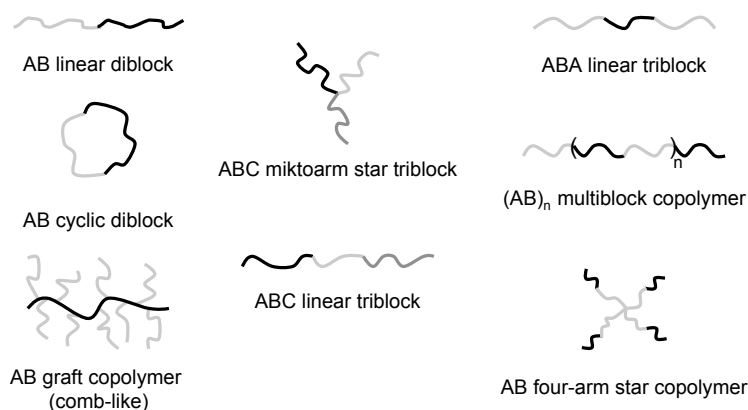


Figure 1.1: Typical architectures of block copolymers.

Block copolymers are made up of blocks of different polymerized monomers. The simplest block copolymer, a diblock copolymer, consists of two chemically bonded homopolymers blocks. For example, PS-*b*-PEO is an acronym form of poly(styrene)-*b*-poly(ethylene oxide) and is made by first polymerizing styrene, and then subsequently polymerizing ethylene oxide from the reactive end of the poly(styrene) chains. This polymer is a “diblock copolymer” because it contains two chemically different blocks. More than two chemically different blocks can be also present in a block copolymer leading to ABC triblock terpolymers, tetrablocks, multiblocks, etc (see Fig 1.1). Diblock or triblock copolymers are essentially made using living cationic or living anionic polymerization techniques, which ensure a narrow molecular weight distribution. Controlled radical polymerization such as atom transfer radical polymerization (ATRP),

reversible addition fragmentation chain transfer (RAFT) and nitroxide mediated polymerization (NMP) can be also employed.

The field of block copolymers seems to be almost limitless since they can be designed as promising materials for numerous applications. For instance, they are widely used industrially in the solid and rubbery states as well as in solution. In the former case, they are used as thermoplastic elastomers, with applications such as impact modification and compatibilization, whereas in the latter case they are exploited for their surfactant properties. A lot of books [1–3] or reviews [4–9] are devoted to this field.

1.2 Highlights on the self-assembly properties

By just joining polymer chains together, researchers have access to a nanoscale organization of polymers leading to new structures with defined physical and chemical properties. Due to the inherent immiscibility of the majority of polymer blocks, phase separation is usually observed in block copolymers. Because the polymer blocks are tethered to each others, macroscopic phase separation cannot occur and a structural organization appears with domain periodicities in the range of the nanometer, either in the melt, bulk state or in solution. Therefore, a large range of nanosized structures can be obtained from block copolymers (see Fig 1.2).

1.2.1 In solution

Micellization and gelation are the two basic processes that characterize the phase behavior of block copolymers in solution. Micellization occurs due to the microscopic separation of the polymer blocks in a selective solvent in dilute solution. A selective solvent is designed as a thermodynamical good solvent for one block and a precipitant for the other one. In such a solvent, the copolymer chains may associate reversibly to form micellar aggregates with a core formed by the insoluble or poorly solvated block, while the corona contains the selectively solvated block. Therefore, those micelles are generally formed from the self-assembly of amphiphilic block copolymers (from Greek, *amphi*: both *philic*: attraction). Although micellization of amphiphilic block copoly-

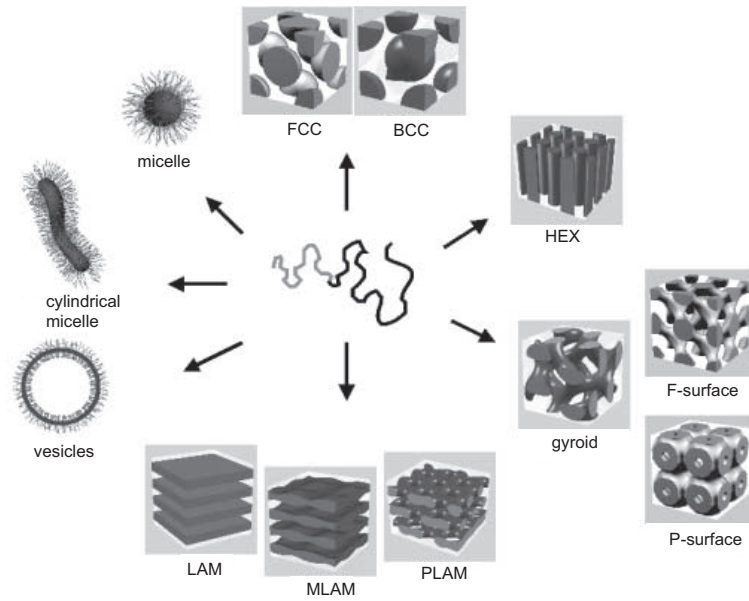


Figure 1.2: Typical self-organized structures obtained from block copolymers: spherical micelles, cylindrical micelles, vesicles, fcc- and bcc-packed spheres (FCC, BCC), hexagonally packed cylinders (HEX), various minimal surfaces (gyroid, F surface, P surface), simple lamellae (LAM), as well as modulated and perforated lamellae (MLAM, PLAM). From Ref. [10].

mers is generally considered in water, it is not limited to aqueous media and can be also conducted in organic solvents. A schematic view of a block copolymer micelle is reproduced in Figure 1.3.

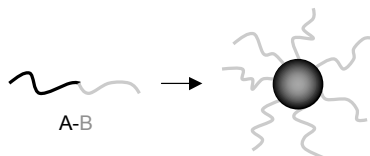


Figure 1.3: Schematic representation of a micelle formed in a selective solvent for the B block.

Since block copolymers mimic low molecular weight surfactants, their behavior is quite similar to the latter ones. At a fixed temperature, the first micelle forms above a concentration 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 non-associated block copolymer 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 phenomenologically the CMC as the concentration at which a sufficient number of micelles is formed to be detected by a given method and not as a thermodynamic property of the system [11]. For instance, fluorescence probe techniques have been successfully applied to determine the micelle characteristic of the investigated system using e.g. pyrene as a fluorescence dye [12–14].

The second parameter of interest is the critical micellar temperature (CMT). At a fixed concentration, micellization can occur above or below the CMT depending on whether the self-assembly process is endothermic or exothermic respectively. Finally, the micellization process is designed as a closed-association assembly, leading to a dynamic equilibrium between micelles with a narrow molar mass and size distribution and free copolymer chains (unimers). However, for a micelle with a glassy core, i.e. with a glass transition temperature of the core-constituting block

that is sufficiently high, e.g. poly(styrene), the structure is “kinetically frozen” and may not represent the thermodynamic equilibrium. Theories for dilute block copolymer solutions have been established since the seventies, including both scaling models and mean-field theories [15–21]. They offered us the possibility to design materials with the desired characteristics. More details about the classification of micelles can be found in Section 4.2.

At higher concentrations, the micelles can order onto a lattice above a critical gel concentration (CGC). Soft and hard gels are distinguished from each other, and from micellar solutions, since they are characterized by a finite yield stress. The notation “hard-gel” follows Hvidt et al. [22,23] and refers to a micellar solution with a dynamic elastic shear modulus $G' \gtrsim 10^3 \text{ Pa}$. Figure 1.4 summarizes the different previously described regimes.

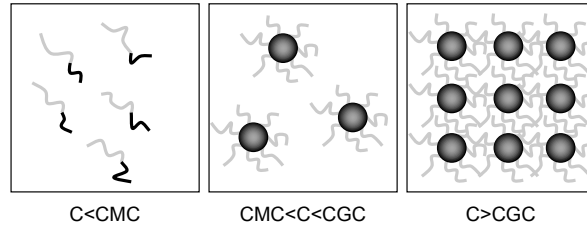


Figure 1.4: Illustration of the critical micelle concentration (CMC) and critical gel concentration (CGC) in a block copolymer solution. From Ref. [2].

1.2.2 In bulk

In bulk, block copolymers are generally observed in a microphase-separated state. A large variety of copolymer morphologies including lamellae (LAM), hexagonally ordered cylinders (HEX), arrays of spherical microdomains (BCC, FCC), modulated (MLAM) and perforated layers (PLAM), and ordered bicontinuous structures such as the gyroid have been studied extensively from both experimental and theoretical point of view over the past decades (see Fig 1.2) [24–27]. In bulk AB diblock copolymers, the phase behavior is determined by a combination of the translational entropy of the chains and the enthalpic interactions between the A and B constituents. In fact, thermodynamic incompatibility between the A and B blocks drives a collection of AB-diblock molecules to self-organize in microphase separated microstructures in which the contacts between similar and dissimilar blocks are maximized and minimized, respectively. Macrophase separation is thus prevented by the covalent bond holding the A and B blocks together.

For AB-diblock copolymers the basic parameters that determine the pattern characteristics are the degree of polymerization $N = N_A + N_B$, the volume fractions of the constituent blocks (f_A and f_B , $f_A = 1 - f_B$), and the Flory-Huggins interaction parameter χ_{AB} . The enthalpy of the system is related to χ_{AB} which is found to be inversely proportional to temperature ($\chi \sim 1/T$). The value χN that expresses the enthalpic-entropic balance is then used to determine the degree of microphase separation. On the other hand, the volume fraction of one component, f , determines which ordered structures are accessed below the ordered-disordered transition (ODT). Depending on χN , three different regimes are distinguished:

- i the weak-segregation limit (WSL) for $\chi N < 10$;
- ii the intermediate segregation region (ISR) for $10 < \chi N \leq 50$;
- iii the strong segregation limit (SSL) for $\chi N \rightarrow \infty$.

Most of the experimental work on the phase behavior of diblock copolymers has been performed in the SSL. The bulk morphologies can be mapped into a phase diagram parameterized in terms of χN versus

f. These phase diagrams give an excellent overview of the types of morphologies that are available for the construction of the ordered materials described above. An example of such phase diagram is shown in Figure 1.5 for poly(styrene-*b*-isoprene) (PS-*b*-PI), a system that has been thoroughly investigated [28,29]. The microphase morphology is strongly influenced by the copolymer composition. For example, diblock copolymers having blocks of comparable volume exhibit a lamellar morphology. Increasing the degree of compositional asymmetry leads to the gyroid, cylindrical, and finally, spherical phases.

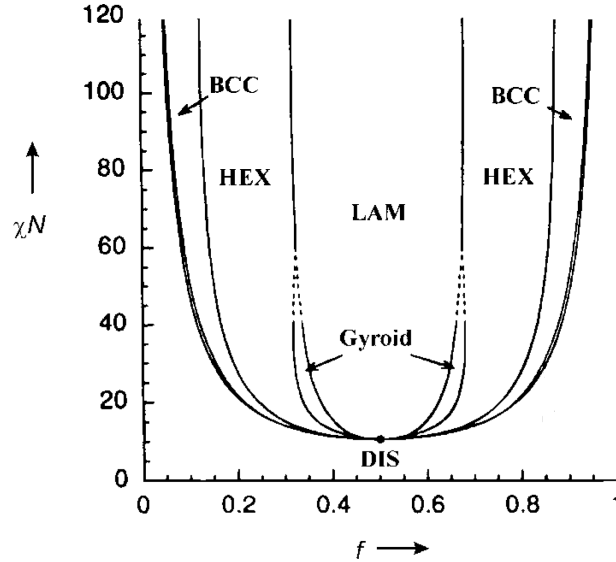


Figure 1.5: χN versus f phase diagram for poly(isoprene-*b*-styrene) diblock copolymers. Five different ordered microstructures (LAM, HEX, BCC, gyroid) are observed. From Ref. [30].

In the strong segregation limit (SSL) at larger values of χN it is commonly assumed that only the “classical” morphologies LAM, HEX, and BCC are stable. Moreover, the periodic length scale of the morphologies can be adjusted over the whole mesoscopic range (from a few up to several hundred nanometers) by simply varying the degree of polymerization. Finally, by using the phase diagrams one can specifically adjust the morphology of these structures through the choice of block

lengths and polymer composition leading to tailor-made nanostructured materials.

1.2.3 Thin films

In thin films, in addition to composition and molecular weight, the final morphology is also dependent on the surface energies of the blocks and on geometrical constraints induced by the confinement in a thin film. A well-documented review from Fasolka and Mayes sheds light on the physics underpinning structure formation in block copolymer films [31]. They highlight the enhanced role of surface/interfacial energetics, as well as the interplay between the copolymer characteristic length scale and the film thickness itself as the main features governing the final film structure. Indeed, the more the thickness of the film decreases, the more these effects become increasingly consequential. In contrast to block copolymer bulk morphologies, block copolymer thin films are often characterized by highly oriented domains as a direct result of surface and interfacial energy minimization [32–34]. In thin films, the lamellae formed by symmetric block copolymers can orient either parallel or perpendicular to the substrate. The component with the lower surface energy typically resides at the free surface. If the other component resides at the substrate then the lamellae generally orient normal to the substrate. On our application point of view, the cylindrical morphology is of particular interest since it can be transformed into an array of nanopores after elimination of the minor component [35, 36]

Block copolymer thin films are usually prepared by the spin coating technique, where drops of a solution of the polymer are deposited onto a spinning solid substrate (often silicon wafers are used due to their uniform flatness). The polymer film spreads by centrifugal forces, and the volatile solvent is rapidly driven off. The film thickness can be controlled through the spin speed, the concentration of the block copolymer solution or the volatility of the solvent [37]. Dip-coating is another reliable method for fabricating uniform thin films [38]. One can notice also recently the emergence of a new thin film depositing technique based on drop casting, ink-jet printing, that offers a new control over the general properties [39, 40]. Whatever the deposition technique, if the surface

energy of the block copolymer is much greater than that of the substrate, then dewetting will occur [41–43]. This latter point can be easily circumvented with an appropriate choice of the substrate.

1.3 Towards the formation of nanostructured devices

The fabrication of systems having characteristic dimensions smaller than 100 nm requires the ability to obtain, control and modify structure at the nanometer scale. Block copolymers represent promising nanoscale tools since their morphologies are rather well-defined, i.e., show long-range order, and their characteristic size is related to the dimensions of the constituent polymer blocks and can be predetermined in a systematic fashion between 10 and 250 nm both in bulk and in solution. All these breakthroughs have been learned from Nature which uses self-assembly processes to create nanometer-sized functional nanomaterials such as proteins and enzymes.

Top-down and bottom-up approaches can be used for assembling nanoscale materials and devices. Bottom-up approaches seek to have smaller (usually molecular) components that arrange themselves into more complex assemblies, while top-down approaches seek to create nanoscale devices by using larger, externally-controlled ones to direct their assembly (Figure 1.6).

The bottom-up strategy is based upon the stepwise synthesis of ordered structures with the help of self-organization processes. In contrast, top-down strategies often use the traditional workshop or microfabrication methods such as photolithography and ink-jet printing based on down-sizing technologies. The possible chemical modifications of self-assembly structures as a starting point for the synthesis of advanced materials are numerous, e.g., degradation of one microphase would result in ordered porous materials and crosslinking of one of the components leads to colloidal structures. In this thesis, bottom-up strategies will be only considered.

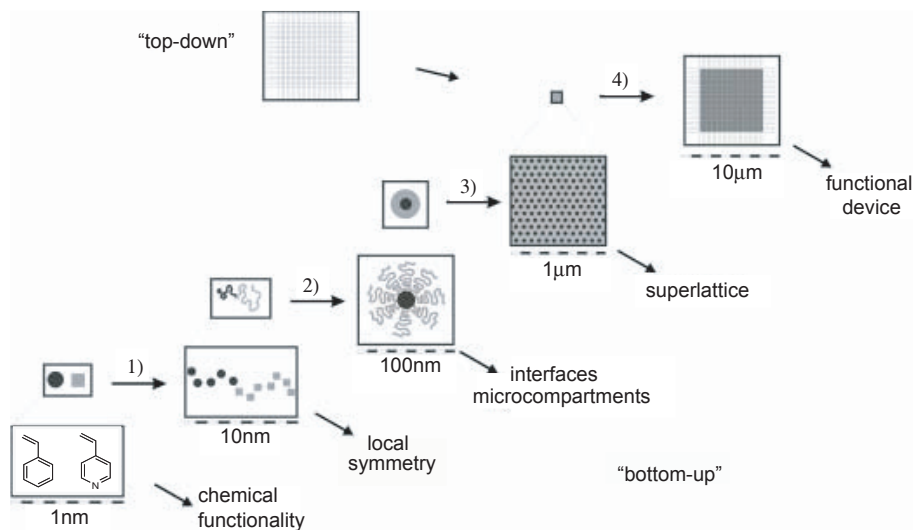


Figure 1.6: Bottom-up versus top-down strategy. Reproduced from Ref. [10]

1.4 Metallo-supramolecular block copolymers

1.4.1 Introduction

In the past twenty years, since the Nobel prize of Lehn, Pedersen and Cram, supramolecular chemistry has become increasingly important, and is now a major field in chemical research. Self-recognition and self-assembly are the two pillars on which supramolecular chemistry is based, involving mainly interactions of non-covalent nature (van der Waals, hydrogen bonding, coordinative interactions...). The large range of interaction strength, directionality, and reversibility offered by these interactions (cf. Table 1.1) allows unprecedented control over the structure and properties of materials, enabling the synthesis of large and complex structures with diverse functions interesting for many different fields.

In recent years, supramolecular polymer chemistry, applying the principles of supramolecular chemistry to the synthesis of macromolecules, has gained special interest, as indicated by the almost exponential in-

Interaction	Energy (kJ/mol)	Distance dependence	Stability	Illustration
Ion-ion	40-360	r^{-1}	High	
Ion-dipole	40-200	r^{-2}, r^{-4}	High	
Dipole-dipole	4-150	r^{-3}, r^{-6}	Medium	
Cation- π	4-80	r^{-2}, r^{-4}	Medium	
π - π stacking	4-20	r^{-3}, r^{-6}	Low	
Dispersion	4-20	r^{-6}	Low	
Solvent effects	4-40		High	

Table 1.1: Supramolecular recognition interactions (Reproduced from Ref. [44]).

crease of publications and citations in this field (Figure 1.7). Various approaches towards supramolecular polymers have been considered so far. They can be classified according to the nature of the non-covalent interaction (i.e. hydrogen bonding, coordinative interactions...) and to the structure of the supramolecular polymer (i.e. polycondensation-type supramolecular polymers vs. supramolecular block copolymers).

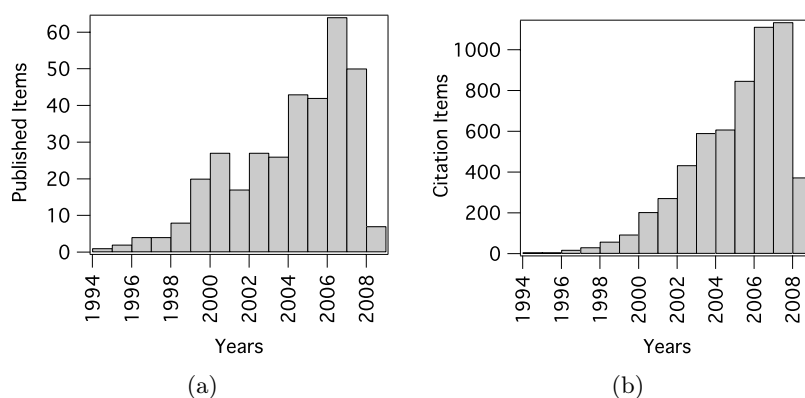


Figure 1.7: Number of publications (a) and citations (b) on metallo-supramolecular polymers, sorted by year (updated on March 25, 2008) [45].

In polycondensation-type polymers, each monomer or macromonomer are linked by non-covalent interactions. This approach requires the use of monomers or macromonomers bearing at least two binding sites that could be further condensed through supramolecular interactions (Figure 1.8). This approach leads to polymers containing many supramolecular linkers along the main-chain, and has been successfully applied to the synthesis of supramolecular polymers using hydrogen bonds [46–48] and metal-ligand coordination [49–52]. Many reports have been devoted to this approach which represents by far the main route to supramolecular polymers [53]. This route will not be considered in the present chapter.

In the second approach, supramolecular linkers are introduced at specific locations in block copolymer architectures leading to supramolecular block copolymers. This should lead to systems combining the character-

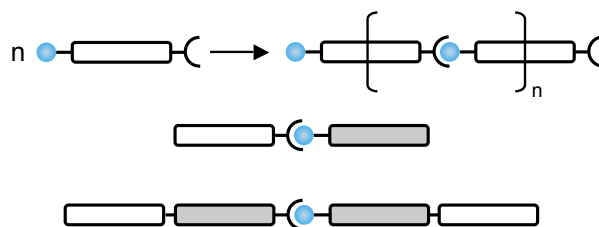


Figure 1.8: Schematic representation of a polycondensation-type supramolecular polymer (top), of a supramolecular block copolymer where the linker is located at the junction of the two blocks (middle), and of a supramolecular block copolymer where the linker holds two copolymer chains together (bottom).

istic features of block copolymers (e.g. microphase separation between immiscible constituent blocks) to the ones of supramolecular polymers (e.g. reversibility and tunability of the strength of the supramolecular bonds). The supramolecular linkers can be used to either bridge together different homopolymer blocks, or to link together different block copolymers. The first approach leads to diblock copolymers containing a supramolecular linker between the constituent blocks (Figure 1.8). The integrity of the block copolymer is in this case directly related to the supramolecular linker. In this respect, microphase separation between the polymer blocks is expected whenever the supramolecular interactions are operative, while macrophase separation between free polymer blocks should occur if the supramolecular interactions are turned off. The second strategy is based on the use of block copolymers containing a linking group specifically introduced at a defined locus of the copolymer chain (generally at the chain end or the block junction). These linking groups can further promote the formation of a supramolecular structure by bridging two or more copolymer chains together (Figure 1.8). In this case, microphase separation still occurs upon disruption of the supramolecular interactions.

In principle, all the supramolecular interactions listed in the Table 1.1 can be used for the preparation of block copolymers. For example, the mixing of a carboxylic acid end-functionalized poly(styrene) with a ter-

tiary amine end-functionalized poly(isoprene) led to a supramolecular AB diblock copolymer based on ionic interactions (cf. Figure 1.9a) [54]. However, such supramolecular interactions are not directional and not selective. Furthermore, taking into account the complementary hydrogen-bonded units in biological systems such as in DNA and RNA, researchers have imagined to synthesize supramolecular hydrogen-bonded AB copolymers (cf. Figure 1.9b). Although H-bonded systems are essentially found in polycondensation-type polymers, two examples of heteroleptic diblock copolymers have been reported so far. The first example deals with two polymers end-functionalized by two different oligoamide strands leading to a *hexa*-hydrogen bonded block copolymer [55]. The second example is based on bio-complementary hydrogen bonding. This supramolecular copolymer was obtained by decorating two different homopolymers with complementary oligonucleotides [56]. However, the strength of hydrogen-bonds is still rather weak compared to ionic and ion-dipole interactions.

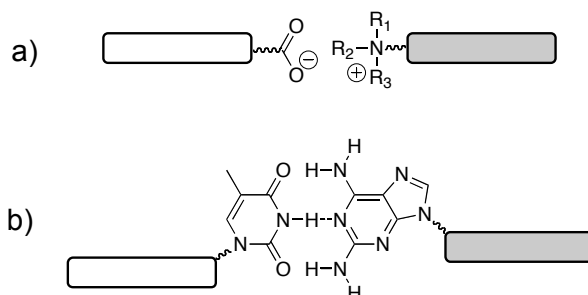


Figure 1.9: Possible complementary supramolecular interactions for the construction of heteroleptic AB-block copolymers based on a) ionic interactions and b) hydrogen bonding motives.

Metal-ligand coordination is particularly interesting for the synthesis of both types of supramolecular block copolymers because the coordination bond is highly directional, a wide range of ligands, rather easily functionalized, are available, and the interaction strength can be fine-tuned by choosing the appropriate metal ions. Such supramolecular copolymers, coined metallo-supramolecular block copolymers, offer

several advantages compared to their covalent counterparts. The reversibility of the supramolecular bond allows an improved control over the material properties and the construction of “smart” materials. Moreover, the presence of a metal complex in the copolymer structure introduces additional electrochemical, photophysical, catalytic and magnetic properties, and potentially allows to use those copolymers as precursors for the generation of inorganic or hybrid structures. These novel copolymers represent therefore highly promising candidates for the formation of functional nanostructured materials.

The following sections will deal only with metallo-supramolecular block copolymers. In the following, linear architectures based on 2,2':6',2'' terpyridine ligands (see Ref. [57] for a recent tutorial review about terpyridine chemistry) will be distinguished from star-like architectures based mainly on 2,2'-bipyridine ligands [49]. Moreover, a large part of the literature devoted to metallo-supramolecular polymers deals also with the use of metal-ligand interactions in the side chains of the polymer [58–61]. These side-chain functionalities afford some enhanced properties beyond those traditionally found in organic materials. However, this latter type of functionality will not be further discussed in this section since it does not involve the binding of two polymer blocks unlike for the linear and star-like architectures. Both parts of these sections are devoted to selected recent examples of linear and star-like architectures, respectively.

1.4.2 Linear metallo-supramolecular block copolymers

Linear metallo supramolecular copolymers can be obtained from three different combinations of supramolecular interactions, according to the structure of the building blocks used and to the position of the ligand (A, B represent two different polymer blocks, -[the ligand attached to these blocks and M the metal ion used in the complex):

- A-[and B-[blocks yields A-[M]-B diblock copolymers ;
-]-A-[and B-[blocks yield B-[M]-A-[M]-B triblock copolymers ;
- two A-B-[copolymers yield A-B-[M]-B-A diblock copolymers.

For A-[M]-B and B-[M]-A-[M]-B copolymers, the supramolecular linker -[M]- is located at the junction between the A and B polymer blocks. If these two blocks are immiscible and phase separate, an effect of the metal-ligand complex on the phase separation process might be expected. Since microphase separation in AB block copolymers is known to lead to well-defined nanostructured materials, the characteristic features (morphology, size, etc.) of the resulting self-assembled structures might be strongly influenced by the supramolecular linkers. Some preliminary results on that issue will be discussed. In the case of A-B-[M]-B-A copolymers, the metallo-supramolecular complexes are located in a single polymer phase (in this case B) and should thus have less influence on the microphase separation process than for the case of A-[M]-B copolymers.

The first step towards the synthesis of such metallo-supramolecular architectures is of course the attachment of the ligand, i.e., a terpyridine, to a polymer chain end. Two main strategies have been reported so far to reach this goal. The first one involves the grafting of a terpyridine functionalized at the 4'-position on the reactive chain end of a polymer [62, 63]. The commercially available 4'-chloro-2,2':6',2''-terpyridine is a very useful compound in that respect to react with α - or ω -hydroxyl-functionalized polymers. A variation of this approach has been recently reported, where the authors terminated the anionic polymerization of styrene with the chloro-terpyridine, avoiding thus the post-functionalization step [64]. The second synthetic strategy consists in using a terpyridine-functionalized initiator (so-called "supramolecular initiator") for the polymerization of the desired polymer. This method has the advantage of producing polymer chains with a theoretical functionalization degree of 1. Two examples of such initiators for controlled radical polymerization have been reported; one developed for nitroxide mediated polymerization (NMP) [65–67], and the other for reversible addition fragmentation chain transfer polymerization (RAFT) [68]. Recently, a library of hydroxy- and amino-functionalized Kröhnke-type terpyridines has been used to synthesize new terpyridine end-functionalized poly(ϵ -caprolactone)s and poly(L-lactide)s, via Sn(II)-catalyzed ring-opening polymerization [69].

The synthesis of A-[M]-B and B-[M]-A-[M]-B metallo-supramolecular block copolymers requires the formation of heteroleptic complexes. In

case of the A-[M]-B system, this means that the reaction between A-[, B-[and M should only selectively lead to A-[M]-B complexes and that the formation of homoleptic A-[M]-A and B-[M]-B complexes should be avoided. Very few metals (Ru, Os, Ir, Co) are suitable for this approach, among which only Ru has been used for the synthesis of metallo-supramolecular block copolymers [70]. Such a selective complexation process requires a two-step complexation procedure. Indeed, ruthenium(III) ions are known for forming a stable *mono*-complex with terpyridine, while ruthenium(II) ions do form a stable *bis*-complex with the same ligand [71]. Therefore, the synthesis of A-[Ru^{II}]-B metallo-supramolecular block copolymers can be selectively achieved by first making the A-[Ru^{III}] (or B-[Ru^{III}]) *mono*-complex, which is further reacted under the appropriate reducing conditions with the free terpyridine block B-[(or A-[) to form the desired A-[Ru^{II}]-B *bis*-complex (Figure 1.10). The high selectivity of this two-step process was demonstrated by using several analytical and spectrometric methods such as ¹H-NMR, UV/vis spectroscopy, MALDI-TOFMS, and size-exclusion chromatography [70]. The high stability of the *bis*-2,2':6',2''-terpyridine ruthenium(II) complexes allows the integrity of the block copolymers formed to be kept in various environments, such as organic solvents or water, even under extreme pH and salt concentration [72]. In the following, the metallo-supramolecular block copolymers will be designated by the acronym A_x-[Ru]-B_y, where A and B are the two different polymer blocks, -[Ru]- stands for the *bis*-2,2':6',2''-terpyridine-ruthenium(II) linkage between the A and B blocks and x and y represent the average degree of polymerization of the A and B blocks, respectively.

The most studied system is the poly(styrene)-[Ru]-poly(ethylene oxide) (PS-[Ru]-PEO) block copolymer, and in particular the PS₂₀-[Ru]-PEO₇₀ composition. For this copolymer, the macroligands were prepared by reacting chloro-terpyridine with the hydroxy chain end of PEO and PS (which was end-capped with one unit of ethylene oxide at the end of the anionic polymerization) [73]. Formation of micelles from this amphiphilic copolymer has been studied by different techniques. Dynamic light scattering (DLS) revealed the presence of two populations, one with a hydrodynamic diameter of about 65 nm, and one around 200 nm [72]. A cryo-TEM investigation enabled the identification of these two pop-

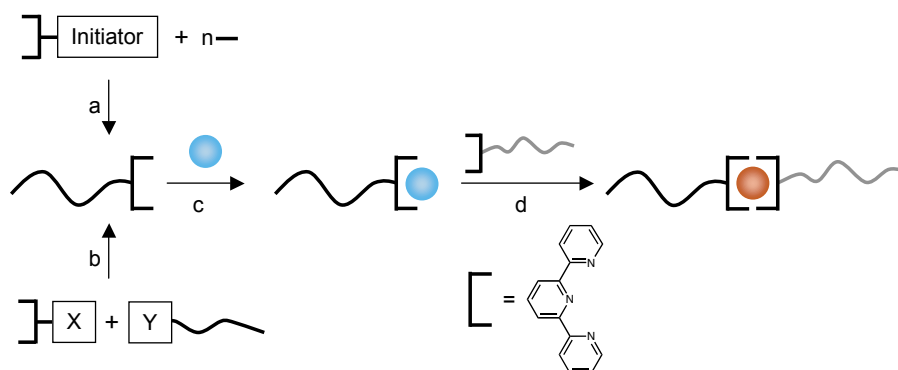


Figure 1.10: Schematic representation of the synthetic strategy to prepare linear metallo-supramolecular block copolymers. The first step is the synthesis of the macroligands by either using a functionalized (supramolecular) initiator (a), or grafting a terpyridine on a reactive chain end (b). The second 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).

ulations [74]. The first one is not attributed to individual micelles but to a mixture of micelles and small aggregates, while the population with larger size results from the clustering of a large number of micelles. The characteristic features of the micelles formed by the $\text{PS}_{20}\text{-[Ru]-PEO}_{70}$ copolymer were also compared to the ones formed by a classical covalent block copolymer: $\text{PS}_{22}\text{-}b\text{-PEO}_{70}$ [72]. The diameter of the PS core was found to be the same for the covalent and metallo-supramolecular samples, but in the case of the covalent counterpart, only individual micelles were formed, showing that micelles formed by metallo-supramolecular PS-[Ru]-PEO copolymers have a strong tendency to aggregate. In a more recent paper, it was shown that the formation of micellar aggregates could almost be totally suppressed by modifying the method of preparation of the micelles [75]. Indeed, a slow and regular addition of water, with the help of a syringe pump, to an initial DMF solution of the $\text{PS}_{20}\text{-[Ru]-PEO}_{70}$ copolymer resulted in a well-defined micellar solution with almost no further aggregation of micelles. The micelles thus formed were analyzed by analytical ultracentrifugation, revealing unimodal size

distribution with an average molar mass of 318,000 g/mol , corresponding to an aggregation number of 53 copolymer chains per micelle.

The PS₂₀-[Ru]-PEO₇₀ copolymer was not only studied in solution but also in the melt. A small-angle X-ray scattering investigation revealed that when hexafluorophosphate (PF₆⁻) is used as counterion, the morphology observed is spherical, and not the expected lamellar morphology considering the composition of the copolymer [76]. This is due to the aggregation of the terpyridine-ruthenium(II) complexes and of the counterions, forming spherical aggregates with a radius of about 1.5 nm, surrounded by a polymer shell with an outer radius of about 2.4 nm. If the more bulky tetraphenylborate (BPh₄⁻) is used as counterion, a highly ordered lamellar melt with a period of 11.9 nm is obtained after annealing at 55 °C for 40 h [77]. The lamellar structure is composed of segregated domains of PS and PEO blocks with the metal ions and their associated counterions confined to the lamellar interfaces. The order-disorder temperature (ODT) of this system was found to be around 70 °C, in agreement with Leibler's random phase approximation theory. This transition is reversible upon cooling, but more and more time is needed to achieve the lamellar morphology when increasing the annealing temperature. Schematic drawings of the morphologies obtained for both type of counterions are shown in Figure 1.11.

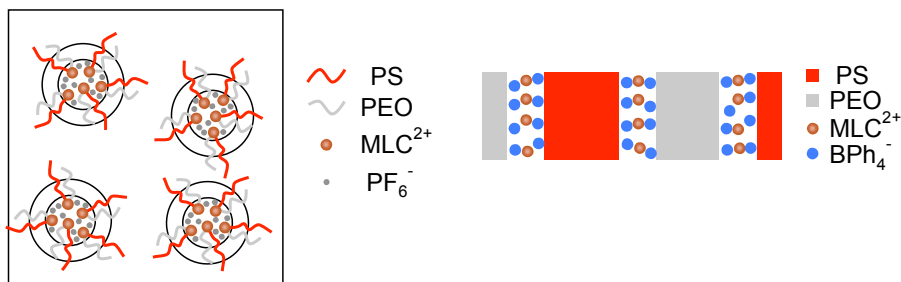


Figure 1.11: Schematic drawing of the model of the melt morphology of PS₂₀-[Ru]-PEO₇₀ with either PF₆⁻ counterions (left) or BPh₄⁻ counterions (right). Reproduced from Ref. [77].

These initial investigations on the nano-scale organization of the PS₂₀-[Ru]-PEO₇₀ metallo-supramolecular copolymer in both a selective

solvent and in the bulk revealed a deep influence of the *bis*-terpyridine ruthenium complexes on the microphase separation between the PS and PEO blocks. Therefore, other compositions than the PS₂₀-[Ru]-PEO₇₀ have to be synthesized and characterized. A deep look into synthesis and characterization of a library of metallo-supramolecular block copolymers will be further detailed in Chapter 3 and Chapter 4 respectively. Results on a previously synthesized library exhibit a wide variety of morphologies with tunable domain size as investigated by scanning force microscopy (SFM). The SFM images obtained on those thin films are shown in Figure 1.12. This combinatorial approach is certainly an advantage of metallo-supramolecular block copolymers compared to classical covalent ones. Although not discussed in the original work, this study also shows that the PEO microdomains are always oriented perpendicularly to the film surface. This effect, also observed in another study (creation of nanopores, see below), is again most probably linked to interactions between metal-ligand complexes, and the Chapter 8 will be devoted to this part.

Beside the formation of libraries of copolymers, another advantage of metallo-supramolecular block copolymers lies in the reversibility of the *bis*-terpyridine complexes. Indeed, an oxidation of Ru^{II} ions to Ru^{III} ones should be accompanied by a transformation of the initial *bis*-complexes into *mono*-complexes. Such a reversibility could be advantageously used to create well-defined nanoporous structures. In this respect, nanoporous thin films were obtained from a PS₃₇₅-[Ru]-PEO₂₂₅ copolymer [79]. In a first step, cylindrical microdomains oriented normally to the substrate were easily obtained by spin-coating a solution of the copolymer in a non-selective solvent without the need of further treatment. In a second step, the metal-ligand complexes were opened by oxidizing the Ru^{II} ions to Ru^{III} ones, which can only form *mono*-complexes (Figure 1.13). This releases the minor block and creates the nanopores. The removal of the PEO was evidenced by SFM, X-ray photoelectron spectroscopy and X-ray reflectivity.

PS_x-[Ru]-PEO_y were not the only metallo-supramolecular copolymers to be synthesized. An amphiphilic poly(ethylene-*co*-butylene)-[Ru]-PEO copolymer was prepared and its micellization in water was studied [80]. DLS and SFM characterizations revealed a strong tendency to

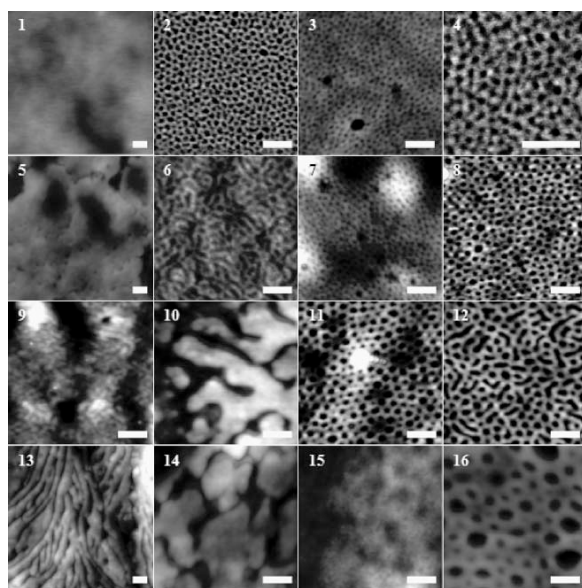


Figure 1.12: SFM phase images of thin films prepared by spin-coating 2 % w/v solutions in toluene of all the $\text{PS}_x\text{-[Ru]-PEO}_y$ block copolymers in the library (with $x = 20, 70, 200$ and 240 respectively, and $y = 70, 125, 225$ and 375 respectively). The white scale bar represents 100 nm. Reproduced from Ref. [78].

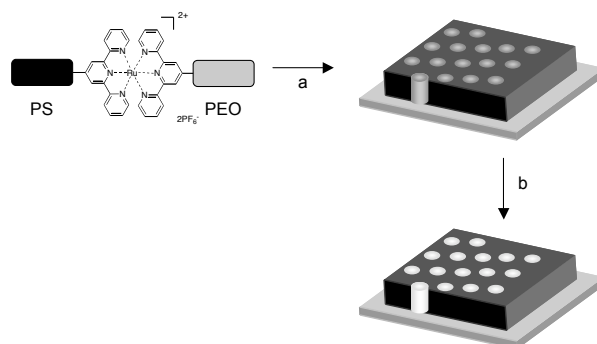


Figure 1.13: General strategy leading to functionalized nanoporous thin films. The cleavable copolymer is first self-assembled as a thin film with a cylindrical morphology (a). The appropriate stimulus is applied in order to cleave the copolymer and the minor block is eliminated by washing with a selective solvent (b).

aggregate, but in the case of the PEB-[Ru]-PEO a quasi equilibrium state between micelles and clusters was found, due presumably to the softness of the micellar core. The addition of a large excess of a water-soluble competitive ligand resulted in the breaking of the *bis*-terpyridine complexes and lead to water-dispersed PEB nanoparticles decorated by charged metal-complexes at their surface [80,81]. Rod-like micelles were obtained from a poly(ferrocenylsilane)-[Ru]-PEO copolymer in water as evidenced by DLS, TEM and SFM [82]. The micelles had a constant diameter but were rather polydisperse in length, and DLS indicated that they are rather flexible. Crystallization of the PFS in these micelles was observed by differential scanning calorimetry (DSC), and is thought to be responsible for the formation of these rod-like structures. Harruna et al. reported the synthesis of an amphiphilic PS-[Ru]-poly(N-isopropylacrylamide) using RAFT polymerization with a terpyridine functionalized chain transfer agent [68]. An ABC triblock copolymer was prepared by complexing a terpyridine-functionalized poly(styrene)-*b*-poly(2-vinylpyridine) with a terpyridine-functionalized PEO [83]. This copolymer was used to prepare stimuli responsive core-shell-corona micelles consisting of a PS core, a P2VP shell and a PEO corona. These micelles can indeed respond to

pH via the protonation/deprotonation of the P2VP shell, increasing or decreasing their size.

1.4.3 Star-like metallo-supramolecular block copolymers

The most frequently used ligand to prepare star-shaped block copolymers is the 2,2'-bipyridine [49]. This ligand forms *tris*-complexes with a large variety of metals, and is an ideal candidate for the preparation of multi-arm stars since bipyridines functionalized at the 4-and/or 4'-position can be rather easily prepared. Stars with 3, 4, 5 or 6 arms could thus in principle be synthesized according to the functionality of the bipyridines used.

Two approaches towards star-like metallo-supramolecular block copolymers can be distinguished: the coordination of different kinds of polymeric ligands around the metal center yielding hetero-arm star copolymers (heteroleptic complexes), or the coordination of identical ligands (homoleptic complexes), each ligand being a block copolymer (Figure 1.14).

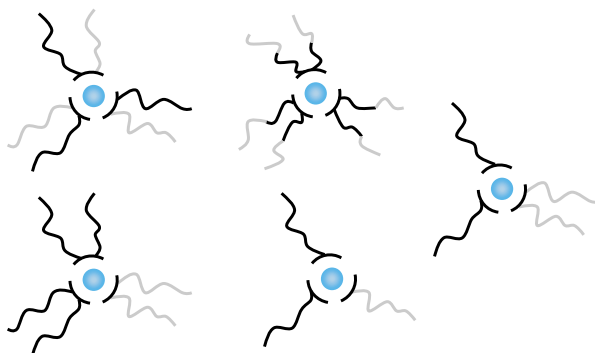


Figure 1.14: Schematic representation of the different architectures based on bipyridine complexes reported in the literature. The two examples at the top are obtained by the homoleptic complex approach, the other three by the heteroleptic complex approach.

After self-assembly, the metal-ligand complexes will be positioned at the domain interface in the case of hetero-arm star copolymers, while

they will be positioned in the core of the domain formed by the block directly attached to the ligand in the other case (Figure 1.15).

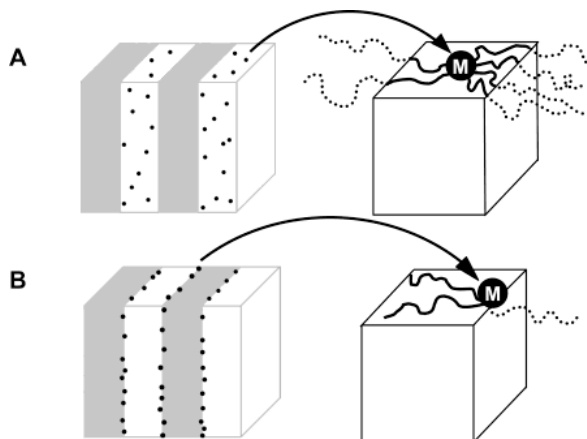


Figure 1.15: Schematic representation of the metal placement predicted for (A) a metal-centered star block copolymer and (B) a metal-centered hetero-arm star in microphase-separated films. (From Ref. [84]).

The preparation of star block copolymers based on homoleptic complexes can be achieved by two strategies. The first one employs a bipyridine-metal *tris*-complex as initiator for the polymerization of the arms, each bipyridine bearing the proper functional group. The second strategy consists in using a bipyridine-metal *tris*-complex as initiator. The second strategy consists of growing the polymer arms not from a *tris*-bipyridine complex but from the free bipyridine ligand. The macroligands thus created are complexed around a metal center in a subsequent step (Figure 1.16).

The synthesis of hetero-arm star copolymers relies on the same principle as the terpyridine-based linear AB copolymers. A *bis*-bipyridine metal complex is first prepared using two identical macroligands. The third, differently functionalized, bipyridine based macroligand is then added in a subsequent step to yield the *tris*-complex (Figure 1.17). As for the linear architectures, the same two strategies, i.e., the grafting of the ligand on a polymer chain end or the use of a functionalized initiator to grow the polymer chain from the ligand, can be applied to obtain a

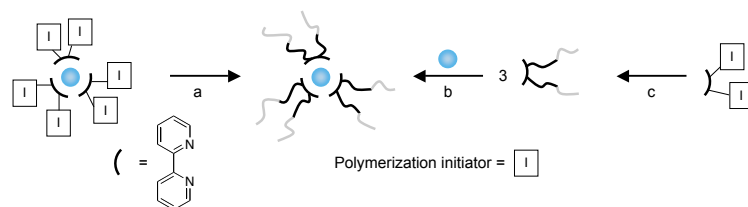


Figure 1.16: Schematic representation of the synthetic strategies to prepare metallo-supramolecular star copolymers. The first strategy (a) consists in growing the polymeric arms using a bipyridine-metal *tris*-complex as initiator. The second strategy involves first the synthesis of the macroligands (c), followed by the complexation with the metal (b).

polymeric ligand. In this context, modified bipyridines have been used as initiator in atom transfer radical polymerization (ATRP) and in ring opening polymerization (ROP). In the following we will describe some examples of the two classes of compounds: homoleptic and heteroleptic complexes.

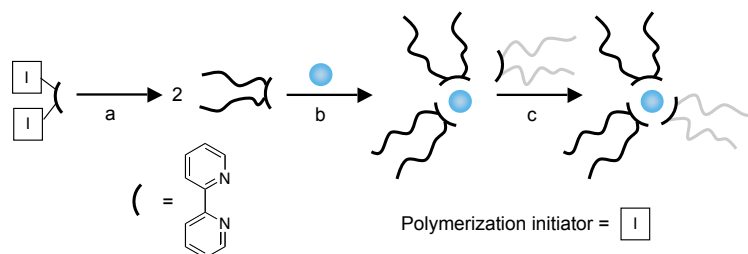


Figure 1.17: Schematic representation of the synthetic strategy to prepare metallo-supramolecular hetero-arm star copolymers. The first step is the synthesis of the macroligands (a). The second step is the preparation of a *bis*-complex with the metal (b). Finally, the second type of macroligand is added to form a bipyridine *tris*-complex (c).

The first reported example of homoleptic complexes was the preparation of six-arm star block copolymers using $[\text{Fe}(\text{bpy}(\text{CH}_2\text{Cl})_2)_3](\text{PF}_6)_2$ as hexafunctional initiator for the polymerization of oxazolines [85]. The first block was made of the hydrophilic 2-ethyl-2-oxazoline (EtOx), and

the second, hydrophobic, block of either 2-phenyl-2-oxazoline (PhOx) or 2-undecyl-2-oxazoline (UnOx). The morphology of thin and thick films of the poly(EtOx)-*b*-poly(UnOx) six-arm star copolymer was later investigated by X-ray scattering (SAXS and WAXS), TEM and SFM [86]. It was found that the pEtOx block forms cylindrical microdomains in a matrix of pUnOx. Upon annealing at 160 °C, iron nanoclusters are formed on top of the pEtOx domains for thin films, and micron size iron-rich clusters form on the surface of bulk samples. Another example of six-arm star copolymer was synthesized by a combination of ROP and ATRP polymerization [87]. The first step of the synthesis was the polymerization of DL-lactide by ROP using [Ru(bpy(CH₂OH)₂)₃](PF₆)₂ as hexafunctional initiator. The OH end groups were then converted to bromoesters, and *tert*-butyl acrylate was polymerized by ATRP. In a final step, PtBA was hydrolyzed into poly(acrylic acid). Six-arm star block copolymers have also been obtained by the macroligand strategy [88]. DL-lactide and ϵ -caprolactone were sequentially polymerized by ROP, using *bis*(hydroxymethyl)-2,2'-bipyridine as initiator, to yield bpy(PCL-DLPLA)₂ and bpy(DLPLA-PCL)₂ copolymers. The macroligands were then complexed with iron(II) ions to yield biocompatible copolymers with a labile metal center, or to ruthenium(II) to generate luminescent copolymers with an inert metal core. This ruthenium *tris*-(bipyridine) core could be useful as a luminescent tag for drug delivery model studies. It was observed that the iron-centered star copolymers decolorize in response to some stimuli (heat, acid, bases, peroxides, ammonia), suggesting interesting possibilities for their use in qualitative and quantitative assays. Other examples of this alternative strategy include the synthesis of macroligands by a combination of ROP (for PCL or DLPLA) and ATRP (for PtBA or poly(methyl methacrylate)), or sequential ATRP to produce bpy(PMMA-PS)₂ and bpy(PS-PMMA)₂ [89]. Those macroligands were then complexed with iron(II) to yield six-arms star copolymers. However, for bpy(PCL-PtBA)₂ and bpy(PLA-PtBA)₂ macroligands, only *bis*-(bpy) complexes resulted. The reasons for these differences between several polymers may originate from variations in chain conformation in the mixture of solvent used inducing steric hindrance around the metal binding site. Hetero-arm star copolymers can also be produced by the homoleptic complex approach.

This requires the orthogonal synthesis of unsymmetrical macroligands from a dual initiator. 4-Chloromethyl-4'-hydroxymethyl-2,2'-bipyridine (bpy-(CH₂Cl)(CH₂OH)) was used as dual initiator for the sequential polymerization of ϵ -caprolactone by ROP and of styrene by ATRP [90]. The bpy(PS)(PCL) macroligand was best prepared by growing the PS block first from the more reactive halide, followed by the generation of the PCL block from the OH site. In a final step, the macroligands were complexed with iron(II). Recently a new bipyridine-functionalized dithioester was successfully synthesized and further used as a RAFT agent in RAFT polymerization of styrene and *N*-isopropylacrylamide to produce bipyridine-terminated poly(styrene) and PNIPAM polymers as macroligands with controlled molecular weights and low polydispersity. The bipyridine end-functionalized polymers were further used as macroligands for the preparation of star-shaped metallopolymer [91].

Several examples of hetero-arm star copolymers based on heteroleptic complexes have been reported. Macroligands bearing one or two PS chains were first synthesized by ATRP using 4-(chloromethyl)-2,2'-bipyridine and 4,4'-*bis*-(chloromethyl)-2,2'-bipyridine as initiator, respectively [92]. *bis*-Bipyridine-ruthenium complexes were then prepared with those macroligands. In a final step, a second type of macroligand, bearing one or two PMMA chains also grown by ATRP, was attached to the *bis*-complexes to yield hetero-arm star copolymers with 3 or 6 arms. It was demonstrated that solvent polarity, influencing the conformation of the polymer chains, is an important parameter to tune in order to achieve control over the assembly of hetero-arm star copolymers. In another example, the synthesis of hetero-arm star copolymers with 4 or 6 arms was reported [93]. Six-arm stars were obtained by first forming a ruthenium *bis*-complex with bipyridines bearing two PCL chains, grown by ROP, as macroligands, followed by the complexation with a bipyridine bearing either two PS chains (grown by ATRP) or two poly(ethylene glycol) chains prepared by grafting PEG onto 4,4'-*bis*-(chloromethyl)-2,2'-bipyridine by the Williamson reaction. Four-arm stars were prepared by complexing to a ruthenium-bipyridine *bis*-complex bearing one PS chain on each bipyridine, a bipyridine bearing either two PLA chains (grown by ATRP) or two PEG chains.

The synthesis of a hetero-arm star copolymer with ligands other than

bipyridines has also been reported. Ligands of the β -diketonate family, in conjunction with a bipyridine were chosen to build a heteroleptic complex with a lanthanide ion [94]. The macroligands were obtained by polymerizing DL-lactide by ROP with dibenzoylmethane functionalized with a hydroxyl site as initiator. Three macroligands were then chelated to europium(III) to yield a three-arm star. A bipyridine bearing two PCL chains was finally complexed to this *tris*-complex to obtain a five-arm star block copolymer.

1.4.4 Conclusions

As shown by the results already available in the literature, important progress has been made in the development of synthetic strategies towards metallo-supramolecular block copolymers. From these preliminary reports, it is clear that the presence of metal-ligand complexes in block copolymers has a deep impact at several levels, ranging from the synthetic aspects to the final structure and functionality of the accordingly obtained materials. Indeed, the sequential self-assembly process used for the synthesis of metallo-supramolecular block copolymers is compatible with a combinatorial approach towards libraries of copolymers. In such an approach various parameters, including the length of the precursor blocks, the nature of the metal-ion in the complex, as well as the architecture of the copolymer can be easily screened. Having in mind that the final properties of the accordingly obtained materials critically depend on these parameters, metallo-supramolecular copolymers will certainly play an important role within the next few years in polymer-based materials with tunable properties. The combination of a highly modular synthetic approach, enabling the preparation of various architectures, with the presence of a metal center having particular properties, make of metallo-supramolecular block copolymers ideal candidates for the assembly of new, stimuli-responsive, functional materials. However, it is still an emerging field and a lot of work still need to be done in order to get a clear correlation of structure-property relationships and gain better understanding and control over the parameters governing the self-assembly and nanostructure formation.

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OBJECTIVES

THIS thesis focuses on the study of a new family of diblock copolymers, containing a supramolecular connection between the two blocks. A metal/ligand complex is used as a supramolecular linker between the two different blocks giving rise to metallo-supramolecular block copolymers.

Terpyridine is used as the ligand in our approach. Two terpyridines can coordinate to a transition metal ion in an octahedral geometry. Whenever two polymer blocks, both end-functionalized by a terpyridine ligand, are reacted with a transition metal, a *bis*-2,2':6',2''- terpyridine metal complex is formed, which acts as a reversible supramolecular linker between the two constituent blocks.

In this thesis, we are planning, in a first step, to optimize the incorporation of terpyridine ligands into polymer blocks. To this aim, we will graft the terpyridine ligand to the terminal group of ω -hydroxy polymer blocks. This approach will be however limited to rather low molecular weight (MW) polymer blocks (MW below 10,000 *g/mol*) due to the dilution of the reactive groups with increasing MW. In addition, we will implement the use of terpyridine-functionalized initiator for nitroxide-mediated radical polymerization (NMP). Since the terpyridine group is attached to the initiator and does not interfere with the polymerization mechanism, this approach has the advantage to lead to a quantitative functionalization of the accordingly obtained polymer blocks. This initiator will be further used to polymerize various monomers, including styrene, *tert*-butyl acrylate, dimethylamino-ethyl acrylate (Chapter 3).

After optimization, these two methods (terpyridine *post*-grafting and terpyridine-functionalized initiator) will provide us, in a second step, with a collection of terpyridine-functionalized polymer blocks of varying chemical nature and MW. These blocks will be then systematically self-assembled by using the coordination chemistry based on ruthenium ions, as described above. A library of metallo-supramolecular block copolymer will be accordingly obtained (see Figure 2.1).

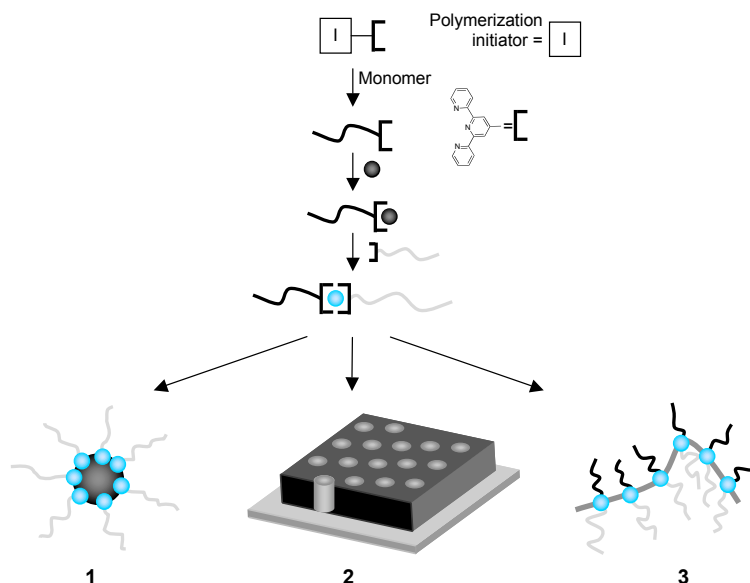


Figure 2.1: Schematic pathways of the formation of diblock copolymers with a metallo-supramolecular junction binding the two blocks. These copolymers can be self-assembled in several ways: amphiphilic micelles in water (1), thin films (2) and more complex brush-like architectures (3).

The Chapter 4 of this thesis will consist in the preparation of nano-materials based on the library of metallo-supramolecular block copolymers. Special attention will be paid to metallo-supramolecular block copolymers containing a hydrophobic block (poly(styrene)) linked to a hydrophilic one (poly(ethylene oxide)) via a *bis*-terpyridine ruthenium complex. These copolymers will be characterized by an amphiphilic char-

acter that will be further exploited for the formation of block copolymer micelles in aqueous medium (see **1**, Figure 2.1). One of the central target of this study will be to understand the influence of the *bis*-terpyridine ruthenium complexes located at the core-corona interface on the characteristic features of the micelles. The MW of the constituent blocks will also be systematically varied and the influence on the micellar dimensions will be evaluated. These results will be compared to those obtained on micelles formed by the “classical” poly(styrene)-*b*-poly(ethylene oxide) copolymers with a covalent C-C bond at the block junction.

The following chapters are devoted to recent applications taking advantages of the metallo-supramolecular interactions. Firstly, Chapter 5 highlights the exchange of low-molecular counterions by polymeric ones leading to novel amphiphilic structures in water (see **3**, Figure 2.1). Furthermore, Chapter 6 describes the terpyridine-metal interactions located at the extremity of a classical block copolymer, poly(styrene)-*b*-poly(*tert*-butyl acrylate) (see **1**, Figure 2.2). The formation of stimuli-responsive systems will be described in this part as an extension of the versatility related to this type of interactions. Chapter 7 focuses on the same system than in the previous chapter, but in more concentrated solution, leading to the formation of a supramolecular gel with enhanced properties (see **2**, Figure 2.2). Finally, the last chapter is devoted to the formation of thin films starting from a PS-[Ru]-PEO copolymer, and will focus on the parameters controlling the orientation of the nanodomains found in these systems (see **3**, Figure 2.1).

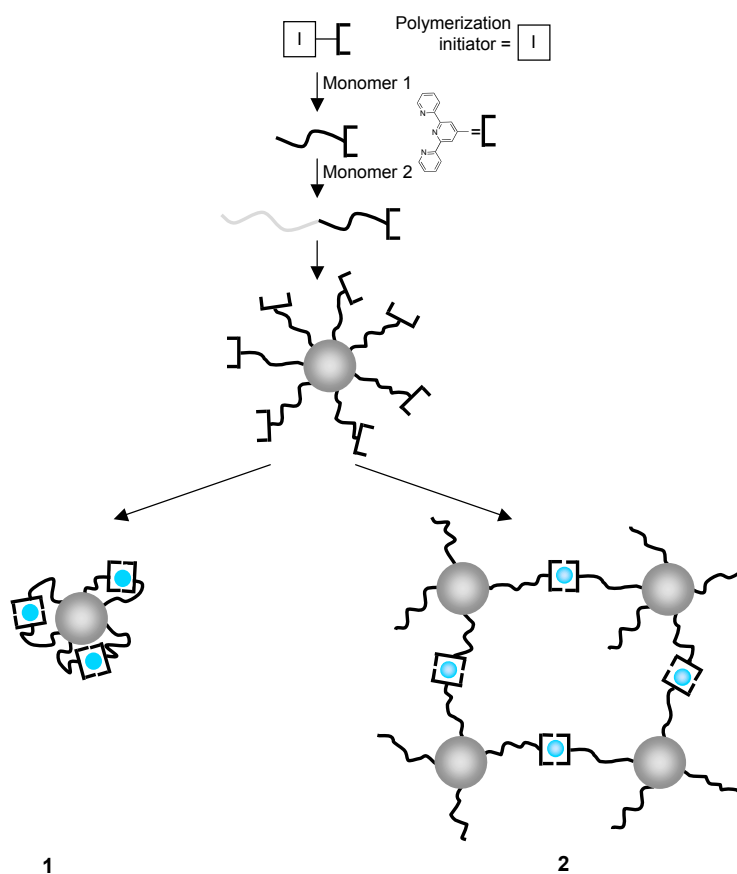


Figure 2.2: Schematic pathways of the second strategy involving metallo-supramolecular polymers. Classical block copolymers are synthesized and metal-ligand interactions are used both in diluted (1) and more concentrated solutions (2) to create a hierarchical self-assembly.

SYNTHESIS OF METALLO-SUPRAMOLECULAR COPOLYMERS

Abstract

The synthesis of metallo-supramolecular amphiphilic block copolymers containing a hydrophilic poly(ethylene oxide) block, PEO, linked to a hydrophobic poly(styrene) block, PS, through a metal-ligand complex is described in this chapter. 2,2':6',2''-terpyridine acts as the ligand. In a first step, the synthesis of the building blocks end-functionalized with this ligand is performed on the one hand using controlled radical polymerization, and on the other hand, using chain-end modification. In a second step, the PS and PEO building blocks are self-assembled to lead to a block copolymer. The use of ruthenium ions allows the exclusive formation of PS-[Ru]-PEO hetero-dimers, through a sequential two-step self-assembly process of the terpyridine-functionalized blocks. The last part of this chapter is devoted to another example of these peculiar copolymers, and deals with the synthesis of easily reversible copolymers using terpyridine-cobalt bis-complexes.

3.1 Introduction

This chapter focuses on the synthesis of a new family of diblock copolymers, containing a supramolecular connection between the two blocks [1]. A metal/ligand complex is used as a supramolecular linker between the two different blocks giving rise to a metallo-supramolecular block copolymer. Terpyridine is used as the ligand in our approach. Two terpyridines can coordinate to a transition metal ion in an octahedral geometry. Whenever two polymer blocks, both end-functionalized by a terpyridine ligand, are reacted with a transition metal, a *bis*-2,2':6',2''-terpyridine metal complex is formed, which acts as a reversible supramolecular linker between the two constituent blocks [2].

The first step deals thus with the incorporation of terpyridine ligands into polymer blocks. To this aim, the terpyridine ligand can be grafted to the terminal group of ω -hydroxy polymer blocks. This approach is however limited to rather low molecular weight (MW) polymer blocks (MW below 10,000 *g/mol*) due to the dilution of the reactive end groups with increasing MW. In addition, we will implement the use of terpyridine-functionalized initiator for nitroxide-mediated radical polymerization (NMP). Starting from an universal alkoxyamine developed by Hawker [3], the synthesis of a modified version of this molecule bearing the terpyridine moiety will be performed. Since the terpyridine group is attached to the initiator and does not interfere with the polymerization mechanism, this approach has the advantage to lead to a quantitative functionalization of the accordingly obtained polymer blocks. This initiator will be further used to polymerize various monomers, including styrene, *tert*-butyl acrylate and 2-(dimethylamino)ethyl acrylate. The "living" character of the NMP will be highlighted with the synthesis of a diblock copolymer poly(styrene)-*b*-poly(*tert*-butyl acrylate) end-functionalized with the terpyridine ligand.

After optimization, these two methods (terpyridine post-grafting and terpyridine-functionalized initiator) will provide us, in a second step, with a collection of terpyridine-functionalized polymer blocks of varying chemical nature and MW. These blocks will be then systematically self-assembled by using coordination chemistry based on ruthenium ions, leading to the formation of A-[Ru]-B hetero-dimers, through a sequential

two-step self-assembly process [2]. Starting from the initial methodology developed by Lohmeijer et al. [1], the initial procedure will be extended to polymers with higher molecular weights. Optimisation of the coupling synthesis as well as the purification process is highlighted in this chapter.

Compared to other transition metals, *bis*-2,2':6',2''-terpyridine-Ru(II) complexes are extremely stable and are good candidates to replace classical A-*b*-B covalent block copolymers for the formation of nanostructured materials. However, as further explained, these metallo supramolecular copolymers are not prone to ligand exchange once the *bis*-terpyridine ruthenium complexes are formed. Since the reversibility of these peculiar copolymers is an important parameter, the last part of this chapter will be devoted to the formation of easily reversible supramolecular block copolymers, using a cobalt(III)-terpyridine *bis*-complex as the junction between the two blocks.

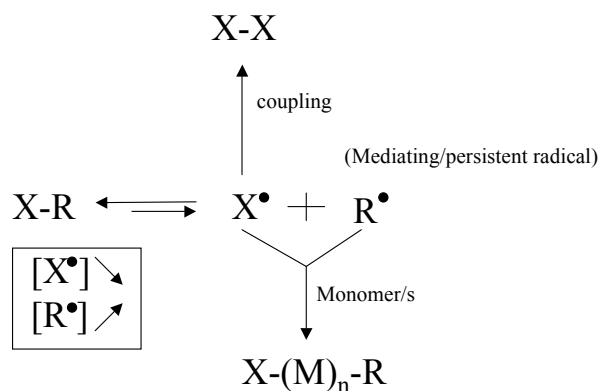
3.2 Incorporation of terpyridine ligands into polymers

3.2.1 Highlights on the nitroxide mediated polymerization process

Functional groups can be introduced into polymer blocks by several methods, including the use of functionalized initiators (i), the termination of polymerization reaction by a molecule bearing the desired functional group (ii) and the transformation of a *pre*-existing end-group into the desired functional group (iii). In this thesis, strategies (i) and (iii) will be used. It should be however mentioned that synthetic route (ii) was described recently, where the anionic polymerization of styrene was terminated by a terpyridine derivative, providing a highly efficient functionalization [4]. Nevertheless, the stringent reaction conditions required for the living anionic polymerization are not available within our laboratory and this route will not be further considered in the present thesis.

Since we are aiming for well-defined polymer blocks with a pre-determined molecular weight (MW) and a narrow MW distribution, controlled radical polymerization techniques using functionalized initiators are a valuable approach if strategy (i) is considered. In the last

decade, important breakthroughs have been made in the field of controlled radical polymerization. It is now quite straightforward to obtain polymers with narrow molecular weight distribution and high end-group functionality with techniques such as Atom Transfer Radical Polymerization (ATRP) [5], Nitroxide Mediated Polymerization (NMP) [6] and Reversible Addition Fragmentation Chain Transfer Polymerization (RAFT) [7, 8]. Although ATRP polymerization is not suitable in our case due to the competitive complexation between the metal ion catalyst and the terpyridine ligand, NMP and RAFT have been successfully developed by Lohmeijer [9] and Zhou [10, 11], respectively. In the following, we will concentrate on NMP polymerization using a terpyridine-functionalized initiator. A number of groups have demonstrated that alkoxyamine based unimolecular initiators give accurate control over molecular weight, chain end functional groups, polydispersity and macromolecular architecture in nitroxide mediated living free radical systems [6]. The basic operation principle of NMP is depicted in Scheme 3.1 and is based on the establishment of an equilibrium between an active species and a dormant one. The dormant species contains an alkoxyamine that



Scheme 3.1: Simplified reaction scheme for the NMP.

can decompose into a growing radical and a nitroxide one. The equilibrium is strongly shifted towards the dormant species and the instantaneous concentration of growing radicals is therefore low, and irreversible termination (by disproportionation or recombination) is minimized. Since

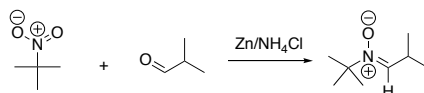
the global polymerization rate is considerably slowed down due to this active-dormant species equilibrium, the initiation step becomes fast compared to the propagation one and low polydispersity polymers are finally obtained with this method. Moreover, if the monomer conversion is known, the MW of the obtained polymer can simply be calculated by the [monomer] to [initiator] ratio multiplied by the conversion. The initiator in NMP is an alkoxyamine that decomposes into an initiating radical and a nitroxide one (see Scheme 3.1). The nitroxide radical is unable to initiate any polymerization. A polymer chain is growing from the initiating radical (active species), that is further reversibly terminated by recombination with the nitroxyl radical (leading to the dormant species). At the beginning of the NMP process, the active/dormant species equilibrium is not well established and some irreversible terminations can occur. This leads to an excess of persistent nitroxide radicals. Finally, this excess mediates in an equilibrium reaction between growing and dormant chains, the so-called persistent radical effect [12]. The dormant chains are turned into growing chains by continuous addition and fragmentation of the nitroxide radical, leading to an equal growth of the different chains until high conversions are obtained (Scheme 3.1).

3.2.2 Synthesis of the terpyridine functionalized initiator

Hawker has developed an universal alkoxyamine with a *chloro*-functionality capable of polymerizing via NMP styrenes, acrylates, dienes, acrylamides and vinylpyridines. This alkoxyamine is an interesting precursor for the synthesis of functionalized polymer blocks thanks to the chloride group. As shown by Lohmeijer, a terpyridine functionalized initiator can be obtained by reacting the 2,6-*bis*-(2'-pyridyl)-4-pyridon with this alkoxyamine. This initiator has been further used in nitroxide mediated polymerization in order to build different terpyridine end-functionalized polymers with a narrow molecular weight distribution and a high end-functionality [9, 13].

After some synthetic perseverance, we have reproduced the synthesis of this initiator, since it is not commercially available. We are detailing in the following the different required steps in order to obtain the macroinitiator with the terpyridine moiety [3, 14].

The first step corresponds to the reductive condensation of a nitropropane with an aldehyde to give the desired nitron (Scheme 3.2)



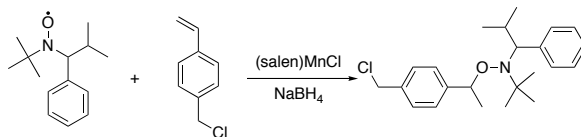
Scheme 3.2: Synthesis of the nitron.

For the second step, leading to the nitroxide, we have realized the addition of a Grignard reagent on the nitron according to the method of Reznikov and Volodarsky [15], followed by copper(II) catalyzed oxidation under ambient atmosphere (Scheme 3.3).



Scheme 3.3: Synthesis of the nitroxide.

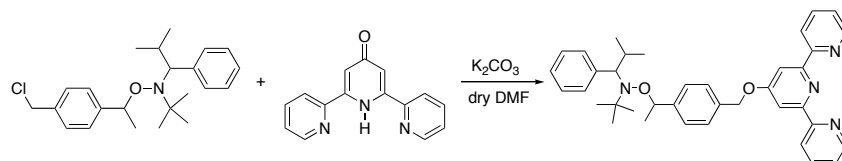
Different strategies have been previously studied in order to generate a centered-carbon radical followed by the trapping of this radical by a nitroxide derivative. The method developed by Dao and al. [14] has been used. In this case, Jacobsen's reagent, manganese (III) salen, is employed to promote the addition of nitroxide across the activated double bond of the styrene, leading to the alkoxyamine in high-yield (Scheme 3.4).



Scheme 3.4: Synthesis of the alkoxyamine.

In a last step, pyridon was reacted with the previously formed alkoxyamine yielding a unimolecular initiator bearing a terpyridine moiety. The

mild base K_2CO_3 deprotonates the pyridon and then undergoes a SN_2 reaction with the *chloro*-group on the alkoxyamine (Scheme 3.5).



Scheme 3.5: Synthesis of the unimolecular initiator.

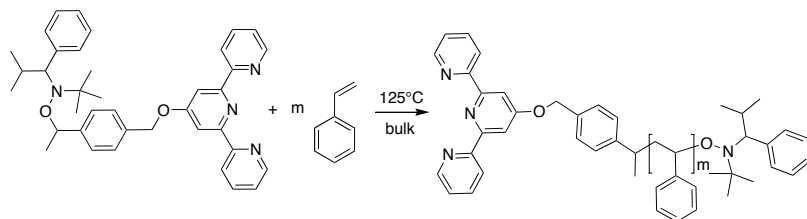
This four-step sequence has been realized on a large scale to prepare a stock of the desired terpyridine end-functionalized initiator.

3.2.3 Synthesis of terpyridine functionalized polymers via NMP

3.2.3.1 Polymerization of styrene

As previously introduced, terpyridine ligands can be attached at the chain end of polymers by NMP using an unimolecular initiator bearing a terpyridine moiety (Scheme 3.6). According to the previous study of Lohmeijer et al. on the polymerization of styrene using NMP [13], it was decided to work at seventy percents of conversion. Actually, it is better to limit the conversion to obviate an increase of the polydispersity index. Moreover, styrene is subjected to *auto*-polymerization, which starts at 60 °C. Therefore, a purification via column chromatography is needed for the elimination of this *non*-functionalized poly(styrene). However, it has been shown, that this polymerization is not a real issue since the auto-initiation of styrene is a slow-process [16, 17], and high terpyridine incorporation degrees are thus obtained (>90 %). We have deduced the time of reaction from Figure 3.1 with $\ln([M_0]/[M])=1.2$ (conversion=70 %).

A series of terpyridine-functionalized poly(styrene) chains of various MW ranging from 10,000 to 35,000 *g/mol* was synthesized by using this method (see Table 3.1). In this study, the polymers were consistently analysed by GPC and 1H -NMR. 1H -NMR spectra (see Figure 3.2) were



Scheme 3.6: Synthesis of terpyridine functionalized poly(styrene) by NMP.

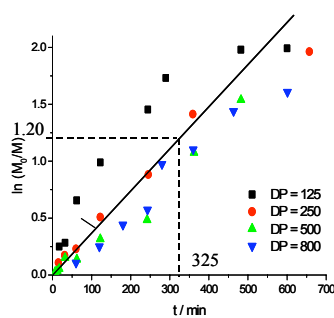


Figure 3.1: Plot of $\ln([M_0]/[M])$ as a function of time for four differently targeted degrees of polymerization [13].

used for the determination of the degree of polymerization of polymers by careful integration of the polymer backbone to the terpyridine signals (see inset on Figure 3.2). On the other hand, polydispersity indices were measured by size exclusion chromatography. Moreover one can notice that the results obtained by NMR and GPC are closed since our GPC system was calibrated with poly(styrene) standards. These poly(styrene) building blocks will be further used for the building-up of metallo-supramolecular block copolymers.

Sample	Polymerization conditions ^a	$M_{n,th}^{b,c}$	M_w^b (GPC)	PDI (GPC)	M_n^b NMR	Conversion ^d (%)
1	355 min in bulk	14,900	11,700	1.06	10,900	73
2	355 min in bulk	45,000	29,200	1.06	35,000	77

^a Polymerizations were always performed at 125 °C in argon-filled Schlenck tubes, without any further additions of nitroxide.

^b Values are indicated in *g/mol*.

^c Theoretical molecular weight is calculated at a final conversion of 100 %.

^d Conversion is determined from the ratio $M_n(NMR)/M_{n,th}$.

Table 3.1: Representative results obtained for the polymerization of styrene by the terpyridine functionalized initiator.

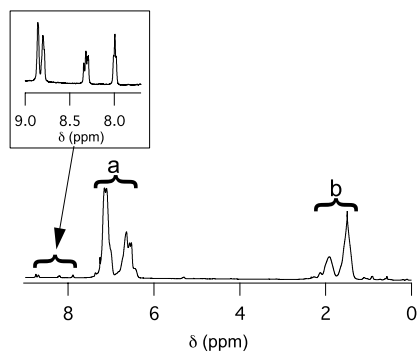


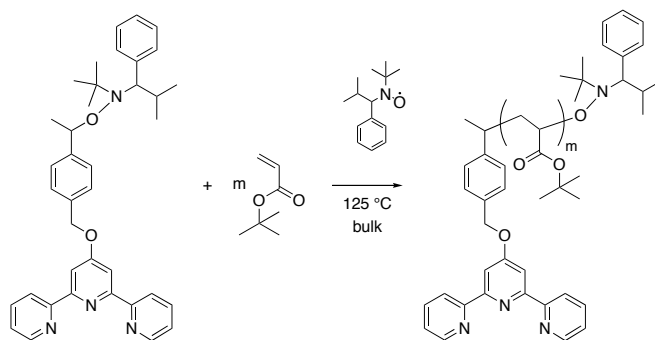
Figure 3.2: ^1H -NMR of the terpyridine functionalized poly(styrene) in CDCl_3 . The typical terpyridine signals are highlighted in the inset. The (a) and (b) areas correspond to the aromatic and aliphatic regions of the PS backbone, respectively.

3.2.3.2 Polymerization of *tert*-butyl acrylate

Polymerization of acrylate monomers in a controlled radical manner has always been a challenge since acrylates are not subjected to *auto*-initiation and *auto*-polymerization as for styrene derivatives. In the case of styrene, a steady-state between termination reactions (consuming existing transient radicals) and *auto*-initiation reactions (producing new transient radicals) lead to a controlled growth of the poly(styrene) chains. Moreover, the polymerization propagation rate of acrylates is much higher than for styrene (about 6 times at 120°C for *n*-butylacrylate polymerizations [3]). Therefore, an equilibrium is never reached and at a certain point of conversion, polymerization of acrylates could stop if termination reactions occur frequently. Initially, efforts were made to develop new mediating nitroxides [18, 19]. Nevertheless, although they were able to polymerize acrylates at elevated temperature, polydispersity indices were still between 1.40 and 1.67, which is the higher limit for controlled radical polymerization (PDI must be below than 1.5). Additives were also used to ensure a constant concentration of persistent radicals but without any real improvement on the polydispersity indices [20]. Finally, the solution to reach well-defined polymers was obtained by the

addition of an excess of free nitroxide, i.e. the persistent radical, to shift the equilibrium in favor of the dormant chains [3, 16].

The aim of this section is to show the possibility to synthesize various acrylate polymers bearing a terpyridine end-chain functionality (Scheme 3.7). By screening several experimental conditions, we have successfully obtained poly(*tert*-butyl acrylate) of targeted molecular weights with a narrow MW distribution (see a selection of these results in Table 3.2). Polymerizations performed in anisole are efficient for a targeted molecular weight above 30,000 *g/mol*. In fact, experiments revealed that, due to the high viscosity of acrylate monomers, polymerizations in bulk are not suitable for the higher targeted molecular weight polymers, since they are subjected to the “Trommsdorff-Norrish” effect [21].



Scheme 3.7: Synthesis of terpyridine functionalized poly(*tert*-butyl acrylate) by NMP.

Since the M_n values of PtBA shown in Table 3.2 were estimated by PS-calibrated GPC, they are inaccurate on an absolute scale. $^1\text{H-NMR}$ analysis provides more reliable M_n values in this case. Figure 3.3 shows the $^1\text{H-NMR}$ spectrum of a typical terpyridine end-functionalized PtBA (see Experimental Section) with M_n of 26,300 (sample 7 - Table 3.2), as estimated by GPC, where the signals from the protons of the terpyridine moiety at the initiating chain end clearly appear between 8.9 ppm and 7.6 ppm (see inset Figure 3.3). On the other hand, the signals of the protons of the tBA chain are observed in the area at 1.0-2.5 ppm. Since PtBA is not subjected to *homo*-polymerization unlike PS, it can be assumed

Sample	Polymerization conditions ^a	M _{n,th} ^{b,c}	M _n ^b (GPC)	PDI (GPC)	M _n ^b NMR	Conversion ^d (%)
1	360 min in 37 wt% anisole ^e	51,200	18,500	1.17	16,600	32
2	540 min in 37 wt% anisole ^e	51,200	19,200	1.14	18,000	40
3	840 min in 37 wt% DMF ^f	51,200	12,500	1.20	13,600	25
4	1,320 min in bulk ^e	51,200	23,900	1.15	24,600	50
5	1,320 min in bulk ^e	51,200	24,500	1.13	26,700	50
6	1,320 min in bulk ^e	51,200	26,300	1.12	26,400	50
7	1,320 min in bulk ^e	15,400	9,400	1.17	7,700	50

^a Polymerizations are always performed at 125 °C in argon-filled Schlenk tubes.

^b Values are indicated in *g/mol*.

^c Theoretical molecular weight is calculated at a final conversion of 100 %.

^d Conversion is determined from the ratio M_n(NMR)/M_{n,th}.

^e 5 % of free nitroxide were added with respect to the alkoxyamine content.

^f 10 % of free nitroxide were added with respect to the alkoxyamine content.

Table 3.2: Representative results obtained by the polymerization of *tert*-butyl acrylate by the terpyridine functionalized initiator.

that all the polymer chains bear a terpyridine group at the initiating chain end. Therefore, from the intensity of area *a* relative to that of peaks corresponding to the terpyridine functionality, we estimated the M_n to be 26,400 *g/mol* which (accidentally) coincides with the GPC value. Thus, it can be concluded that M_n obtained by GPC in these conditions is close to the actual value.

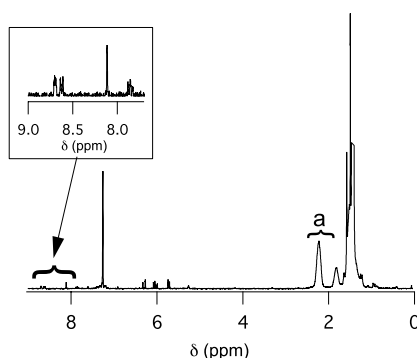


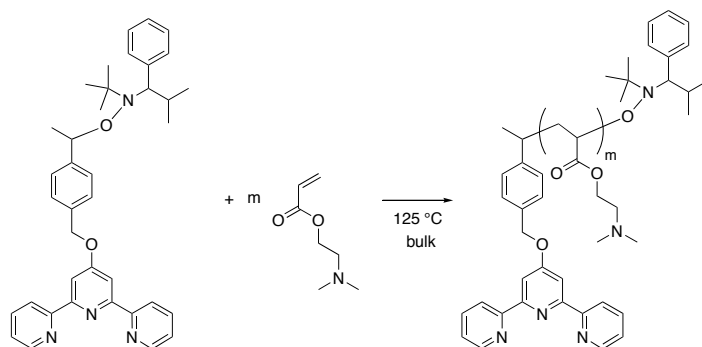
Figure 3.3: ¹H-NMR of the terpyridine functionalized poly(*t*-butyl acrylate) in CDCl₃. The typical terpyridine signals are highlighted in the inset. The (a) area designs the backbone region of the PtBA.

3.2.3.3 Polymerization of 2-(dimethylamino)ethyl acrylate

2-(Dimethylamino)ethyl acrylate (DMAEA) is an important water-soluble monomer bearing a tertiary amine. The DMAEA based polymers and copolymers have wide applications in the pharmaceutical, surfactant, and water treatment industries [22]. Normally, DMAEA polymers are synthesized by conventional free-radical polymerization, which, however, cannot be used to prepare block copolymers. Cunningham et al. were the first to demonstrate the possibility to synthesize well-defined PDMAEA polymers using controlled radical polymerization with nitroxides [23]. However, since they have used a different alkoxyamine-nitroxide system, it remains a challenge to obtain well-defined PDMAEA with our terpyridine functionalized alkoxyamine. To the best of our knowledge, nothing has been yet reported on that issue.

The homopolymerization of 2-(dimethylamino)ethyl acrylate was initiated by the terpyridine end-functionalized alkoxyamine previously described (see Section 3.2.2), in the presence of a small excess of nitroxide (Scheme 3.8). As discussed previously, the additional nitroxide shifts the equilibrium towards the dormant species and hence reduces the rate of propagation. This affords a better control over the polymerization process. Table 3.3 summarizes a selection of results obtained for the polymerization of this monomer. Polymerizations were performed in bulk and high conversions could be reached (see Sample 4) while maintaining rather narrow MW distributions. Polydispersities range from 1.21 to 1.34, higher than for a well-behaved NMP, but still reasonably low for the polymerization of an acrylate bearing a tertiary amine group.

This work was conducted outside the main topic of this thesis, and any mentions to this polymer will be done in the following. However, although no kinetic investigations are provided in this section, it is straightforward to conclude on the versatility of the terpyridine alkoxyamine developed in this chapter. Since the synthesis of polymers based on styrene or *tert*-butyl acrylate by NMP is not a real issue, the success of DMAEA polymerization demonstrates the universality of our alkoxyamine to synthesize well-defined terpyridine end-functionalized polymers.



Scheme 3.8: Synthesis of terpyridine functionalized poly(2-(dimethylamino)ethyl acrylate) by NMP.

Sample	Polymerization conditions ^a	M _{n,th} ^{b,c}	M _n ^b (GPC)	PDI (GPC)	M _n ^b NMR	Conversion ^d (%)
1	240 min in bulk at 110 °C	85,800	9,800	1.29	24,300	28
2	360 min in bulk at 110 °C	85,800	10,400	1.31	32,900	38
3	180 min in bulk at 125 °C	85,800	11,300	1.34	37,200	43
4	360 min in bulk at 125 °C	85,800	10,000	1.21	57,200	67

^a 5 % of free nitroxide were systematically added with respect to the alkoxyamine content.

^b Values are indicated in *g/mol*.

^c Theoretical molecular weight is calculated at a final conversion of 100 %.

^d Conversion is determined from the ratio M_n(NMR)/M_{n,th}.

Table 3.3: Representative results obtained by the polymerization of 2-(dimethylamino)ethyl acrylate by the terpyridine functionalized initiator.

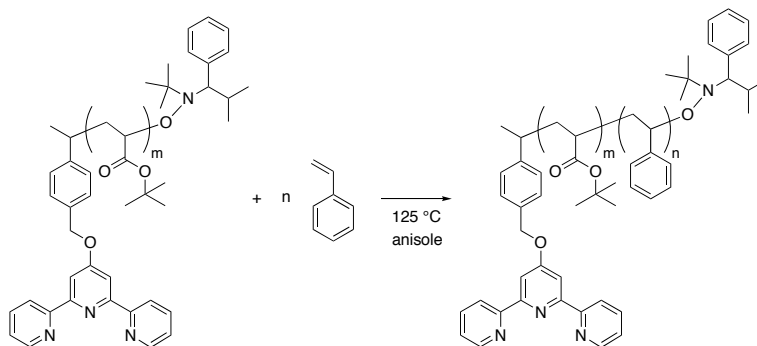
3.2.3.4 Sequential block copolymerization of styrene and *tert*-butyl acrylate

This section aims at demonstrating the “living” character of the used NMP process by performing sequential block copolymerization. As explained in the first section of this chapter (Section 3.2.1) some terminations occur in the beginning of the NMP process, leading to the Persistent Radical Effect [12]. Then, an equilibrium is reached between active species and dormant ones. This steady-state led to well-defined polymers where all polymer chains have the same composition with respect to the initiating fragment, but also to the end group. Hence, after purification steps to remove all the unreacted monomers (polymerizations were commonly stopped at a conversion below 90 % to avoid further terminations), this end group can reinitiate the polymerization of a second monomer.

This is one of the interesting features of preparing block copolymers by nitroxide-mediated, ATRP, or RAFT procedures that the initial block

can be fully characterized and stored before proceeding to the polymerization of the second block. This is totally unlike anionic procedures, and is extremely useful from a synthetic viewpoint. However, the same criteria than the ones previously described (Section 3.2.3.2) are also valuable implying a fast initiation towards the propagation rate. Moreover, one should pay attention to the relative reactivities of the different comonomers. In this respect, polymerization of acrylates starting from a poly(styrene) should not be as easy than the polymerization of styrene starting from poly(acrylates). Moreover, the former case requires the use of an excess of free nitroxide as previously demonstrated [24].

In this section, we deal with the synthesis of terpyridine end-functionalized PS-*b*-PtBA starting from PtBA macroinitiator (Scheme 3.9). The different screened experimental conditions are summarized in Table 3.4. In this case, the use of solvent is relevant, on the one hand, due to the high viscosity of the initial macroinitiator, and on the other hand, to afford a better control over the polymerization rate.



Scheme 3.9: Synthesis of terpyridine functionalized poly(*tert*-butylacrylate)-*b*-poly(styrene) diblock copolymer via NMP.

GPC traces were helpful to determine polydispersity indices (see Table 3.4), whereas $^1\text{H-NMR}$ was used to calculate the respective block ratio's and molecular weight by integration with respect to the terpyridine signals (see Figure 3.4). No shoulder on the lower molecular weight side of the distribution was observed. This demonstrates that the PtBA macroinitiator totally initiates the polymerization of styrene and that no

Sample	Polymerization conditions ^a	M _{n,th} ^{b,c}	M _n ^b (GPC)	PDI (GPC)	M _n ^b NMR	Conversion ^d (%)
1	315 min in 40 wt% anisole ^e	19,900	25,700	1.16	23,400	21
2	360 min in 40 wt% anisole ^e	29,600	27,400	1.15	25,400	21
3	960 min in 63 wt% anisole ^f	25,000	34,700	1.16	39,100	54
4	1,140 min in 70 wt% anisole ^f	13,500	28,500	1.11	30,800	38

^a Polymerizations are always performed at 125 °C in argon-filled Schlenk tubes, without any further additions of nitroxide.

^b Values are indicated in *g/mol*.

^c Theoretical molecular weight is calculated at a final conversion of 100 %.

^d Conversion is determined from the ratio M_n(NMR)/M_{n,th}.

^e The DP of the macroinitiator was 150.

^f The DP of the macroinitiator was 200.

Table 3.4: Representative results obtained for the polymerization of styrene by the terpyridine functionalized poly(*tert*-butyl acrylate) macroinitiator.

unreacted PtBA macroinitiator is observed after the polymerization of the PS block. Moreover, this also suggests that no auto-initiation of styrene occurs since no homopolymerization is observed.

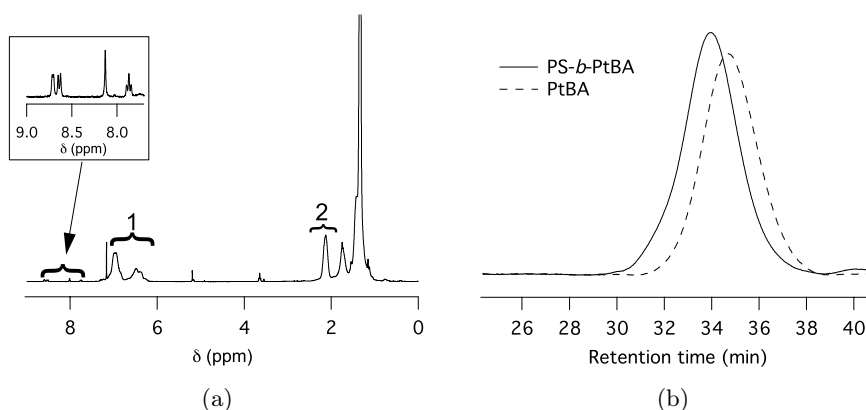
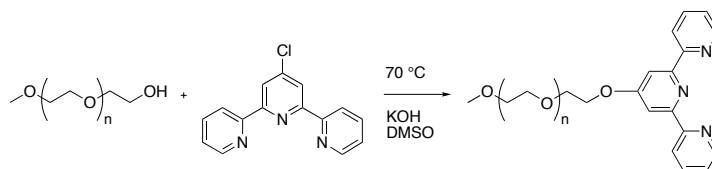


Figure 3.4: (a) ^1H -NMR in CDCl_3 and (b) GPC traces of a terpyridine functionalized poly(*tert*-butyl acrylate)-*b*-poly(styrene) diblock copolymer. The NMR typical terpyridine signals are highlighted in the inset. The (1) and (2) areas correspond to the aromatic region of the PS and the characteristic backbone signal of the PtBA, respectively.

3.2.4 Synthesis of terpyridine functionalized poly(ethylene oxide)

In this thesis, we are planning the coupling of hydrophobic polymer blocks (poly(styrene)) to a hydrophilic one (poly(ethylene oxide)) in order to obtain amphiphilic block copolymers. Terpyridine functionalized poly(ethylene oxide) blocks have been obtained via synthetic route (iii), i.e. the introduction of the terpyridine unit through chemical modification of an existing end-group on the polymer. In this respect, we took advantage of the commercial availability (Polymer Source, Inc.) of well-defined ω -hydroxy-functionalized poly(ethylene oxide) blocks, prepared by living anionic polymerization and thus characterized by a very low polydispersity index. These functional poly(ethylene oxide)s were end-capped with a terpyridine via an etherification reaction starting from 4'-chloroterpyridine and hydroxy functionalized poly(ethylene oxide) (Scheme 3.10). They will be further used for the preparation of metallo-supramolecular copolymers (see Section 3.3).



Scheme 3.10: Synthesis of the terpyridine functionalized poly(ethylene oxide).

3.3 Synthesis and characterization of PS-[Ru^{II}]-PEO diblock copolymers

3.3.1 Introduction: the “key and lock” principle

The self-association of synthetic molecules via non-covalent interactions into well-defined architectures is the field of supramolecular chemistry, also known as “*chemistry beyond molecules*” as defined by the Nobel laureate Jean-Marie Lehn [25]. Self-recognition and self-assembly processes represent the basic concepts of supramolecular chemistry and the interactions involved are usually weaker than covalent bonds (e.g., van der Waals forces, hydrogen-bonding, coordinative interactions). In this work we focused on the chelation of one or two tridentate terpyridine ligands around a transition metal ion. The choice of this metal ion is crucial: in order to construct supramolecular AB diblock copolymers, the supramolecular interaction must exclusively lead to an AB “*hetero-assembly*” and not to an AA or BB “*homo-assembly*”. This implies two requirements. Firstly, the self-assembly process should obey to the “key and lock” principle in order to selectively couple A and B. Secondly, if a labile metal complex is used, ligand exchange would take place, and AB, AA, and BB complexes would coexist in a statistical mixture. Therefore, the stability of the metal complex is a key to form “*hetero-assembly*” diblock copolymers. It has been shown [26, 27] that the couple terpyridine/ruthenium is a good candidate. In fact, Ru(III) forms a very stable *mono*-complex with one terpyridine ligand, while Ru(II) forms a very stable *bis*-complex with two terpyridine ligands. Therefore, the stable *mono*-complex can be easily isolated, and in a second step, reacted with another terpyridine moiety, leading exclusively to a heteroleptic complex (see Figure 3.5). Besides ruthenium terpyridine complexes, heteroleptic complexes from cobalt(III)/terpyridine have been developed in this thesis, leading to other AB “*hetero-assembly*” diblock copolymers.

3.3.2 Formation of the *mono*-complex

The general strategy used for the synthesis of *mono*-complexes from low MW terpyridine ligands cannot be translated to polymers. In fact, precipitation of the *mono*-complex in the reaction media is the lead-

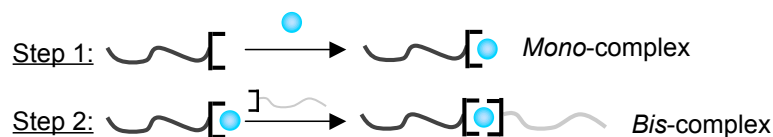


Figure 3.5: Schematic representation of the “key and lock” principle (block A in grey, block B in red, metal ion as blue dots).

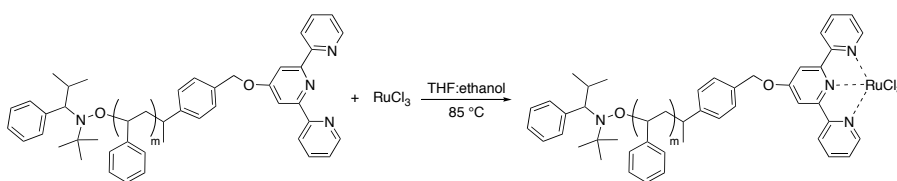
ing force for the formation of low MW *mono*-complexes. When polymers bearing terpyridine are used as ligands, there is no difference in solubility between the free terpyridine functionalized polymer and the *mono*-complex, since the solubility of the system is only governed by the solubility of the polymer backbone. Therefore, an initial strategy has been developed by Lohmeijer and Schubert, using dry degassed *N,N*-dimethylformamide (DMF) and by adding the dried terpyridine functionalized polymer dropwise [1]. However, the yield of the *mono*-complex was low.

Firstly, in collaboration with the group of Prof. Schubert, we have used *N,N*-dimethylacetamide (DMA) instead of DMF, and the initial results seemed promising, leading to very high yields (>85 %). In contrast to DMF, DMA has no hydrogen in alpha of the carbonyl, and cannot thus undergo decarbonylation reaction, forming CO and dimethylamine. Since the carbonyl moiety can act as ligand, it could substitute one or more chloride around Ru(III) [28].

However, unreproducible results were obtained after several attempts realized on the terpyridine end-functionalized poly(ethylene oxide). A new strategy has been therefore developed, starting from poly(styrene) instead of poly(ethylene oxide) as the initial block and RuCl₃·xH₂O as the metal salt. These compounds have been stirred in a THF:ethanol mixture at a lower temperature (85 °C) than in the case of the DMA-strategy (120 °C) to circumvent the problem of nitroxide chain-end reactivity. The obtained yields are still very high (~90 %) and sorts out problems of reproducibility previously encountered.

In the first step, terpyridine-functionalized poly(styrene) was reacted with ruthenium chloride in THF:ethanol mixture leading to a stable

mono-complex (Scheme 3.11). The formation of the *mono*-complex can be followed essentially by UV/Vis spectroscopy and ^1H -NMR. In UV/Vis spectroscopy, a band appears at ca. 400 nm, that can be attributed to the metal-to-ligand charge transfer band (MLCT), whereas in NMR, the signals of the terpyridine disappear due to the paramagnetic nature of the metal-ion [29]. Figure 3.6 shows the UV/Vis and the ^1H -NMR spectrum of the PS-[RuCl₃]. Finally, Gel Permeation Chromatography (GPC) was systematically performed to check the purity of the *mono*-complex.



Scheme 3.11: Formation of the *mono*-complex from the poly(styrene) block.

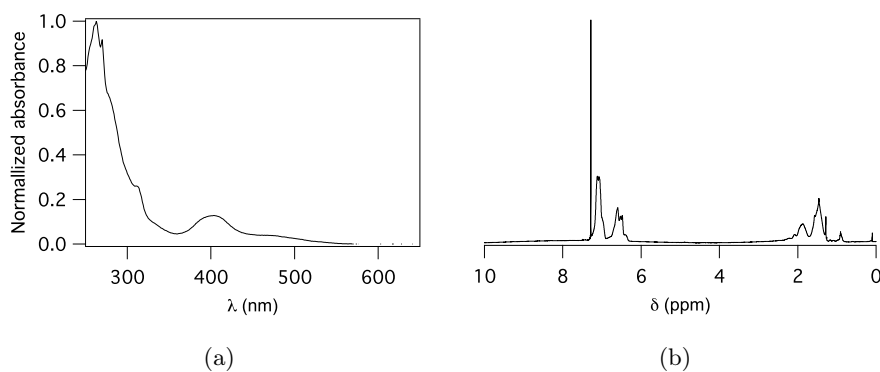
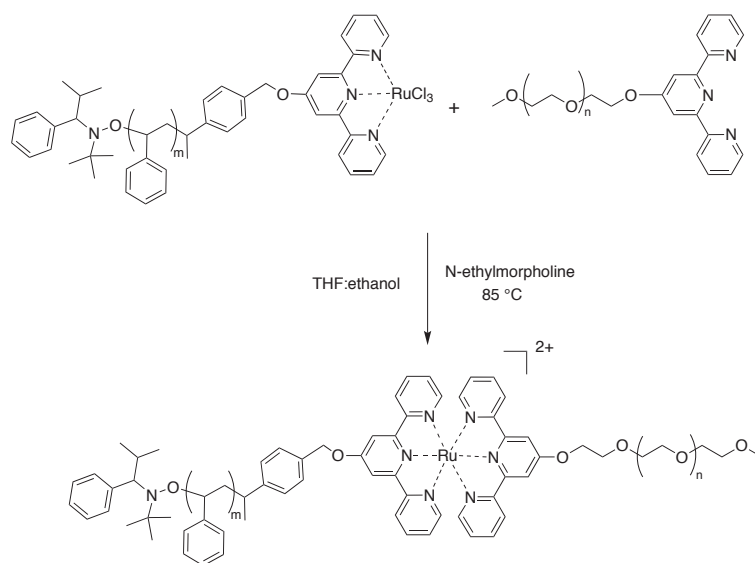


Figure 3.6: UV/Vis spectrum in CHCl₃ (a) and NMR spectrum in CDCl₃ (b) of the *mono*-complex from the poly(styrene) block.

3.3.3 Formation of the *bis*-complex

The last step deals with the formation of the *bis*-complex, starting from the poly(styrene)-based *mono*-complex and from a poly(ethylene oxide) bearing the free terpyridine group (Scheme 3.12).



Scheme 3.12: Formation of the heteroleptic Ru(II) *bis*-complex starting from the poly(styrene)-based *mono*-complex and the free terpyridine end-functionalized poly(ethylene oxide) block.

The mechanism of this reaction is more complex than for the *mono*-complex formation. Roughly, Ru(III) is reduced to Ru(II), and the free terpyridine-functionalized polymer displaces the remaining chloride. Due to the low concentration of the chain ends, the reaction is kept several days at high temperature, in a very small amount of solvent. Then, a large excess of counter-ions (NH_4PF_6) is added at room temperature, in order to enhance the solubility of the complex in organic media. The original procedure developed by Lohmeijer et al. [1] was designed for the synthesis of low-weight supramolecular block copolymers ($\text{PS}_{20}\text{-[Ru]-PEO}_{70}$). However, an improved methodology has been further developed in this PhD-thesis for the synthesis of higher MW supramolecular block copolymers, since the previous one led to very low yields after purifica-

tion (<10 %). Firstly, the use of *mono*-complex of poly(styrene) has the advantage to lead to an increased yield compared to the reverse situation, i.e. the coupling between PEO-[RuCl₃ with PS-. This difference is tentatively attributed to an enhanced solubility and/or accessibility of the ruthenium terpyridine *mono*-complex whenever it is associated to a PS chain. In this respect, a PEO chain could somewhat interact with the -[RuCl₃ *mono*-complex and create a shielding shell around it that would be detrimental for the next coupling reaction. Similar effects have already been reported in the literature for the synthesis of metallo-supramolecular *star*-like block copolymers [30, 31]. The concentration of the polymer plays a significant role since the higher the concentration, the better the yield. Compared to the previously used methodology, a larger amount of alcohol is used. Since it acts as a reducing agent, it also promotes the *bis*-complex formation. However, the amount of ethanol cannot be increased too much because it acts also as a precipitant for the poly(styrene) block. The reaction is conducted in a THF:ethanol (3:2) mixture at 80 °C until no more changes are observed in the UV/Vis spectrum. The UV/Vis spectrum then reveals a metal-to-ligand charge transfer band at 490 nm and a new-band at 307 nm (π - π^* transitions) [32], which are typical for *bis*-terpyridine ruthenium(II) complexes (Figure 3.7) [33]. The characteristic band at 400 nm of the *mono*-complex has disappeared, indicating the success of the reaction.

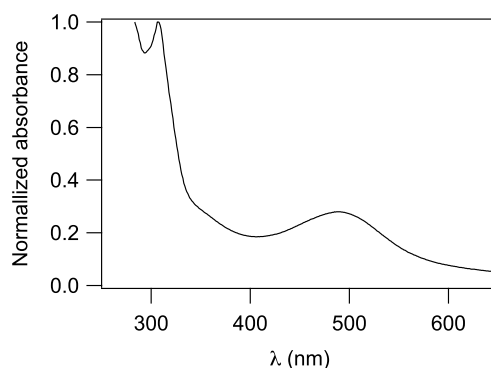


Figure 3.7: UV/Vis spectrum in CHCl_3 of a poly(styrene)-[Ru]-poly(ethylene oxide) metallo-supramolecular block copolymer.

Since the yield of the coupling reaction is not 100 %, the accordingly obtained PS-[Ru]-PEO metallo-supramolecular block copolymer is contaminated by PS-[RuCl₃] and PEO-[] blocks that should be separated from the desired product. Several techniques could be applied:

- i gel permeation chromatography on columns ;
- ii dialysis ;
- iii preparative gel permeation chromatography ;
- iv washing techniques.

For polymers with molecular weight up to 10,000 *g/mol*, gel permeation chromatography on columns (Bio-Beads, SX1) is a reliable method, as previously shown by Lohmeijer et al. [1]. However, this method could not be translated to higher MW polymers. Also silica columns cannot be used because of the strong interactions between the polymers to be separated and the column material. Dialysis is a valuable method but it implies to find a proper cut-off of the dialysis bag. The third technique described in this section concerns the use of preparative gel permeation chromatography. In collaboration with the group of Prof. du Prez (Ghent, Belgium), we have successfully applied this technique to purify

our products. Nevertheless, as it has been already published in the literature [34], *bis*-terpyrine metal-complexes exhibit strong interactions with GPC columns, and therefore, the use of *N,N*-dimethylformamide with additives like NH_4PF_6 is required as eluent. Moreover, this preparative gel permeation chromatography technique requires tedious evaporation processes to remove DMF, as well as, further extractions to remove all the added salt.¹

All these limitations convinced us to develop a better purification process based on several extractions with selective solvents of either the PS or the PEO blocks. The results are very convincing according to ^1H -NMR and gel permeation chromatography (Figure 3.3.3). In a first step, the products of the reaction are washed with water during several days, in order to get rid off the uncomplexed poly(ethylene oxide). Then, in a second step, reaction products are treated with diethylether, since this solvent is selective for uncomplexed poly(styrene). As shown in Figure 3.3.3-(a), the residue of water shows only some poly(ethylene oxide) signals, and the residue of diethylether exhibits only poly(styrene) signals. After these purifications, the ^1H -NMR spectrum of the product reveals a poly(styrene)/poly(ethylene oxide) ratio which is in agreement with the one expected for the desired PS-[Ru]-PEO block copolymer.

Finally, efforts have been made in order to improve the yield of this synthesis to reach about 30% after purification procedures. It should be emphasized that the major limit of this coupling reaction is the stringent purification procedure.

Finally, this coupling reaction can be easily followed by GPC (Figure 3.3.3-(b)). A lower retention time is indeed observed for the PS-[Ru]-PEO copolymers compared to the starting PEO- and PS-[RuCl₃] blocks. Although PS-[RuCl₃] exhibits a higher molecular weight than the PEO-, its retention time is larger than for PEO-. This difference can be accounted for a smaller hydrodynamic volume of a PS chain in *N,N*-dimethylformamide compared to a PEO one [36].

¹It should be noticed that recently, the group of Prof. U.S. Schubert has improved the preparative gel permeation chromatography technique [35] by using THF instead of DMF coupled with a PSS Gram preparative 100 Å column.

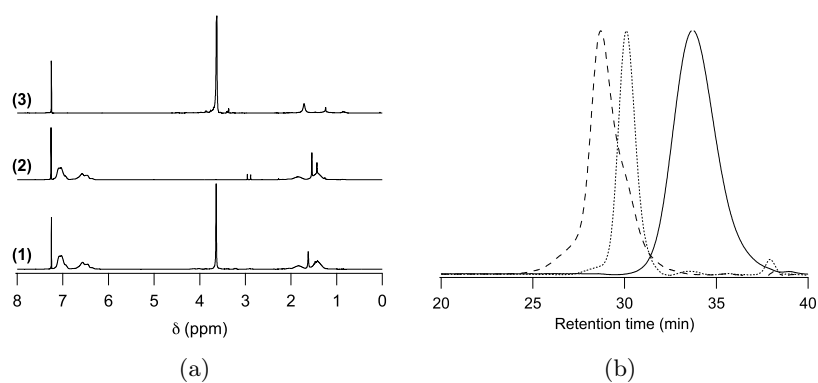


Figure 3.8: (a) ¹H-NMR spectra in CDCl₃: metallo-supramolecular block copolymer poly(styrene)-[Ru]-poly(ethylene oxide) after purification (1); residue after washing with diethylether (2); residue after washing with water (3) and (b) GPC traces (eluent; 5 mM NH₄PF₆ in *N,N*-dimethylformamide) of a poly(styrene)-[Ru]-poly(ethylene oxide) metallo-supramolecular block copolymer after purification (*dashed*-line) and its precursors RuCl₃ *mono*-complex of poly(styrene) (*solid*-line) and terpyridine terminated poly(ethylene oxide) (*dotted*-line).

3.4 Towards the synthesis of PS-[Co^{III}]-PEO diblock copolymers

3.4.1 Motivations

The previous section dealt with the formation of heteroleptic *bis*-complexes starting from ruthenium(III) chloride. In the first step, a *mono*-complex of Ru^{III} was isolated and characterized by UV/vis analysis. In a second step, this *mono*-complex was reduced to Ru^{II} in the presence of an organic reductor, and the chlorides were replaced by the second terpyridine ligand leading to a heteroleptic *bis*-complex. However, these Ru^{II} *bis*-complexes are not prone to ligand exchange. This latter point is in contradiction with reversibility properties. There are several options available to open the metal-terpyridine complexes:

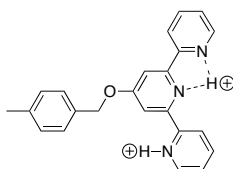
- i modification of the pH ;
- ii oxidation/reduction of the metal complex ;
- iii addition of a competitive ligand.

By adjusting the pH of the metal complex, ligand protonation (see Scheme 3.13) and metal hydroxide formation may take place leading to the opening of the complex [37]. Lohmeijer has previously shown that all the terpyridine metal-complexes remain intact by varying the pH from 3.0 to 10.0 whatever the metal used (Mn^{II}, Fe^{II}, Ru^{II}, Co^{II}, Co^{III}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, Hg^{II}) but decompose at extreme pH [38]. Moreover, Ru^{II} and Ni^{II} terpyridine complexes are stable over the whole pH-range.

The second strategy implies the use of redox reactions. By choosing an appropriate oxidant/reductor couple, it may be possible to change the oxidation state of the metal coordinated to the terpyridine and therefore, to open the complex. For instance, since the oxidation potential of Ce^{III}/Ce^{IV} (1.43 V vs. saturated calomel electrode (SCE)) is higher than Ru^{II}/Ru^{III} (1.19 vs. SCE), Cerium(IV) can be used as an oxidant for the terpyridine-ruthenium(II) complexes. This method was successfully applied by Fustin et al. for the formation of nanoporous thin films [39]. Starting from a PS-[Ru]-PEO metallo-supramolecular

block copolymer bearing the *bis*-terpyridine ruthenium(II) at the junction of the two blocks, thin films with cylindrical PEO microdomains oriented normal to the substrate were obtained, and after immersing the films in a CeSO₄. 0.1 M H₂SO₄ solution, PEO blocks were successfully removed as further evidenced by AFM, XPS and X-ray reflectivity measurements [39]. However, due to the instability of Ce^{IV} at pH higher than 1.0, the opening of the complexes, implies harsh conditions that limit the range of possible applications.

The third strategy requires the use of a competitive ligand. This task seems not as easy as the two former strategies since terpyridine is a tridentate chelating ligand leading to rather high ion-dipole interactions and hence to very high stability constants for the complexes. Some experiments have however shown that the addition of a large excess of a competitive ligand (hydroxyethyl ethylene-diaminetriacetic acid sodium salt HEEDTA) did allow the opening of the initial *bis*-2,2':6',2''-terpyridine ruthenium(II) complex [40]. However, a very large excess of the competitive ligand (10⁵ molar excess) was required and the sample needed to be heated at 60 °C for a few hours. HEEDTA is also known to be an oxidant, and therefore the integrity of the polymer backbone is not guaranteed. Here again, harsh conditions are needed to open the complexes.



Scheme 3.13: Doubly-protonated form of the terpyridine ligand.

In any case, ruthenium(II) complexes have been shown to be highly stable, and therefore are really difficult to open. Thus, the use of a terpyridine metal complex that could be more easily opened is required for the formation of “smart” stimuli-responsive systems. As previously explained in Section 3.3.1, the strategy to obtain heteroleptic *bis*-complex is based, in a first step, on the formation and isolation of a *mono*-complex, followed in a second step by the addition of a free ligand leading to the

bis-complex. *Mono*-complexes of terpyridine have been reported with a variety of transition metal ions such as Fe^{III} , Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} [41–46]. However, the formation of a heteroleptic *bis*-complex is not suitable with these metal ions due to the lability of the metal-ligand *mono*- or *bis*-complexes. Indeed, formation of a *bis*-complex starting from these *mono*-complexes will lead to a mixture of A-A, B-B, and A-B dimers.

In contrast to cobalt(II) complexes, which are labile and undergo ligand exchange very rapidly, statistical cobalt(III) complexes are kinetically inert and undergo ligand exchange very slowly. Thus, a selective approach could be developed in principle for the formation of heteroleptic *bis*-complexes of terpyridine- Co^{III} . A very common procedure for the synthesis of cobalt(III) complexes involves oxidation of the corresponding cobalt(II) salt in the presence of the desired ligands. Two different strategies will be described in the following sections: the first one is based on a synthesis in aqueous medium, whereas the second one takes place in organic medium.

Firstly, the formation of *mono*- and *bis*-complexes will be studied using model ligands (see Figure 3.4.1) in order to gain a closer look onto the characteristic features (^1H -NMR, UV/Vis) of these peculiar metal complexes. Furthermore, these model ligands bear an oxygen-substituent at the 4'-position in order to mimic the terpyridine-polymer functionality.

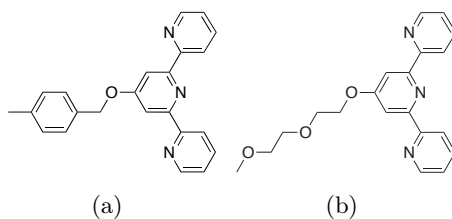


Figure 3.9: (a) Chemical structure of the 4'-(4-methylbenzyloxy)-2,2';6',2''-terpyridine and (b) 4'-(2-[1-methoxyethoxy]ethoxy)-2,2';6',2''-terpyridine.

3.4.2 Synthesis and characterization of heteroleptic Co^{III} model complexes

This work, conducted in our laboratory, has been developed by C. Mugemana within the framework of his master-thesis [47].

3.4.2.1 In aqueous media

Firstly, a solution containing Co^{II}-ions and 4'-(2-[1-methoxyethoxy]-ethoxy)-2,2';6',2''-terpyridine was oxidized by bubbling air in the presence of sodium nitrite in an aqueous buffer (pH=6). In fact, the nitro-counterions are of special interest since they are considered as strong field ligands, resulting in an increase of the splitting parameter, Δ_o (see Figure 3.10), and thus, an increase of the stability of the formed complex [48]. This first step leads to the formation of a *mono*-terpyridine-trinitrocobalt(III) complex.

By far, the largest number of cobalt(III) complexes are prepared by oxidation of the cobalt(II) ion in the presence of the ligand. Such a procedure is well suited for ligands which are inert toward oxidation and show a relatively strong coordinating ability. In our case, the complex was isolated in the +3 oxidation state and was observed to be diamagnetic, in agreement with a d⁶ low spin configuration. As shown in Figure 3.11, the ¹H-NMR spectrum is sharp, well-resolved and fully assigned (see Experimental section for further details).

However, the main drawback with the nitro-ligands is their too strong coordination ability which prevent the efficient substitution of those 3 ligands by a terpyridine, needed to obtain an heteroleptic *bis*-complex. Therefore, the nitro-ligands must be replaced by more labile ones, like chloride ones. The initial *mono*-terpyridine-trinitrocobalt(III) complex was thus treated with a concentrated aqueous hydrochloric solution for several minutes. The resulting trichloro-compound precipitated from the solution as a grey product.

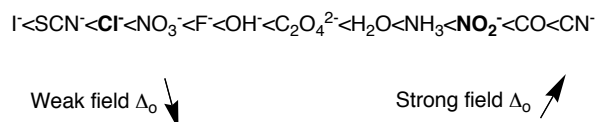


Figure 3.10: Classification of the hardness of classical ligands: from “weak-field” ligands to “strong-field” ones.

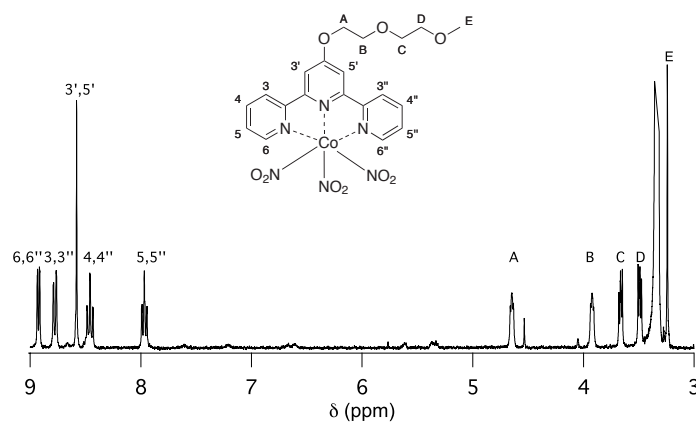


Figure 3.11: ^1H -NMR spectrum (300 MHz/DMSO- d_6) of the 4'-(2-[1-methoxyethoxy]ethoxy)-2,2';6',2''-terpyridine trinitro cobalt(III).

The final step concerns the formation of the heteroleptic *bis*-complex by addition of the second terpyridine ligand. As chloride ligands are considered as weak ligands (see Figure 3.10), they should be easily replaced by the tridentate chelating terpyridine giving rise to a heteroleptic cobalt(III) *bis*-complex. Several experimental setups (temperature, reaction time, solvent) have been screened to determine the best conditions. However, the formation of the two homoleptic complexes beside the heteroleptic one has been always observed in all our attempts. This could be explained by the moderate inertness of the cobalt(III) complexes over a prolonged time scale. Nevertheless, the compounds are easily purified through a flash chromatography column to afford 50 % of pure heteroleptic *bis*-terpyridine cobalt complex (III), which has been further characterized with ¹H-NMR, as depicted in Figure 3.12.

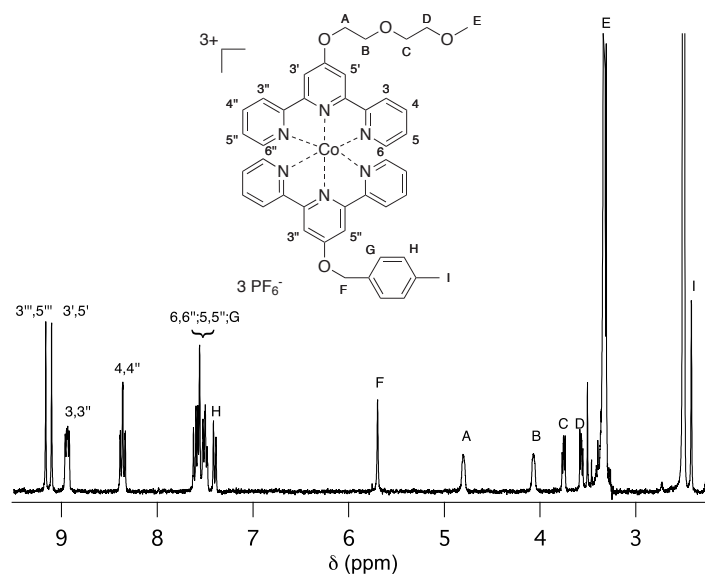
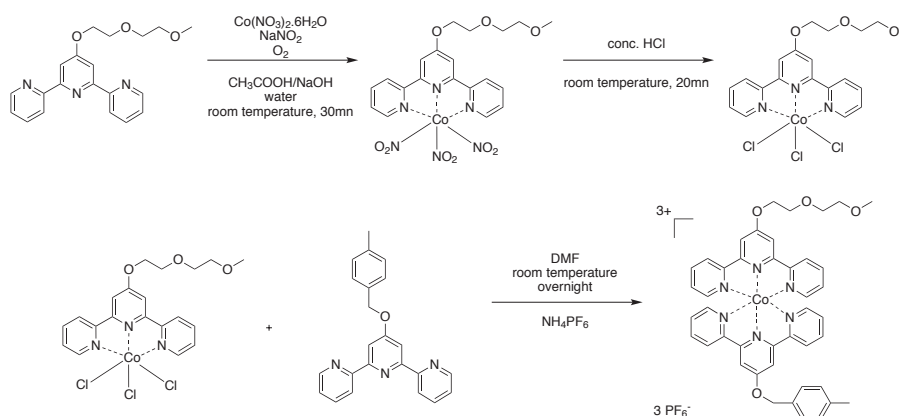


Figure 3.12: ¹H-NMR spectrum (300 MHz/DMSO-d⁶) of the heteroleptic *bis*-terpyridine cobalt complex (III).

The general synthetic pathway leading to the formation of the heteroleptic *bis*-complex is summarized in Scheme 3.14.



Scheme 3.14: Synthetic pathway for the formation of heteroleptic *bis*-complexes of terpyridine-cobalt(III) in aqueous media.

3.4.2.2 In organic media

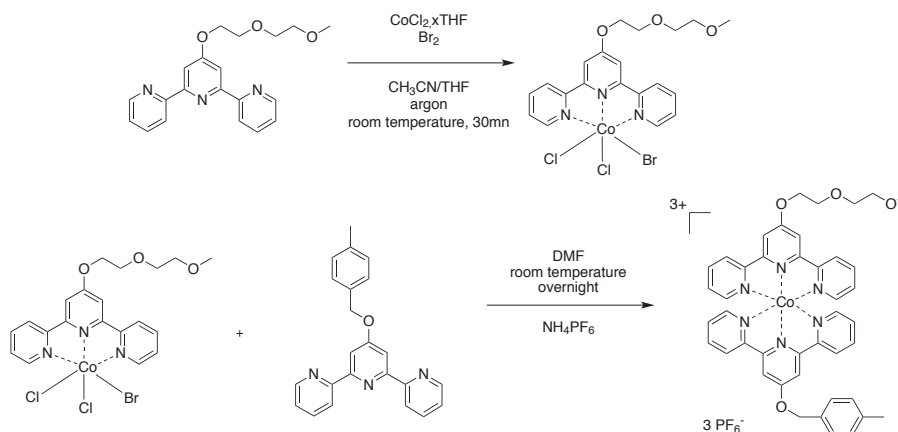
Tetrahydrofuran reacts readily with dihalides of the first transition metal series to form complexes which are thermally stable at room temperature [49, 50]. We took advantage of this situation to prepare $\text{CoCl}_2 \cdot x\text{THF}$ as initial metal complex. Unlike more polar solvents, THF is a weak ligand, and therefore, requires the use of anhydrous conditions to prepare the complex. In fact, water molecules could easily displace THF ones as ligands.

As shown in the following scheme (Scheme 3.15), the reaction was carried out in two steps. Firstly, the anhydrous cobalt chloride salt and freshly distilled THF were mixed together in a Schlenk tube filled with argon. In a second step, the terpyridine ligand was added in CH_3CN , since the *mono*-complex of terpyridine-cobalt(II) is not readily soluble in THF. Finally, a 5-fold excess of a bromine solution was added to oxidize the cobalt(II) complexes into cobalt(III) complexes. The use of bromine is relevant in this case since it also acts as a ligand for cobalt(III).

Although purification was still needed at the end of this reaction to separate the desired *mono*-complex from the *bis*-complex, the yield was better (85 %) than in the previously described aqueous procedure (see Section 3.4.2.1). Water could be used to separate these 2 compounds

because, due to its non-ionic nature, the *mono*-complex precipitates out from an aqueous solution, whereas the *bis*-complex is still soluble. However, this purification procedure is not well suited since water molecules displace the chlorine ligands leading to *bis*-complex formation.

Thus, taking into account that the proportion of homoleptic *bis*-complex is quite low at the end of the *mono*-complex synthesis (15 %), it was decided to use the *mono*-complex without any further purification to synthesize the heteroleptic *bis*-complex. The synthesis of the *bis*-complex was performed in the same conditions than for the aqueous procedure, but it leads to a better yield (60 %).



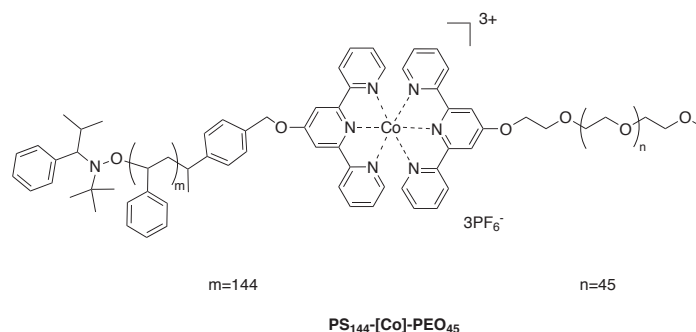
Scheme 3.15: Synthetic pathway for the formation of heteroleptic *bis*-complexes of terpyridine-cobalt(III) in organic media.

Finally, it has been shown that it is possible to prepare *mono*-terpyridine cobalt(III) complexes as well as heteroleptic *bis*-terpyridine cobalt(III) complexes starting from model compounds with two different synthetic pathways, the first one with an aqueous precursor of Co^{II} and the second one with an organic precursor, $\text{CoCl}_2 \cdot x\text{THF}$. The latter route is much more versatile, since it does not rely on a difference of solubility between the *mono*- and the *bis*-complex. This should be an advantage considering the construction of new polymeric materials where the two building blocks are held together through a *bis*-terpyridine cobalt(III) complex. In fact, when using polymers, the solubility is no longer gov-

erned by the metal complex but rather by the polymer backbone. Therefore, a simple precipitation-based strategy will fail.

3.4.3 Towards the formation of easily reversible heteroleptic diblock copolymers

The last step of this study deals with the construction of supramolecular block copolymers with a *bis*-terpyridine cobalt(III) complex at the junction between the two blocks in order to lead to easily reversible block copolymers (see Scheme 3.16). Preliminary experiments have been performed to translate the synthesis of *mono* and *bis*-complexes from model ligands to terpyridine end-functionalized polymers. Starting from the work performed with the model ligands, two strategies can be applied: the first one in aqueous medium and the second one in organic medium.



Scheme 3.16: Chemical structure of the supramolecular block copolymer containing a *bis*-terpyridine Co^{III} complex at the block junction.

As previously described in Section 3.4.2.2, the formation of *mono*-complexes in THF could be easily applied to polymers, since it is no longer based on a precipitation strategy. Several conditions have been screened to determine the best setup as reported in Table 3.5. After reaction, the solvents have been systematically concentrated under vacuum, the residue has been precipitated from THF into diethylether, and then analyzed by ¹H-NMR in DMSO-d₆. Whatever the used conditions (solvent, reaction time), a small amount (<35 %) of homoleptic *bis*-complex has been encountered, and, for the shorter reaction times, the signals of

free terpyridine have been detected. However, it is difficult to conclude at this stage whether the formation of *bis*-complex is due to the presence of water in the deuterated solvent (DMSO-d⁶). It has been thus decided to prepare the heteroleptic *bis*-complex directly after the *mono*-complex formation without any further purification. Therefore a solution of PS-[in THF has been added into the bromine solution containing essentially the *mono*-complex of Co^{III}. The mixture has been then allowed to stand for several minutes, followed by a precipitation of the residue into hexane. The purification procedure based on successive washings developed in Section 3.3.3 has been then applied leading to a yellowish powder. ¹H-NMR has been performed in order to determine the structure of the final product. Although the terpyridine signals were not well resolved, the ratio between the characteristic aromatic poly(styrene) signals and the characteristic aliphatic poly(ethylene oxide) signals was in agreement with the formation of a pure PS-[Co]-PEO heteroleptic complex.

	Solvent for CoCl ₂	Solvent for PEO ₄₅	Complexation time (min)	Oxidation time (min)	Results ^a
1	0.5 mL CH ₃ CN	1.0 mL THF	15	15	5 %
2	0.5 mL THF	1.0 mL THF	15	15	15 % ^b
3	0.5 mL CH ₃ CN	1.0 mL CH ₃ CN	15	overnight	20 %
4	0.5 mL CH ₃ CN	1.0 mL CH ₃ CN	1	1	35 %
5	1.0 mL CH ₃ CN	0.5 mL THF	1	1	10 % ^b
6	0.5 mL CH ₃ CN	1.0 mL THF	1	1	20 % ^b
7	1.0 mL CH ₃ CN	2.0 mL CH ₃ CN	5	5	10 % ^b

^a Results correspond to the amount of homoleptic *bis*-complex formed.

^b Presence of free terpyridine ligand was noticed on the ¹H-NMR spectrum.

Table 3.5: Selection of several experimental conditions screened out in order to study the complexation of PEO₄₅ by CoCl₂.

To further prove that a heteroleptic *bis*-complex was formed, micelles were prepared in water from the amphiphilic PS-[Co]-PEO metallo-supramolecular copolymer. Water was added dropwise to an initial DMF solution of the previously purified PS-[Co]-PEO copolymer in order to induce micellization. The solution was then dialyzed against water during several days. That amphiphilic PS-[Co]-PEO copolymer is indeed

formed has been ascertained by the presence of micellar objects in water as evidenced by dynamic light scattering (DLS) (see Figure 3.13). DLS measurements indicated the formation of micelles with a hydrodynamic radius, R_h , of 16 nm and a polydispersity index (PDI) of 0.11 (as determined by the Cumulant method) in agreement with the formation of rather monodisperse well-defined objects.

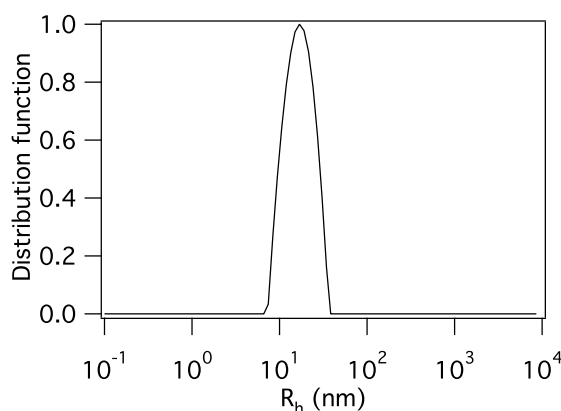


Figure 3.13: Typical Contin distribution obtained for micelles formed by the PS-[Co^{III}]-PEO supramolecular block copolymer in water.

Furthermore, it must be stressed that this final part relies on preliminary results. The synthesis of the heteroleptic PS-[Co^{III}]-PEO *bis*-complexes is not yet optimized and some questions remain on the interpretation of the NMR spectrum (absence of terpyridine signals). As an indirect proof, DLS measurements evidence the formation of micelles confirming the amphiphilic character of the synthesized PS-[Co^{III}]-PEO copolymer. To the best of our knowledge, this is the first time than such an amphiphilic copolymer is reported.

3.5 Conclusions

The synthesis of well-defined metallo-supramolecular block copolymers has been extensively described in this chapter. Starting from a universal alkoxyamine, an initiator bearing the terpyridine functionality has been synthesized, as a first step towards the formation of terpyridine end-functionalized polymers by NMP. This controlled radical polymerization process has been further extended to the formation of classical diblock copolymers. On the other hand, polymers with a lower molecular weight have been functionalized by end-group modification on the hydroxyl functionality of the chain end.

These building blocks have been further linked together by a two step self-assembly process, driven by the high stability of terpyridine-ruthenium(III) complexes. Thus, by reacting an isolated *mono*-complex with a second free terpyridine block, supramolecular diblock copolymers have been successfully obtained leading to *bis*-terpyridine(II) ruthenium complexes. The improvement of the synthesis as well as the purification process have been realized.

Finally, further investigation has been carried out to develop a new type of easily reversible diblock copolymers based on heteroleptic *bis*-complexes of cobalt(III)-terpyridine. An initial study has been performed on model ligands and then, successfully extended to polymers. The amphiphilic behaviour of such copolymers has been evidenced by DLS measurements. These final results definitively pave the way towards the formation of easily reversible diblock copolymers, since terpyridine-cobalt(III) *bis*-complexes can be opened under milder conditions than terpyridine-ruthenium(II) ones.

Experimental part

General: All reactions were run under argon unless otherwise noted. Solvents were distilled under argon over calcium hydride. Analytical thin-layer chromatography (TLC) was performed on commercial Merck plates coated with silica gel GF254 (0.25 mm thick). Silica gel for chromatography was either Rocc Silica gel 60Å (200-500 µm) or (40-63 µm) for the flash one. Aluminium oxide for chromatography was purchased from Acros (activated neutral/50-200 µm). Nuclear magnetic resonance (NMR) spectroscopy was performed on a Bruker AC 250, Bruker Avance 300 MHz, or Bruker Avance 500 MHz NMR spectrometer using mainly deuterated chloroform (CDCl₃) as solvent, the internal solvent peak acting as the reference. Gel permeation chromatography (GPC) was carried out on a Waters chromatograph (two PSS Gram columns 100 Å and 1000 Å in series) connected to a Waters 410 differential refractometer and a Waters UV detector with DMF or DMF+NH₄PF₆ as the carrier solvent. Preparative gel chromatography was performed in collaboration with the group of Prof. du Prez (UGhent-Belgium) on a Varian PLgel 10 µm-10³ Å.

Synthesis of the *N*-tert-Butyl- α -iso-propylnitrone: A mixture of 2-methyl-2-nitropropane (25,0 g, 242 mmol), isobutylaldehyde (17,5 g, 242 mmol), ammonium chloride (12,9 g, 242 mmol), and 1000 mL of water were cooled to 0 °C in an ice bath, and 500 mL of diethyl ether were then added in order to dissolve partially the crystallized 2-methyl-2-nitropropane. Zinc powder (63,3 g, 968 mmol) was added in small portions over 1 hour under vigorous stirring. After 8 hours the mixture was filtered through a sintered glass filter and a layer of celite, and the residue was washed three times with 300 mL of methanol. The product was extracted four times with 500 mL of dichloromethane. The organic phases were combined and washed with 800 mL of brine (27 wt% NaCl saturated water), dried over magnesium sulfate, and concentrated in vacuo. After drying, a pale yellow oil was obtained (17,3 g, yield 50 %). ¹H-NMR (CDCl₃): δ = 6.53 (d, 1H; NOCH), 3.04 (m, 1H; CH₃CHCH₃), 1.36 (s, 9H; C(CH₃)₃), 0.97 (d, 6H; CH(CH₃)₂). TLC 10:1 ethyl acetate/methanol, R_f = 0.76

Synthesis of the 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide: *N*-tert-Butyl- α -iso-propylnitrone (27 g, 189 mmol) was dissolved in 500 mL of THF and the solution was cooled to 0 °C in an ice bath. A 3.0 M solution of phenylmagnesium bromide (126 mL, 378 mmol) in diethylether was added by a cannula at this temperature over 5 min. During the addition, some precipitate formed. The mixture was allowed to warm to room temperature. After 12 h, excess Grignard reagent was decomposed by the addition of 100 mL of concentrated ammonium chloride solution, followed by 300 mL of water until all solids had dissolved. The organic layers were combined, dried over magnesium sulfate, filtered, and concentrated in vacuo. Then, the residue was treated with a mixture of 2000 mL of methanol, 150 mL of concentrated NH₄OH, and

1,88 g (9,45 mmol) of $\text{Cu}(\text{OAc})_2$ to give a pale yellow solution. A stream of air was bubbled through the yellow solution until a change of color of the solution (30 min), and a few drops of *tert*-butyl peroxide were added. This mixture was concentrated in vacuo and the residue dissolved in a mixture of 2000 mL of chloroform, 500 mL of concentrated NaHSO_4 solution, and 2000 mL of water. The organic phase was separated, and the aqueous phase was extracted with 500 mL of chloroform. The organic layers were then combined, washed with 600 mL of saturated sodium bicarbonate solution (9 wt%), dried over magnesium sulfate, and concentrated in vacuo to give the nitroxide. This nitroxide was then purified by a low-flow column chromatography (hexane then 20:1 hexane/ethyl acetate) to afford the pure nitroxide. The compound corresponds to the second fraction, the yellow-orange colored one (Yield 65 %). NMR analysis is not possible here, since the product is paramagnetic. The product was found to be nicely crystalline when stored in the freezer. TLC 10:1 ethyl acetate/methanol, $R_f=0.76$

Synthesis of the 2,2,5-trimethyl-3-(1-(4'-chloromethyl)phenylethoxy)-4-phenyl-3-azahexane: To a solution of *p*-vinyl benzyl chloride (2.00 g, 9 mmol) and 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (1.38 g, 9 mmol) in 1:1 toluene/ethanol (100 mL), [*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminatol] manganese (III) chloride, (represented by the acronym (salen)MnCl), (0.86 g, 1.35 mmol) was added followed by sodium borohydride (0.68 g, 18 mmol) and *di*-*tert*butyl peroxide (1.32 g, 9 mmol). The reaction mixture was then stirred at room temperature for 12 hours, then partitioned between dichloromethane (100 mL) and water (200 mL). The aqueous layer was further extracted with dichloromethane. The combined organic layers were then dried with magnesium sulfate, and concentrated in vacuo. The crude product was purified by flash chromatography eluting with petroleum ether and gradually increasing to a 85:15 mixture of petroleum ether/dichloromethane. The desired compound corresponds to the first phase (2.94 g, yield 87 %). ^1H -NMR (CDCl_3 , both diastereoisomers): $\delta = 7.57\text{--}7.18$ (m, 18H; aromatic), 4.97 (q+q, 2H; HC-ON), 4.62 (s, 2H; Cl-CH_2 , minor), 4.59 (s, 2H; Cl-CH_2 , major), 3.47 (d, 1H; ON-CH , major), 3.36 (d, 1H; ON-CH , minor), 2.38 (m, 1H; $\text{CH}(\text{CH}_3)_2$, major), 1.67 (d, 3H; $\text{CH}_3\text{CH-ON}$, major), 1.58 (d, 3H; $\text{CH}_3\text{CH-ON}$, minor), 1.43 (m, 1H; $\text{CH}(\text{CH}_3)_2$, minor), 1.34 (d, 3H; CH_3CHCH_3 , major), 1.08 (s, 9H; $\text{C}(\text{CH}_3)_3$, minor), 0.93 (d, 3H; CH_3CHCH_3 , major), 0.81 (s, 9H; $\text{C}(\text{CH}_3)_3$, major), 0.56 (d, 3H; CH_3CHCH_3 , minor), 0.27 (d, 3H; CH_3CHCH_3 , minor).

Synthesis of the 2,2,5-trimethyl-3-(1-(4'-(4''-terpyridinyloxy)-methyl)-phenyl-ethoxy)-4-phenyl-3-azahexane: To a suspension of 2,6-bis-(2'-pyridyl)-4-pyridon (0,43 g, 1,71 mmol) and K_2CO_3 (0,92 g, 6,862 mmol) in dry DMF (10 mL) at 50 °C, a solution of 2,2,5-trimethyl-3-(1-(4'-(4''-terpyridinyloxy)-methyl)-phenyl-ethoxy)-4-phenyl-3-azahexane (0,63 g, 1,71 mmol) in dry

DMF (10 *mL*) was added dropwise. The reaction was stirred overnight under argon at 50 °C. The reaction mixture was then cooled, poured into cold water (100 *mL*) and extracted with dichloromethane (3*200 *mL*). The combined organic layers were dried over magnesium sulfate, filtered and concentrated in vacuo. The light brown residue was subjected to an AlO_x column filtration (1:1, hexane/dichloromethane) and recrystallized twice from ethanol to give a polycrystalline white powder (65 % yield). $^1\text{H-NMR}$ (CDCl_3 , both diastereoisomers): δ = 8.69 (m, 4H; $\text{H}_{6,6''}$), 8.62 (d, 4H; $\text{H}_{3,3''}$), 8.17 (s, 2H; $\text{H}_{3',5'}$, major), 8.16 (s, 2H; $\text{H}_{3',5'}$, minor), 7.82 (t, 4H; $\text{H}_{4,4''}$), 7.57-7.18 (m, 22H; aromatic, $\text{H}_{5,5''}$), 5.35 (s, 2H; tpyOCH_2 , major), 5.30 (s, 2H; tpyOCH_2 , minor), 4.97 (q+q, 2H; HC-ON), 3.47 (d, 1H; ON-CH , major), 3.36 (d, 1H; ON-CH , minor), 2.38 (m, 1H; $\text{CH}(\text{CH}_3)_2$, major), 1.67 (d, 3H; $\text{CH}_3\text{CH-ON}$, major), 1.58 (d, 3H; $\text{CH}_3\text{CH-ON}$, minor), 1.43 (m, 1H; $\text{CH}(\text{CH}_3)_2$, minor), 1.34 (d, 3H; CH_3CHCH_3 , major), 1.08 (s, 9H; $\text{C}(\text{CH}_3)_3$, minor), 0.93 (d, 3H; CH_3CHCH_3 , major), 0.81 (s, 9H; $\text{C}(\text{CH}_3)_3$, major), 0.56 (d, 3H; CH_3CHCH_3 , minor), 0.27 (d, 3H; CH_3CHCH_3 , minor).

General procedure for the polymerization of styrene: Styrene was subjected to an AlO_x -filtration before use in order to remove the stabilizer. A solution of the initiator, 2,2,5-trimethyl-3-(1-(4'-(4''-terpyridinyloxy)methyl)phenylethoxy)-4-phenyl-3-azahexane, in 3.0 *g* of purified styrene ($2.88 \cdot 10^{-2}$ *mol*) was prepared. Three freeze-pump-thaw-cycles were applied to remove oxygen before immersing the reaction vessels in an oil bath at 125 °C. The polymerization was carried out during 3-4 hours. Molecular weights and polydispersity indices were determined by size exclusion chromatography, whereas $^1\text{H-NMR}$ was used for the determination of end group functionality by careful integration of the polymer backbone to the terpyridine signals. Purification by column chromatography was carried out on silica to remove non-functionalized polystyrene eluting first with hexane: CH_2Cl_2 (1/3), then CH_2Cl_2 and finally increase the gradient with THF. After analysis, poly(styrene) was precipitated twice from chloroform into methanol. Analytical data are for PS_{300} : $^1\text{H-NMR}$ (CDCl_3): δ = 8.69 (m, 2H; $\text{H}_{6,6''}$), 8.62 (m, 2H; $\text{H}_{3,3''}$), 8.20 (m, 2H; $\text{H}_{3',5'}$), 7.93 (m, 2H; $\text{H}_{4,4''}$), 7.57-6.32 (m, 1500H; H_{PS} backbone aromatics; $\text{H}_{\text{aromatics}}$, $\text{H}_{5,5''}$), 5.35 (m, 2H; tpyOCH_2), 2.45-0.53 (m, 900H; H_{PS} backbone aliphatics).

General procedure for the polymerization of *tert*-butyl acrylate: *tert*-butyl Acrylate was subjected to an AlO_x -filtration before use in order to remove the stabilizer. A solution of the initiator, 2,2,5-trimethyl-3-(1-(4'-(4''-terpyridinyloxy)methyl)phenylethoxy)-4-phenyl-3-azahexane, in 3.6 *g* of purified *tert*-butyl acrylate ($2.34 \cdot 10^{-2}$ *mol*) was prepared. For a degree of polymerisation (DP) of 400 (100 % conversion), the corresponding amount of initiator was 38 *mg* ($6.47 \cdot 10^{-5}$ *mol*) and $7.0 \cdot 10^{-4}$ *g* ($6.47 \cdot 10^{-6}$ *mmol*) for the free nitroxide (5 % with respect to the initial initiator amount). Ten freeze-pump-thaw-cycles were applied to remove oxygen before immersing the reaction ves-

sels in an oil bath at 125 °C. The polymerization was carried out during 22 hours. Polydispersity indices were determined by size exclusion chromatography, whereas $^1\text{H-NMR}$ was used for the determination of end group functionality by careful integration of the polymer backbone to the terpyridine signals. After analysis, $\text{pol}(\text{tert-butylacrylate})$ was precipitated twice from THF into methanol/water (50:50). Analytical data are for PtBA_{200} : $^1\text{H-NMR}$ (CDCl_3): $\delta = 8.66$ (m, 2H; $\text{H}_{6,6''}$), 8.58 (m, 2H; $\text{H}_{3,3''}$), 8.08 (m, 2H; $\text{H}_{3',5'}$), 7.83 (m, 2H; $\text{H}_{4,4''}$), 7.57-7.18 (m, 22H; $\text{H}_{\text{aromatics}}$, $\text{H}_{5,5''}$), 5.35 (m, 2H; tpyOCH_2), 2.45-0.53 (m, 2400H; $\text{H}_{\text{PtBA backbone aliphatics}}$).

General procedure for the polymerization of 2-(dimethylamino)-ethyl acrylate: 2-(Dimethylamino)ethyl acrylate was subjected to an AlO_x -filtration before use in order to remove the stabilizer. A solution of the initiator, 2,2,5-trimethyl-3-(1-(4'-(4''-terpyridinyloxy)methyl)phenylethoxy)-4-phenyl-3-azahexane, in 1.6 g of purified 2-(dimethylamino)ethyl acrylate ($1.12 \times 10^{-2} \text{ mol}$) was prepared. For a degree of polymerisation (DP) of 400 (100 % conversion), the corresponding amount of initiator was 11 mg ($1.87 \times 10^{-5} \text{ mol}$) and $2.1 \times 10^{-4} \text{ g}$ ($9.50 \times 10^{-7} \text{ mmol}$) for the free nitroxide (5 % in respect to the initial initiator amount). Ten freeze-pump-thaw-cycles were applied to remove oxygen before immersing the reaction vessels in an oil bath at 125 °C. The polymerization was carried out during 6 hours. Polydispersity indices were determined by size exclusion chromatography, whereas $^1\text{H-NMR}$ was used for the determination of end group functionality by careful integration of the polymer backbone to the terpyridine signals. After analysis, $\text{pol}(\text{2-(dimethylamino)ethyl acrylate})$ was precipitated twice from THF into hexane. Analytical data are for PDMAEA_{400} : $^1\text{H-NMR}$ (CDCl_3): $\delta = 8.66$ (m, 2H; $\text{H}_{6,6''}$), 8.58 (m, 2H; $\text{H}_{3,3''}$), 8.08 (m, 2H; $\text{H}_{3',5'}$), 7.83 (m, 2H; $\text{H}_{4,4''}$), 7.57-7.18 (m, 22H; $\text{H}_{\text{aromatics}}$, $\text{H}_{5,5''}$), 5.35 (m, 2H; tpyOCH_2), 4.10 (m, 800H; C(O)OCH_2), 2.55-0.53 (m, 4400H; CH_2CH , CH_2CH , $\text{CH}_2\text{N}(\text{CH}_3)_2$, $\text{CH}_2\text{N}(\text{CH}_3)_2$).

General procedure for the synthesis of poly(*tert*-butyl acrylate)-*b*-poly(styrene): A terpyridine functionalized poly(*tert*-butyl acrylate) macro-initiator (350 mg, DP=200, $1.37 \times 10^{-5} \text{ mol}$), anisole (1.2 mL) and styrene (180 mg, 1.73 mmol) were transferred into a Schlenck tube. After ten freeze-pump-thaw-cycles the vessel was transferred in an oil bath at 125 °C. The polymerization was carried out during 19 hours. Polydispersity indices were determined by size exclusion chromatography, whereas $^1\text{H-NMR}$ was used for the determination of end group functionality by careful integration of the polymer backbone to the terpyridine signals. After analysis, $\text{poly}(\text{tert-butyl acrylate})\text{-}b\text{-poly}(\text{styrene})$ was precipitated twice from THF into methanol/water (50:50). Analytical data are for $\text{PtBA}_{200}\text{-}b\text{-PS}_{80}$: $^1\text{H-NMR}$ (CDCl_3): $\delta = 8.69$ (m, 2H; $\text{H}_{6,6''}$), 8.62 (m, 2H; $\text{H}_{3,3''}$), 8.20 (m, 2H; $\text{H}_{3',5'}$), 7.93 (m, 2H; $\text{H}_{4,4''}$), 7.57-6.32 (m, 400H; $\text{H}_{\text{PS backbone aromatics}}$; $\text{H}_{\text{aromatics}}$, $\text{H}_{5,5''}$), 5.35 (m, 2H; tpyOCH_2), 2.45-0.53 (m, 2640H; $\text{H}_{\text{PS backbone aliphatics}}$, $\text{H}_{\text{PtBA backbone aliphatics}}$).

General procedure for the synthesis of terpyridine end-functionalized poly(ethylene oxide): Hydroxy end-functionalized poly(ethylene oxide) and KOH (5 eq.) were heated for 30 minutes in dry DMSO under argon at 70 °C. Via an addition funnel, a 2-fold excess of 4'-chloro-2,2':6',2''-terpyridine was added to the solution and the mixture was heated overnight. The reaction mixture was then partitioned between water and CH₂Cl₂, and the organic phase was then dried over Na₂SO₄ and condensed in vacuo. The resulting solid was precipitated from THF into diethyl ether. This last operation was repeated twice.

General procedure for the synthesis of PS_x-[RuCl₃ *mono-complex*: Terpyridine-terminated polystyrene, PS-[(1 eq.) and a eight fold-excess of RuCl₃.xH₂O were charged into a Schlenk flask with a mixture of EtOH/THF (1:1). The reaction medium was deoxygenated by purging argon during one hour and then heated at 85 °C under argon for 24 hours and allowed to cool to room temperature. The final mixture was then partitioned between chloroform and water. The water layer was washed three times with CHCl₃, and the combined organic phases were dried over MgSO₄, and condensed in vacuo. ¹H-NMR was checked to verify the absence of the terpyridine signals due to the paramagnetic nature of the pure *mono-complex*. The resulting solid was reprecipitated from THF into methanol/water (2:1) (2 times), and placed in an oven overnight at 40 °C. Yields were between 80-90 %.

General procedure for the synthesis of PS_x-[Ru]-PEO_y *bis-complex*: A solution of terpyridine functionalized PEO-[(1.2 eq.) and PS-[RuCl₃ (1 eq.) in a mixture of THF/EtOH (3:2) (20 mL) was heated under argon at 80 °C for 60 minutes. A few drops of *N*-ethylmorpholine were added after one hour and stirring at 80 °C was continued during 24 hours. Then an excess of solid NH₄PF₆ (10 eq.) was added and the solution was allowed to cool to room temperature. Stirring was continued during one hour, and subsequently, the solvents were removed in vacuo. The residue was extracted with CHCl₃ and water (0.01 M NH₄PF₆). The organic layers were dried over MgSO₄ and concentrated in vacuo. The compound was further precipitated into hexane starting from THF. The precipitate was filtered and water was added. The aqueous suspension was stirred at room temperature during two days to remove unreacted PEO, then filtered off. In a last step, diethylether was added and stirred at room temperature during two days to remove unreacted PS. Finally, the product was filtered, and solubilized in a minimum amount of THF and reprecipitated in hexane to yield the PS-[Ru]-PEO copolymer (Yield~30 %). ¹H-NMR (CDCl₃): δ = 8.41 (m, 2H; H_{3,3''} PEO), 8.34-8.22 (m, 6H; H_{3,3''} PS, H_{3',5'} PS&PEO), 7.83 (m, 4H; H_{4,4''} PS&PEO), 7.47 (m, 2H; *H*-PhCH₂Otpy), 7.36 (m, 6H; H_{5,5''} PS&PEO, *H*-PhCH₂Otpy), 7.21-6.28 (m, 1511H; H_{PS} backbone aromatics, H_{6,6''} PS&PEO), 5.58 (m, 2H; tpyOCH₂ PS),

4.77 (m, 2H; tpyOCH₂ PEO), 4.11-3.30 (m, 864H, H_{PEO} backbone), 2.20-1.20 (m, 922H; H_{PS} backbone aliphatics).

Synthesis of 4'-(2-[1-methoxyethoxy]ethoxy)-2,2';6',2''-terpyridine trinitro cobalt(III): A buffer solution is prepared starting from NaOH (1.46 mmol, 2.57 eq.) in 3 mL of water, followed by the addition of CH₃COOH (3.31 mmol, 5.17 eq.). The Co(NO₃)₂·xH₂O (0.74 mmol, 1.30 eq.) and sodium nitrite (3.31 mmol, 5.82 eq.) were then added to the initial buffer. A stream of air was bubbled through the solution during several minutes, until the colour of the solution has turned from brown to orange. At this moment, a solution of 4'-(2-[1-methoxyethoxy]ethoxy)-2,2';6',2''-terpyridine (0.57 mmol, 1 eq.) in ethanol (6 mL) is added dropwise, followed by the formation of an orange precipitate. After 15 minutes, the precipitate is filtered off, and subsequently washed with ethanol (3x), water (3x) and diethyl ether (3x). After drying in vacuum, the yield was 51 %. ¹H-NMR (DMSO-d₆): δ = 8.91 (d, 2H, J = 5.1 Hz; H_(5,5'')), 8.75 (d, 2H, J = 6.9 Hz; H_(3,3'')), 8.57 (s, 2H; H_(3',5')), 8.45 (t, 2H, J = 6.6 Hz; H_(4,4'')), 7.95 (t, 2H, J = 7.5 Hz; H_(5,5'')), 4.63 (t, 2H, J = 4.2; H_A), 3.91 (t, 2H, J = 4.5; H_B), 3.64 (m, 2H; H_C), 3.48 (m, 2H; H_D), 3.23 (s, 3H; H_E). λ / nm (CH₃CN): 256, 274, 282, 308, 365. FT/IR ν / cm⁻¹: 1409 (N=O), 1311 (N-O).

Synthesis of 4'-(2-[1-methoxyethoxy]ethoxy)-2,2';6',2''-terpyridine trichloro cobalt(III) (aqueous procedure): Concentrated hydrochloric acid (18 mmol, 200 eq.) was added to the previously prepared *mono*-complex of trinitro cobalt(III) (91 μmol, 1 eq.). A stream of air was bubbled through the solution for several minutes (20 min). A brown precipitate was then filtered off, then washed with concentrated HCl (2x), HCl 1M (2x), H₂O (4x), acetone (3x) and diethyl ether (2x). After drying in vacuum, the yield was 51 %. ¹H-NMR (DMSO-d₆): δ = 9.65 (d, 2H, J = 5.1 Hz; H_(6,6'')), 8.80 (d, 2H, J = 7.8 Hz; H_(3,3'')), 8.58 (s, 2H; H_(3',5')), 8.37 (t, 2H, J = 7.8 Hz; H_(4,4'')), 7.91 (t, 2H, J = 6.0 Hz; H_(5,5'')), 4.64 (t, 2H, J = 4.2; H_A), 3.91 (t, 2H, J = 4.5; H_B), 3.65 (m, 2H; H_C), 3.49 (m, 2H; H_D), 3.23 (s, 3H; H_E). λ / nm: 264, 305, 320, 530.

Synthesis of 4'-(4-methylbenzyloxy)-2,2';6',2''-terpyridine-4'-(2-[1-methoxyethoxy]ethoxy)-2,2';6',2''-terpyridine cobalt(III) trihexafluorophosphate (aqueous procedure): A solution of 4'-(2-[1-methoxyethoxy]ethoxy)-2,2';6',2''-terpyridine trichloro cobalt(III) (47.4 μmol, 1 eq.) and 4'-(4-methylbenzyloxy)-2,2';6',2''-terpyridine (49.7 μmol, 1.05 eq.) in DMF (1.5 mL) was stirred overnight at room temperature. Then an excess of NH₄PF₆ (0.4 mmol, 10 eq.) was added, and the final mixture was allowed to stir overnight again. At the end of the reaction, the solution exhibits a yellow colour. The final mixture was then partitioned between dichloromethane and a 0.01M NH₄PF₆ solution in water. The organic layer was separated, washed with water (2x), dried over Na₂SO₄ and removed *in vacuo*. TLC-analysis of the crude product revealed three spots and thus the compound was subjected to a col-

umn chromatography (silica, acetonitrile:water:KNO₃ in a 14:2:1 ratio). The purification led to the desired heteroleptic *bis*-complex, but also the homoleptic complexes. All three complexes were extracted from a 0.01M NH₄PF₆ solution in water into CH₂Cl₂. The organic layer was finally washed three times with water, dried over Na₂SO₄ and condensed *in vacuo*. The desired product was obtained with a 48 % yield. ¹H-NMR (DMSO-d₆): δ = 9.16 (s, 2H; H_(3'',5'')), 9.10 (s, 2H; H_(3',5')), 8.93 (m, 4H; H_(3',3'')), 8.36 (t, 4H, J=7.8 Hz; H_(4,4'')), 7.62-7.47 (m, 10H; H_(6,6''), H_(5,5'')), 7.39 (d, 2H, J=8.1; H_H), 5.70 (s, 3H; H_F), 4.80 (t, 2H, J=4.2; H_A), 4.06 (t, 2H, J=4.2; H_B), 3.75 (m, 2H; H_C), 3.56 (m, 2H; H_D), 3.30 (s, 3H; H_E), 2.41 (s, 3H; H_I). λ / nm (H₂O): 215, 280, 323, 338, 450.

Synthesis of 4'-(2-[1-methoxyethoxy]ethoxy)-2,2';6',2''-terpyridine bromodichloro cobalt(III) (organic procedure): Anhydrous cobalt chloride(II) (161 μmol, 1.1 eq.) was placed in a Schlenk tube under argon. Then 2 mL of freshly distilled THF were added leading to a blue solution. On the other hand, 4'-(2-[1-methoxyethoxy]ethoxy)-2,2';6',2''-terpyridine was dried with three azeotropic cycles from toluene, dissolved in 6 mL of anhydrous CH₃CN, and added dropwise to the cobalt chloride solution. After the color of the solution changed from blue to green to brown, the solution was allowed to stir 15 minutes again. Finally few drops of bromide solution in THF (723 μmol, 5 eq.) were added, leading to a green solution. 10 minutes later, the solution was evaporated under vacuum. The residue was dissolved in water and allowed to stand one hour in an ice-cold bath. A precipitate appeared corresponding to the desired *mono*-complex and was subsequently washed with diethylether (2x). The desired product was obtained with a 85 % yield. ¹H-NMR (DMSO-d₆): δ = 9.39 (d, 2H, J=4.8 Hz; H_(6,6'')), 8.89 (d, 2H, J=6.9 Hz; H_(3,3'')), 8.62 (s, 2H; H_(3',5')), 8.37 (t, 2H, J=7.5 Hz; H_(4,4'')), 7.97 (t, 2H, J=6.0 Hz; H_(5,5'')), 4.64 (t, 2H, J=4.8; H_A), 3.92 (t, 2H, J=3.9; H_B), 3.65 (m, 2H; H_C), 3.49 (m, 2H; H_D), 3.23 (s, 3H; H_E). λ / nm: 206, 216, 270, 311, 393, 530.

Synthesis of 4'-(4-methylbenzyloxy)-2,2';6',2''-terpyridine-4'-(2-[1-methoxyethoxy]ethoxy)-2,2';6',2''-terpyridine cobalt(III) trihexafluorophosphate (organic procedure): A solution of 4'-(2-[1-methoxyethoxy]ethoxy)-2,2';6',2''-terpyridine bromodichloro cobalt(III) (26.0 μmol, 1 eq.) and 4'-(4-methylbenzyloxy)-2,2';6',2''-terpyridine (26.0 μmol, 1.05 eq.) in DMF (1.5 mL) was stirred overnight. Then an excess of NH₄PF₆ (0.4 mmol, 10 eq.) was added, and the final mixture was allowed to stir overnight again. At the end of the reaction, the solution exhibits a yellow colour. The final mixture was then partitioned between dichloromethane and a 0.01M NH₄PF₆ solution in water. The organic layer was separated, washed with water (2x), dried over Na₂SO₄ and removed *in vacuo*. TLC-analysis of the crude product revealed three spots and thus the compound was subjected to a column chromatography (silica, acetonitrile:water:KNO₃ in a 14:2:1 ratio). The purification led to

the desired heteroleptic *bis*-complex, but also the homoleptic complexes. All three complexes were extracted from a 0.01M NH_4PF_6 solution in water into CH_2Cl_2 . The organic layer was finally washed three times with water, dried over Na_2SO_4 and condensed *in vacuo*. The desired product was obtained with a 60 % yield. $^1\text{H-NMR}$ (DMSO-d_6): δ = 9.16 (s, 2H; $\text{H}_{(3'',5'')}$), 9.10 (s, 2H; $\text{H}_{3',5'}$), 8.93 (m, 4H; $\text{H}_{3',3''}$), 8.36 (t, 4H, $J=7.8$ Hz; $\text{H}_{4,4''}$), 7.62-7.47 (m, 10H; $\text{H}_{6,6''}$, $\text{H}_{5,5''}$), 7.39 (d, 2H, $J=8.1$; H_H), 5.70 (s, 3H; H_F), 4.80 (t, 2H, $J=4.2$; H_A), 4.06 (t, 2H, $J=4.2$; H_B), 3.75 (m, 2H; H_C), 3.56 (m, 2H; H_D), 3.30 (s, 3H; H_E), 2.41 (s, 3H; H_I). λ / nm (H_2O): 215, 280, 323, 338, 450.

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INFLUENCE OF THE METAL-LIGAND COMPLEX
ON THE SIZE OF AQUEOUS
METALLO-SUPRAMOLECULAR MICELLES

Abstract

A library of metallo-supramolecular block copolymers has been synthesized and the micellization behavior of those copolymers in water has been studied. A series of amphiphilic block copolymers composed of poly(styrene) and poly(ethylene oxide) blocks linked by a bis-terpyridine ruthenium complex was prepared. The micelles formed from these copolymers were characterized by AFM and TEM. The results evidence that the classical scaling laws relating the micelle size with the size of the hydrophobic block are not valid for metallo-supramolecular copolymers. This different behavior is due to electrostatic repulsions between the charged and bulky metal-ligand complexes located at the core-corona interface. If those repulsions are screened by increasing the ionic strength during micelle formation, the classical behavior is observed.

4.1 Introduction

Aqueous block copolymer micelles have been the subject of intense research for more than 30 years [1, 2]. Most of the interest arises from the capability of these systems to confine a hydrophobic nanodomain of precise size and shape in an aqueous environment. These nano-objects consist of a core formed by insoluble hydrophobic blocks, surrounded by a corona formed by water-soluble blocks. Depending on the chemical nature and block composition of the initial amphiphilic copolymer, a wide variety of micellar morphologies has been observed [3]. In a recent set of papers, the synthesis and characterization of a new type of amphiphilic block copolymers, namely metallo-supramolecular amphiphilic block copolymers, has been described. These compounds are formed by hydrophilic poly(ethylene oxide) [4–7] or poly(*N*-isopropylacrylamide) [8–10] *A* blocks linked to hydrophobic *B* blocks such as poly(styrene) or poly(ethylene-*co*-butylene) through a *bis*-2,2':6',2''-terpyridine ruthenium (II) complex. The terpyridine ligand can easily be introduced at the chain end of different polymers, thus giving rise to many possible combinations of different blocks [8–12]. Since the method for preparing metallo-supramolecular block copolymers relies on the coupling of two polymer blocks via a simple two-step synthesis using principles from coordination chemistry around a ruthenium metal ion, it is straightforward to prepare a library of block copolymers [13]. Compared to “classical” covalent block copolymers, metallo-supramolecular block copolymers offer many advantages. Besides the formation via self-organization processes, the reversibility of the supramolecular bond allows the construction of “smart materials” with tunable properties [14]. Moreover, the electrochemical and photochemical properties of the complexes can be engineered by choosing the appropriate metal ion and counter-ion [15, 16].

For micelles prepared from classical covalent copolymers, the micellar characteristic features (size and shape) are mainly controlled by three independent parameters: the stretching of the core-forming chains, the interfacial tension between the micellar core and the solvent, and the repulsions among chains in the corona [17–20]. In the case of micelles prepared from metallo-supramolecular copolymers the presence of the charged and bulky complex (around 1 nm³) [21, 22] at the interface be-

tween the two immiscible blocks is expected to play an important role, strongly affecting the self-assembly and hence the micellar characteristic features.

The purpose of this chapter is thus to study in detail the role of the charged metal complexes on the supramolecular organization of the metallo-supramolecular copolymers. We have investigated the formation of micelles in water from metallo-supramolecular copolymers with PS as the hydrophobic block and PEO as the hydrophilic block. Micelles prepared from this kind of supramolecular copolymers have already been studied but only one composition was considered [4, 11, 23, 24]. In this chapter, we took advantage of the library approach and investigated micelles prepared from different PS-[Ru]-PEO (where -[Ru]- is the *bis*-terpyridine-ruthenium(II) complex), varying the relative length of both blocks. The micelles thus formed have been characterized by Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM).

4.2 The library of investigated supramolecular block copolymers

For block copolymers in the bulk, the obtained morphology depends on the interaction parameter between the blocks, the volume fraction of the constituent blocks and the overall molecular weight of the copolymer [2]. Whenever diblock copolymers are dissolved in a selective solvent of one of the blocks, block copolymer micelles are formed that consist of a core formed by the insoluble blocks surrounded by a corona formed by the soluble blocks [25]. With the recent development of nanotechnology, focuses have been made on the ability of micelles to exhibit an hydrophobic nanodomain of precise shape and size in aqueous media that could be further used for various applications, e.g., templating, drug release, etc. For instance, in water, the micelles formed by the poly(styrene)-*block*-poly(ethylene oxide) diblock copolymers are constituted of an hydrophobic PS core and surrounded by an hydrophilic PEO corona [26]. In the following, the PS-[Ru]-PEO metallo-supramolecular block copolymers will be used to prepare aqueous micelles. Since the method of preparation of these copolymers relies on a two step reaction

as described in the chapter 3, it is straightforward to obtain a library of such block copolymers with different volume fractions and molecular weights [7]. Indeed, a 4x4 library of 16 compounds would only require 8 starting blocks (see e.g. Figure 4.1). In this respect, we have developed a library of 12 metallo-supramolecular copolymers, as depicted in Table 4.1. These copolymers have been chosen in order to study in detail the role of the charged metal complexes on the supramolecular organization of the metallo-supramolecular copolymers.

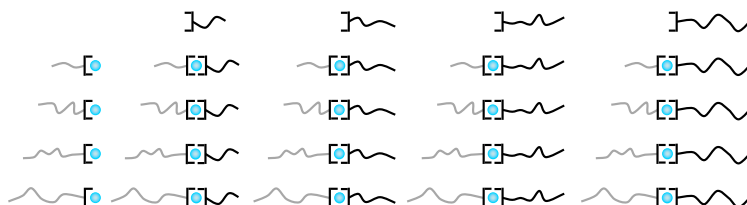


Figure 4.1: Schematic representation of the strategy to obtain a library of 16 compounds starting from 8 initial blocks (first block in grey, second block in black and metal ions as small dots).

PS ₂₀ -[Ru]-PEO ₇₀	PS ₇₀ -[Ru]-PEO ₁₂₅	PS ₁₃₅ -[Ru]-PEO ₂₂₅	PS ₂₄₀ -[Ru]-PEO ₃₇₅
PS ₂₀ -[Ru]-PEO ₁₂₅	PS ₇₀ -[Ru]-PEO ₃₇₅	PS ₂₀₀ -[Ru]-PEO ₂₂₅	PS ₃₀₀ -[Ru]-PEO ₂₂₅
PS ₇₀ -[Ru]-PEO ₇₀	PS ₁₃₅ -[Ru]-PEO ₁₂₅	PS ₂₀₀ -[Ru]-PEO ₃₇₅	PS ₃₀₀ -[Ru]-PEO ₃₇₅

Table 4.1: Library of metallo-supramolecular PS_x-[Ru]-PEO_y block copolymers used in this study.

Depending on the composition of the starting block copolymer, two limiting structures can be drawn (Figure 4.2):

- i “star-like” micelles with a small core compared to the corona ;
- ii “crew-cut” micelles with a large core and highly-stretched coronal chains.

Scaling theories were established by Zhulina and Birshtein [27], who have identified four different regions depending on the copolymer composition. The four regimes are summarized in Table 4.2. According to these

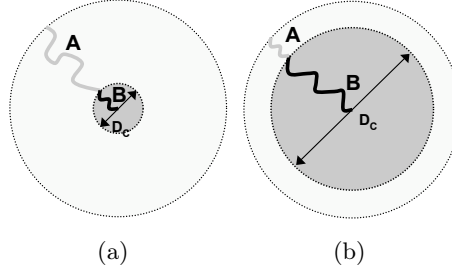


Figure 4.2: Schematic representations of (a) a “star-like” micelle and (b) a “crew-cut” micelle composed of linear diblock copolymers with soluble *A*-block and insoluble *B*-block.

results, all the investigated block copolymers depicted in Table 4.1 belong to the regime IV, because N_{PS} , is always larger than $N_{PEO}^{(1+2\nu)/(5\nu)}$ (where N stands for the degree of polymerization of each block and ν for the scaling exponent for the radius of gyration of linear polymers, respectively). This means that all the investigated micelles will be characterized by a star-like structure. The majority of the investigated samples were not readily soluble in water. Therefore, the preparation method previously introduced by Eisenberg et al. for “crew-cut” micelles was applied, involving the prior dissolution of the copolymer in a non-selective solvent followed by the slow addition of water [3].

Region	Copolymer composition
I	$N_A < N_B^{\nu/6}$
II	$N_B^{\nu/6} < N_A < N_B^{(1+2\nu)/6\nu}$
III	$N_B^{(1+2\nu)/6\nu} < N_A < N_B^{(1+2\nu)/5\nu}$
IV	$N_A > N_B^{(1+2\nu)/5\nu}$

Table 4.2: Classification of micelles prepared from an AB diblock copolymers in a solvent selective for the A block according to Zhulina and Birshstein [27]

4.3 DLS, AFM and TEM results on the library

The aim of this study is to elucidate the influence of the charged and bulky *bis*-terpyridine ruthenium complex on the size of the micelles. We have tried to characterize the micelles in solution by dynamic light scattering (DLS) but the results could not be exploited due to micellar aggregation (Figure 4.3). It has indeed been previously shown that the micelles prepared from metallo-supramolecular block copolymers have a strong tendency to aggregate [23, 24]. In all the investigated samples, deconvolution of the DLS results by the CONTIN algorithm systematically results in two populations of objects: a first one around a R_h of c.a. 40 nm, and a very broad one whose position changes according to the sample but centered above 100 nm. According to a previous study, the second peak corresponds to large micellar aggregates while the first one does not correspond to isolated micelles but rather to a mixture of micelles and small aggregates of micelles [24].

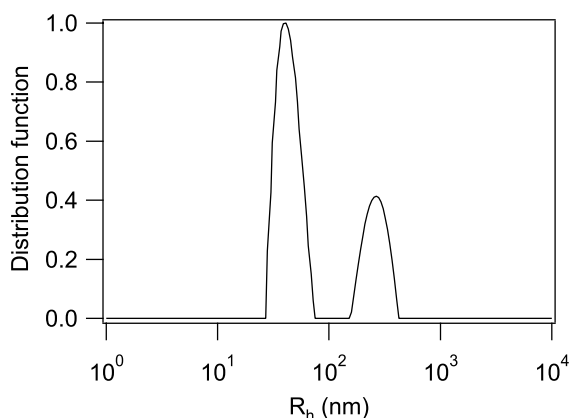


Figure 4.3: Typical Contin size distribution of micelles formed by PS₂₄₀-[Ru]-PEO₃₇₅.

Such a situation is typical of block copolymer micelles stabilized by a corona of PEO blocks. Actually, the steric stabilization provided by those PEO blocks is not effective enough to avoid micellar aggregation. It should also be recalled that CONTIN size distribution histograms rep-

resent the percentage of scattered intensity for each population. Since larger aggregates scatter much more light than the smaller ones, the importance of the population associated to the larger aggregates is overestimated in Figure 4.3.

We have therefore concentrated our efforts in characterizing the core of the micelles, using mainly AFM and TEM imaging. For AFM measurements, the micelles have been deposited on a silicon wafer and their height was measured in order to avoid tip convolution effects. Since the imaging was done in the dry state the flexible PEO coronal chains are expected to be oriented flat on the surface, hence the height of the micelles essentially corresponds to the size of the core (see Figure 4.4).



Figure 4.4: Schematic picture of the micellar structure for AFM characterization.

Since ruthenium ions are present in the complexes located at the core/corona interface, staining is not needed in principle to image the micelles by TEM. Nevertheless, a selective staining of the PS core by RuO_4 was performed in order to improve the contrast and thus increase the precision of the core size measurements [28]. All the studied copolymers formed spherical micelles. Figure 4.5 presents typical TEM and AFM pictures obtained for the $\text{PS}_{240}\text{-[Ru]-PEO}_{375}$ copolymer. We can see clearly on both images isolated micelles but also small clusters, evidencing once again their tendency to aggregate. The core sizes measured by AFM and TEM for the different copolymers are summarized in table 4.3. Both techniques are in good agreement and give similar results even if the sizes determined by TEM are systematically a bit larger (deformations are essentially due to staining or ultra high vacuum conditions in TEM experiments).

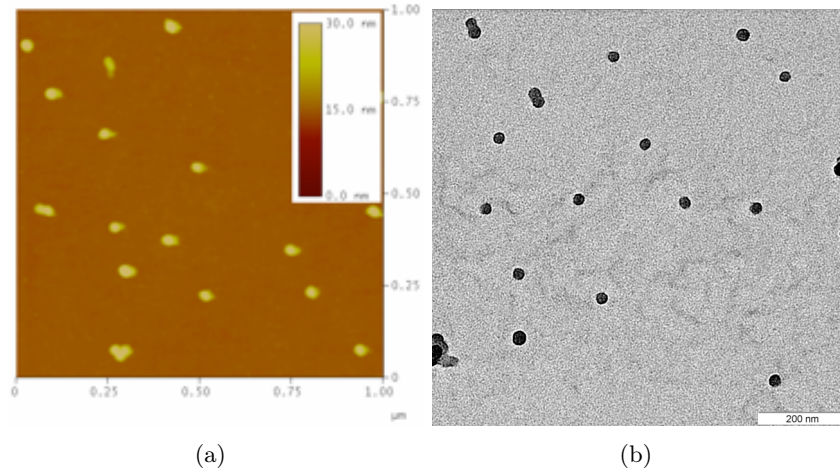


Figure 4.5: AFM (a) and TEM (b) pictures recorded on micelles prepared from the PS₂₀₀-[Ru]-PEO₃₇₅ copolymer in water.

	D_c (nm)		D_c (nm)	
	AFM		TEM	
PS ₂₀ -[Ru]-PEO ₇₀	10 (2)		13 (3)	
PS ₂₀ -[Ru]-PEO ₁₂₅	8.2 (1)		13 (4)	
PS ₇₀ -[Ru]-PEO ₇₀	8.1 (1)		14 (3)	
PS ₇₀ -[Ru]-PEO ₁₂₅	8.7 (1)		15 (4)	
PS ₇₀ -[Ru]-PEO ₂₂₅	9.0 (2)		14 (3)	
PS ₇₀ -[Ru]-PEO ₃₇₅	11 (2)		15 (4)	
PS ₁₃₅ -[Ru]-PEO ₁₂₅	8.8 (1)	19 (3)	14 (4)	25 (4)
PS ₁₃₅ -[Ru]-PEO ₂₂₅	11 (1)	20 (2)	15 (4)	28 (4)
PS ₂₀₀ -[Ru]-PEO ₂₂₅	21 (2)		24 (3)	
PS ₂₀₀ -[Ru]-PEO ₃₇₅	20 (3)		28 (6)	
PS ₂₄₀ -[Ru]-PEO ₃₇₅	19 (3)		28 (4)	

Table 4.3: Diameter of the micellar core as determined by AFM and TEM (the numbers in parentheses are the standard deviations).

4.4 Discussion

From the data reported in Table 4.3, one can immediately notice that the micellar cores are splitted into two populations, one around 10 nm for the small PS blocks (DP of 20 and 70) and one around 20 nm for the PS with a DP of 200 and above, according to the AFM results. For classical “star-like” micelles the size of the core should scale as the $3/5^{th}$ power of the degree of polymerization of the insoluble block [29]. For micelles prepared from *metallo*-supramolecular copolymers this law is clearly not valid since there is a sharp transition between two sizes as the DP gradually increases. This observation evidences that in this case the size of the insoluble block is not the main parameter governing the core size and that an additional parameter has to be taken into account. The electrostatic repulsions and steric hindrance between the charged and bulky (around 1 nm³) *bis*-terpyridine ruthenium complexes are most probably responsible for this unusual behavior. Those two factors will exert constraints on the number of chains aggregating together. One could imagine that the complexes will delimit a sphere that can accommodate the PS blocks inside. When the PS block becomes too large to fit into this sphere a transition will occur to a sphere large enough for the PS chains to fit in. To illustrate this point, we have calculated the degree of stretching of the PS chains in the micellar core. To this end, we have divided the *end-to-end* distance of each PS blocks, calculated by equation 4.1, by the average radius of the core measured by AFM [13].

$$\langle \bar{a}^2 \rangle = nl^2 \frac{1 - \cos \theta}{1 + \cos \theta} \sigma^2 \quad (4.1)$$

n is the number of monomers, l is the length of a C-C bond (0.154 nm), θ is the valence angle between each chain atom (109°), and σ is the steric parameter and equals to 2.23 for PS at room temperature [30]. The results are summarized in Table 4.4. For micelles prepared from copolymers containing 70 units of styrene the *end-to-end* distance of the PS chains is very close to the micellar radius. When the DP of the PS further increases to 200 the chains cannot fit anymore in the volume initially delimited by the complexes, and a transition occurs to a larger core size. To better understand those results we have synthesized two additional

	Average <i>end-to-end</i> distance (nm)	Average core radius (nm)	
PS ₂₀	2.1	4.6	
PS ₇₀	4.0	4.6	
PS ₁₃₅	5.6	5.0	10
PS ₂₀₀	6.8	10	
PS ₂₄₀	7.4	9.5	
PS ₃₀₀	8.3	11	

Table 4.4: Comparison between the *end-to-end* distance of each PS blocks and the average radius of the micellar core measured by AFM.

copolymers with a PS block having a DP in the transition region between 70 and 200, i.e., PS₁₃₅-[Ru]-PEO₁₂₅ and PS₁₃₅-[Ru]-PEO₂₂₅. The size of the micelles formed by these copolymers are reported in Table 4.3. Surprisingly, both samples show two populations with equal abundance, one around 10 nm as for DP 20 and 70, and one around 20 nm as for DP of 200 and above. The existence of these two populations could be due to a size segregation of the PS chains. An average DP of 135 corresponds to an *end-to-end* distance of 5.6 nm, which is slightly larger than the radius of the first population (5 nm) but smaller than the radius of the second population (10 nm) (see Table 4.3). The fraction of the copolymer chains having a smaller PS block could thus aggregate in micelles having a core radius of 5 nm, the rest of the copolymer chains, having a larger PS block, will aggregate to form micelles with a core radius of about 10 nm.

To further prove that the self-assembly of the *metallo*-supramolecular copolymers is mainly controlled by electrostatic repulsions between the charged complexes, we have prepared micelles following the procedure described above, but using 1M NaCl, instead of pure water, for the micellization and the dialysis. The sizes measured by AFM and TEM are reported in Table 4.5.

	D_c (nm) AFM	D_c (nm) TEM
PS ₂₀ -[Ru]-PEO ₇₀	6.1 (0.5)	10 (2)
PS ₇₀ -[Ru]-PEO ₂₂₅	12 (1)	14 (2)
PS ₁₃₅ -[Ru]-PEO ₂₂₅	17 (1)	18 (3)
PS ₂₀₀ -[Ru]-PEO ₂₂₅	21 (1)	23 (2)
PS ₃₀₀ -[Ru]-PEO ₃₇₅	25 (1)	27 (2)

Table 4.5: Diameter of the micellar core prepared in 1M NaCl as determined by AFM and TEM (the numbers in parentheses are the standard deviations).

In this case we see clearly that the micelle size varies continuously with the DP of the PS block. It should also be pointed out that only one population is observed for the PS₁₃₅-[Ru]-PEO₂₂₅ copolymer, instead of two when the micelles are prepared with pure water. In 1M NaCl, the electrostatic repulsions between the complexes are screened, and the *metallo*-supramolecular copolymers behave as their covalent counterpart. To evidence the fact that the *metallo*-supramolecular copolymers indeed behave as their covalent counterpart when the micelles are prepared in the presence of salt, the diameters of the cores, measured by AFM, have been plotted against the $3/5^{th}$ power of the PS block DP (Figure 4.6). The core size scales perfectly with $DP^{3/5}$ in a linear way, as predicted by theory [29]. The same conclusions can be drawn from the TEM results. For comparison, the evolution obtained for micelles prepared in pure water, where only two sizes were observed, has been added to Figure 4.6.

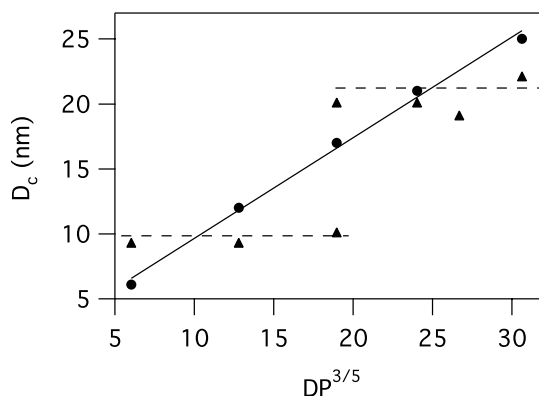


Figure 4.6: Relationship between the measured (AFM) core diameter of the micelles and the $3/5^{th}$ power of the PS block DP, for micelles prepared in pure water (*black-filled triangles*) and in 1M NaCl (*black-filled circles*). The solid line represents the linear regression obtained from the data in 1M NaCl. The dashed lines, evidencing the presence of only two sizes, are only a guide for the eyes.

4.5 Conclusions

The two-step self-assembly process based on ruthenium/terpyridine complexation has been used to self-assemble the terpyridine-functionalized polystyrene blocks to poly(ethylene oxide) ones, resulting in *metallo-supramolecular* PS-[Ru]-PEO block copolymers. The systematic combination of the synthesized polymer blocks has allowed us to create a library of 12 different PS-[Ru]-PEO block copolymers. This library only contains block copolymers with a major PEO block (in term of volume fraction). As a result, star-like micelles have been further obtained from the self-assembly of these PS-[Ru]-PEO block copolymers in water.

The characteristic dimension of the micellar cores have been further measured by AFM and TEM. AFM and TEM characterization of the micelles revealed that the core size does not scale linearly with the DP of the PS block as expected from the theory of classical covalent copolymers. Only two core sizes were observed, one around 10 nm for DP of 70 and below, and one around 20 nm for DP of 200 and above. For copolymers

having a DP in the transition region between 70 and 200, two populations were observed. This unusual behavior is due to electrostatic repulsions between the charged *bis*-terpyridine ruthenium complexes present at the junction of the two blocks which strongly affect the self-assembly. This hypothesis has been confirmed by preparing micelles in the presence of salt to screen the repulsions. In this case, the *metallo*-supramolecular copolymers behaved as their covalent counterpart.

Experimental part

Micelle preparation The copolymers were dissolved in DMF at a concentration of 1 g/L. A volume of water equal to half the DMF volume was then added by steps of 50 μ L to induce aggregation of the insoluble poly(styrene) block, followed by the addition of an equal volume of water in one shot to “freeze” the micelles. Subsequently, the DMF/water solution was dialyzed against water for 24 hours replacing the water at least trice (Spectra-Por dialysis bags, cutoff 6000-8000 Da). The final concentration of the copolymer in pure water was set to 0.3 g/L.

Micelle Characterization Atomic force microscopy (AFM) images were obtained using a Digital Instruments Nanoscope IV scanning force microscope in tapping mode using NCL type cantilevers (Si, 48 N/m, 190 kHz, Nanosensors). The samples were prepared by spin-coating a dilute solution of micelles on a silicon wafer. Transmission electron microscopy (TEM) was performed on a LEO 922 microscope, operating at a 200 kV accelerating voltage in bright field mode. The images were formed by unscattered electrons only. Samples for TEM experiments were prepared by spin-coating a drop of the solution of micelles on a carbon-coated TEM grid. The samples were stained with RuO₄ [28].

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AMPHIPHILIC BRUSHES FROM
METALLO-SUPRAMOLECULAR BLOCK
COPOLYMERS

Abstract

A novel strategy to control the formation of amphiphilic brushes from metallo-supramolecular block copolymers is described. The investigated copolymer consists of a poly(styrene) block linked to a poly(ethylene oxide) one via a charged bis-terpyridine ruthenium (II) complex (PS-[Ru]-PEO). This copolymer forms unimers in DMF and spherical micelles in water consisting of a PS core and a PEO corona. The initial hexafluorophosphate counterions associated to the complex have been exchanged for poly(styrenesulfonate) ones (PSS). In DMF, flexible amphiphilic brushes are observed in which PS-[Ru]-PEO chains decorate the PSS main-chain. These structures have been further transferred into pure water, resulting in the collapse of the PS chains into hydrophobic cores. Spherical or worm-like micelles have been observed in water, depending on the length of the PSS chain.

5.1 Introduction

The design and control of novel polymer architecture and functionality is a key issue while considering applications dedicated to polymeric materials in general [1–3] and can basically be achieved by two methods. The first one is the modification of pre-existing polymers and the second one concerns the development of new polymerization pathways [4–9]. Among the methods for modifying polymers, grafting is one of the promising methods leading to the so-called graft copolymers [10]. Graft copolymers refer to polymer architectures in which polymeric side chains are grafted at various points along the polymer backbone (Fig. 5.1). For very high grafting density, polymer brushes are formed [11].

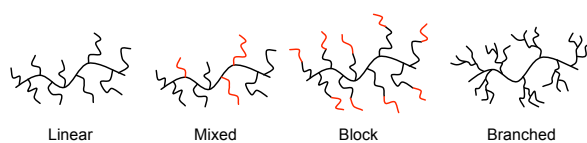


Figure 5.1: Possible architectures of polymer brushes.

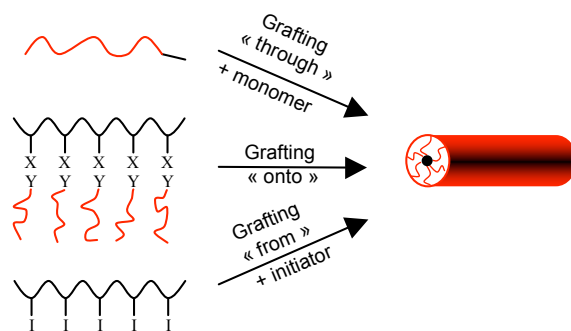


Figure 5.2: Strategies for polymer brushes: “grafting through”, “grafting onto” and “grafting from”.

Three major types of grafting have been considered so far (Fig. 5.2): “grafting from” [12–15], “grafting through” [16–19] and “grafting onto” [20–

23]. The latter one is quite interesting because it allows the use *non-covalent* interactions to graft the side arms onto the polymer backbone. In this respect, supramolecular chemistry has been successfully applied to the design of polymer brushes through secondary interactions such as hydrogen bonding, [24, 25] ionic interaction, [26, 27] and coordination bonding [28]. Ikkala and coworkers have proven the great interest of coordination bonding since it allows the tuning of the self-assembly by playing on both the ligands and the counter-ions. They have applied successfully this technique to obtain multi-comb polymeric supramolecules by forming a complex between poly(4-vinyl pyridine) and zinc dodecylbenzene sulfonate [29]. However, only oligomeric molecules have been complexed with a polymer backbone in order to promote the formation of comb-shaped block copolymer. On the other hand, interactions between polyelectrolytes and oppositely charged surfactants have gained a great interest, due to the possibility to obtain complex formation, often in highly ordered structures. The well-defined supramolecular structures of the polyelectrolyte-surfactants complexes have been widely reviewed, covering complexes at the interfaces, in solution and in solid state [30–37]. Moreover, Eisenberg and coworkers have studied the formation of complexes between block or grafted polyelectrolytes and surfactants. Their work led to a special class of lyophilic colloids that exhibits the combined properties of amphiphilic block copolymers and polyelectrolyte complexes [32, 38–41].

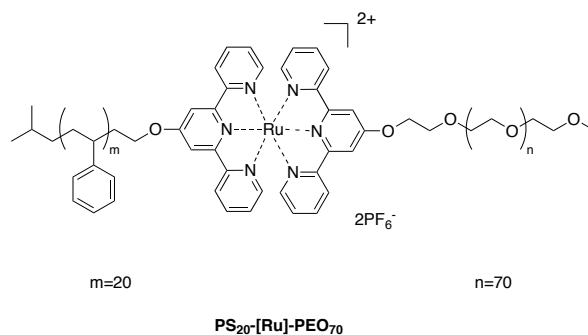
In this chapter, we report on the formation of dynamic graft copolymers using a non-covalent “grafting onto” method [20–23]. Starting from metallo-supramolecular block copolymer chains bearing two positive charges at the junction, we exchange the initial associated low molecular weight counterions by polyanions. Since many negative charges are present on the polyanions, this exchange process results in polyelectrolyte chains decorated by metallo-supramolecular block copolymers. The starting metallo-supramolecular diblock copolymer is made of a poly(styrene) block linked to a poly(ethylene oxide) one via a twice positively charged *bis*-terpyridine-ruthenium(II) complex (PS-[Ru]-PEO) [42]. Due to the presence of a charged and bulky metal-ligand complex, the self assembly properties differ from those obtained with “classical” covalent block copolymers. The results evidenced that the classical scal-

ing laws relating the micelle size to the size of the hydrophobic block were not valid for these metallo-supramolecular copolymers (see Chapter 4). The initial hexafluorophosphate counterions are then exchanged by poly(styrene sulfonate) polyanions (PSS). We firstly investigate the formation of such complexes in *N,N*-dimethylformamide (DMF), a non-selective solvent for the system, by dynamic light scattering. In that respect, PSS of various degree of polymerization (DP) have been selected for this counterion exchange. In addition, the stoichiometric ratio between PS-[Ru]-PEO and PSS has been varied. The second part of this chapter is dedicated to the transfer of these peculiar complexes in water. In fact, due to the collapse of the hydrophobic poly(styrene) chains, formation of micelles is expected and will be followed by dynamic light scattering in combination with cryo-transmission electron microscopy.

5.2 Formation of complexes in a non-selective solvent

In this work we have selected a metallo-supramolecular copolymer in which a α -terpyridine poly(styrene) block with an average degree of polymerization, DP, of 20 (PS₂₀-[]) is coupled with an ω -methoxy, α -terpyridine poly(ethylene oxide) block with an average DP of 70 (PEO₇₀-[]), resulting into a PS₂₀-[Ru]-PEO₇₀ amphiphilic copolymer (Scheme 5.1). The starting PS₂₀ and PEO₇₀ are prepared by living anionic polymerization processes and are characterized by polydispersity indexes as low as 1.1. They were then *end*-functionalized with the terpyridine ligand [42].

The counterion exchange was achieved by mixing known amounts of PS₂₀-[Ru]-PEO₇₀ dissolved in *N,N*-dimethylformamide (DMF) to solutions of PSS in a mixture DMF/water (95/5). The presence of a small amount of water is required in order to guaranty a perfect solubilization of the PSS chains. However, as shown later on, this amount of water is not sufficient to induce the collapse of the PS blocks in the DMF/water mixture. The stoichiometric ratio of styrene sulfonate units per PS₂₀-[Ru]-PEO₇₀ chain was varied in order to study the architecture of the resulting complexes from graft copolymers with a low grafting density [43] to brush-like copolymers with a high grafting density. Be-



Scheme 5.1: Chemical structure of the metallo-supramolecular block copolymer used in this chapter.

cause of the entropy increase resulting from the release of PF_6^- ions in solution, the counterion exchange between PF_6^- and PSS is expected to be effective. The expected structure of the $\text{PS}_{20}\text{-[Ru]-PEO}_{70}$ /PSS complexes in DMF/water (95/5) is schematically depicted in Figure 5.3. Such supramolecular complexes can be either seen as amphiphilic

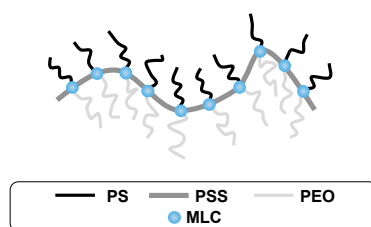


Figure 5.3: Schematic representation of the structure in DMF/water (95/5) of the complex obtained after exchange of the PF_6^- counterions by PSS macromolecular ones.

graft copolymers in which hydrophobic PS and hydrophilic PEO polymer blocks are regularly distributed along a long PSS polymer main-chain or as dynamic graft copolymer since reversible ionic interactions are used between the grafted metallo-supramolecular block copolymers and the polyelectrolyte main-chain. Dynamic light scattering (DLS) has been used in order to measure the hydrodynamic radius (R_h) of the PS_{20} -

[Ru]-PEO₇₀/PSS complexes in DMF/Water (95/5) as a function of the DP of the PSS polyanion. Figure 5.4 shows a typical relaxation curve measured at an angle of 90° and the corresponding relaxation time as obtained from the inverse Laplace relaxation function (Contin analysis). These curves were obtained for a PS₂₀-[Ru]-PEO₇₀/PSS complex

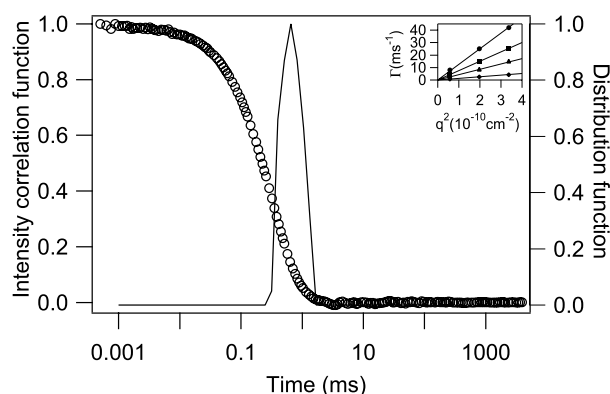


Figure 5.4: Autocorrelation function (open circles) and CONTIN analysis (full line) of PS₂₀-[Ru]-PEO₇₀/PSS₆₀₆ complexes in DMF/water (95/5) at 90°. Inset: Dependence of the frequency (Γ) with the squared magnitude of the scattering vector (q^2) of different PS₂₀-[Ru]-PEO₇₀/PSS complexes in DMF/water (95/5).

in which the PS₂₀-[Ru]-PEO₇₀/SS stoichiometry has been adjusted to 1/2 meaning that all the SS units should have been complexed to the metallo-supramolecular block copolymers. A well-defined monomodal distribution with a translational diffusive behavior is also obtained (see inset Figure 5.4). Such a situation will be referred to the “stoichiometric” ratio for the PS₂₀-[Ru]-PEO₇₀/PSS complexes since all the negative charges of PSS are theoretically compensated only by the positive charges of the metallo-supramolecular block copolymers. Assuming that the counterion exchange is nearly complete, this should result in a highly grafted brush-like complex as depicted in Figure 5.3. Firstly, the observation of a well-defined monomodal distribution is relevant since a solution of PSS chains in the same DMF/water mixture exhibits a bimodal time relaxation distribution function, as usually observed for polyelectrolytes

in high dielectric constant solvents [44, 45]. This typical polyelectrolyte behavior disappears after complexation with the metallo-supramolecular polymer.

	Cumulant		Contin
	R_h (nm)	PDI	R_h (nm)
PSS ₅₃	6.3	0.13	5.7
PSS ₁₂₉	9.5	0.13	8.7
PSS ₁₉₈	11.5	0.20 ^a	10.5
PSS ₃₁₁	12.9	0.09	12.8
PSS ₆₀₇	18.7	0.10	18.2
PSS ₁₄₁₆	27.9	0.16	26.9
PSS ₄₀₀₅	45.3	0.28 ^a	42.6

^a Presence of large aggregates in the Contin distribution

Table 5.1: DLS data of the PS₂₀-[Ru]-PEO₇₀/PSS complexes in DMF/water (95/5)

Another important piece of information is found in the evolution of the R_h of the complexes versus the DP of the PSS as reported in Figure 5.5 (PS₂₀-[Ru]-PEO₇₀/SS stoichiometry of 1/2 in all cases). Considering a stoichiometric ratio between the supramolecular block copolymer and the PSS, the results are dispersed from 6 nm for the PS₂₀-[Ru]-PEO₇₀/PSS₅₃ complexes to 45 nm for the PS₂₀-[Ru]-PEO₇₀/PSS₄₀₀₅ ones (see Table 5.1 for the whole results). The R_h of the complexes is indeed found to increase with the DP of the PSS following the scaling law: $R_h \sim DP^{0.45}$. This result is in agreement with the formation of flexible PS₂₀-[Ru]-PEO₇₀/PSS complexes adopting a random-coil conformation [46]. The same conformation is reported with only the PSS chains in the mixture DMF/water (95/5). This indicates that the grafting of the PS₂₀-[Ru]-PEO₇₀ does not exert an influence on the final conformation of the PSS main-chain but rather decorate it and leads to the formation of a flexible brush-like structure as depicted in Figure 5.3.

In order to elucidate the grafting efficiency, the ratio of PS₂₀-[Ru]-PEO₇₀ versus SS has been varied from a two-time excess (PS₂₀-[Ru]-

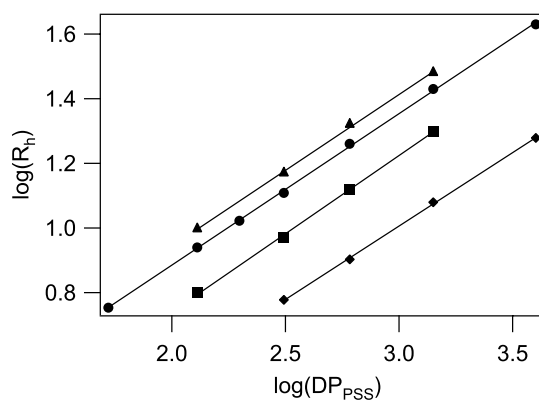


Figure 5.5: Hydrodynamic radii (R_h) of the PS_{20} -[Ru]- PEO_{70} /PSS complexes in DMF/water 95/5 as a function of the DP of the PSS. Full triangles; with an excess of PS_{20} -[Ru]- PEO_{70} copolymer (PS_{20} -[Ru]- PEO_{70} /SS ratio of 1/1). Full circles: stoichiometric ratio (PS_{20} -[Ru]- PEO_{70} /SS ratio of 1/2). Full squares: with a default of PS_{20} -[Ru]- PEO_{70} copolymer (PS_{20} -[Ru]- PEO_{70} /SS ratio of 1/4). Full diamonds: PSS in a mixture DMF/water 95/5 (fast mode only).

PEO₇₀/SS ratio of 1/1) to a two-time default (PS₂₀-[Ru]-PEO₇₀/SS ratio of 1/4) of the metallo-supramolecular block copolymer. These situations have to be compared to the stoichiometric case in which all SS negative charges are only compensated by positive charges from the metallo-supramolecular block copolymer (PS₂₀-[Ru]-PEO₇₀/SS ratio of 1/2). Results are reported in Figure 5.5. Whenever the PS₂₀-[Ru]-PEO₇₀/SS ratio is overvalued (PPS₂₀-[Ru]-PEO₇₀/SS ratio of 1/1), the behavior and the size of the complexes are similar with the stoichiometric ratio (PS₂₀-[Ru]-PEO₇₀/SS ratio of 1/2 ratio). Whereas, when an excess of SS units is present the system, the size of the complexes significantly decreases. These results are in agreement with a relative efficient grafting process and could be easily understood in terms of diffusion coefficient of the complex rather than its R_h . Indeed, the diffusion coefficient of the complex should be higher and hence the R_h smaller whenever only part of the SS units are grafted with PS₂₀-[Ru]-PEO₇₀ chains (PS₂₀-[Ru]-PEO₇₀/SS ratio of 1/4). The grafting of more PS₂₀-[Ru]-PEO₇₀ chains should result in a decrease of the mobility of the complex and thus in a decrease in its diffusion coefficient (and thus in an increase in R_h). It is remarkable to observe that no significant change in diffusion coefficient is observed whenever an excess of PS₂₀-[Ru]-PEO₇₀ copolymer is present in the system (PS₂₀-[Ru]-PEO₇₀/SS ratio of 1/1). This means that the complexes formed with PS₂₀-[Ru]-PEO₇₀/SS ratio of 1/1 and 1/2 should be similar. One could therefore speculate about the localization of the excess of PS₂₀-[Ru]-PEO₇₀ chains in the 1/1 complex. This excess of PS₂₀-[Ru]-PEO₇₀ chains could be present as unimers in solution. In principle, this should lead to a second minor population in the Contin histogram. In fact, this second minor population is clearly evidenced from the main population associated to the complexes obtained from the PS₂₀-[Ru]-PEO₇₀/PSS₅₃ as reported on Figure 5.6.

5.3 Transfer of the complexes in water

In a second step, water was slowly added to the solution of the PS₂₀-[Ru]-PEO₇₀/PSS complexes with a PS₂₀-[Ru]-PEO₇₀/SS ratio of 1/2, and the solutions were dialyzed against water to remove DMF. The accordingly obtained aqueous micelles were then measured by DLS. The

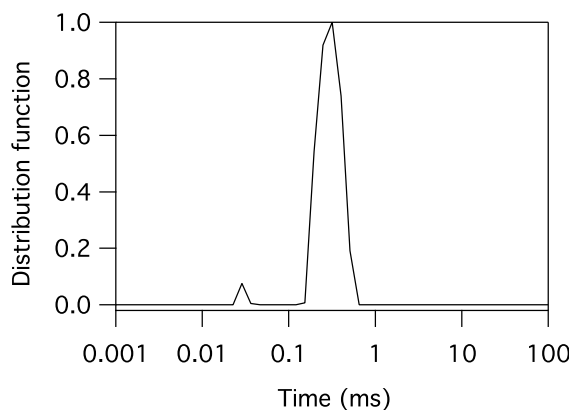


Figure 5.6: Relaxation time distributions for PS₂₀-[Ru]-PEO₇₀/PSS₁₄₁₆ complexes in DMF/water (95/5) with an excess of PS₂₀-[Ru]-PEO₇₀ copolymer (PS₂₀-[Ru]-PEO₇₀/SS ratio of 1/1).

decay rate values obtained at different angles are plotted against q^2 to confirm that the dynamic mode is only a translational motion (see figure 5.7 for several examples).

Moreover, two different regimes are observed in water depending on the DP of the PSS (Figure 5.8). For DP of, and lower than 607, micelles with a R_h around 13 nm, almost independent of the DP of PSS, are detected (see Table 5.2). Spherical micelles are always observed in that regime, as evidenced by transmission electronic microscopy (Figure 5.8).

These observations can be explained by the collapse and further aggregation of the PS blocks when DMF is gradually replaced by water. As it has been shown earlier, PS₂₀-[Ru]-PEO₇₀ copolymers tend to aggregate into spherical micelles in water [47]. However, the R_h (13 nm) in the case of PS₂₀-[Ru]-PEO₇₀/PSS complexes is larger than for the PS₂₀-[Ru]-PEO₇₀ copolymers with PF₆⁻ counterions (R_h of 8 nm). This can be explained by constraints induced by the wrapping of the PSS chains around the PS core (at the PS/PEO interface where the -[Ru]- complexes are located) during micelle formation (see Figure 5.9). Moreover, well-defined micelles are obtained in this case unlike those obtained by the self-assembly of PS₂₀-[Ru]-PEO₇₀ in water. As it was shown earlier [47],

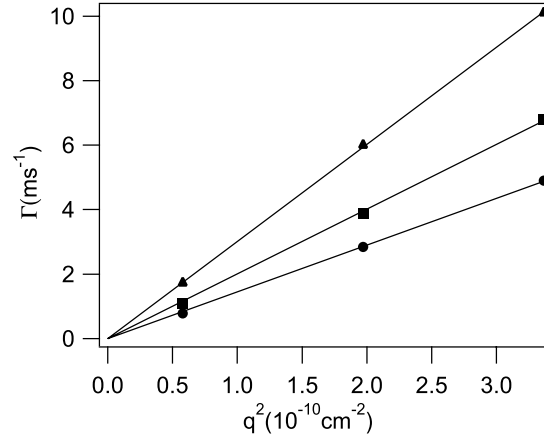


Figure 5.7: The linear dependence of the decay rates on the squared scattering vector q^2 , proving a diffusive process. Full triangles; PS₂₀-[Ru]-PEO₇₀/PSS₃₁₁ complexes. Full squares; PS₂₀-[Ru]-PEO₇₀/PSS₁₄₁₆ complexes. Full circles; PS₂₀-[Ru]-PEO₇₀/PSS₄₀₀₅ complexes.

	Cumulant		Contin
	R_h (nm)	PDI	R_h (nm)
PSS ₅₃	19.6	0.36 ^a	12.5
PSS ₁₂₉	18.9	0.31 ^a	13.1
PSS ₁₉₈	13.1	0.12	12.7
PSS ₃₁₁	18.6	0.30 ^a	14.1
PSS ₆₀₇	13.9	0.12	13.8
PSS ₁₄₁₆	18.9	0.08	18.6
PSS ₄₀₀₅	28.6	0.12	29.1

^a Presence of large aggregates in the Contin distribution

Table 5.2: DLS data of the PS₂₀-[Ru]-PEO₇₀/PSS complexes in water

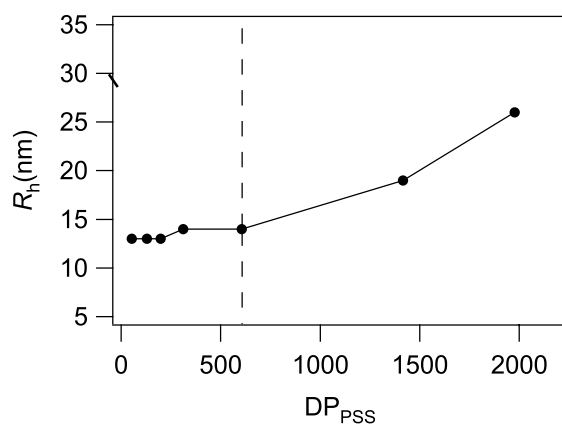


Figure 5.8: Hydrodynamic radii (R_h) of the PS₂₀-[Ru]-PEO₇₀/PSS complexes in water as a function of the DP of the PSS.

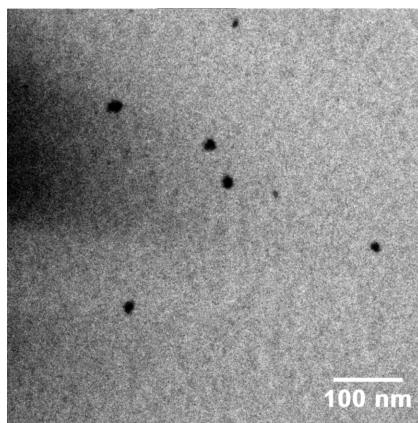


Figure 5.9: Typical TEM picture obtained after transfer in water of PS₂₀-[Ru]-PEO₇₀/PSS₆₀₇ complexes. An average radius of 9 nm was measured for these spherical micelles.

micelles formed by this kind of copolymers have strong tendency to aggregate into larger structures. An additional electrostatic stabilization provided with the presence of the PSS chains in the corona could explain why much less clustering is observed for the $\text{PS}_{20}\text{-[Ru]-PEO}_{70}\text{/PSS}$ composite micelles.

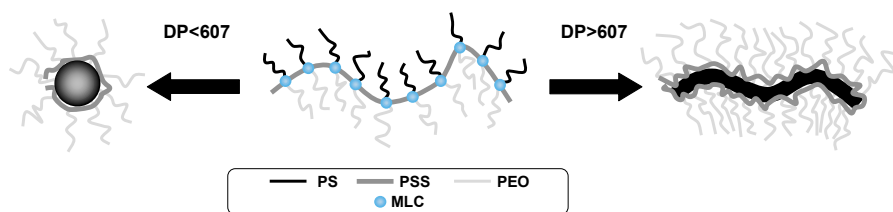


Figure 5.10: Schematic representation of the spherical or worm-like micelles obtained after the transfer of the complexes in water as a function of the DP of the PSS.

Whenever the DP of PSS is larger than 607, cryo-TEM observations reveal that the micelles are no longer spherical but adopt a worm-like morphology. This situation is illustrated in Figure 5.10 for micelles obtained from the $\text{PS}_{20}\text{-[Ru]-PEO}_{70}\text{/PSS}_{4005}$ and $\text{PS}_{20}\text{-[Ru]-PEO}_{70}\text{/PSS}_{1416}$ complexes.

Among the factors influencing the morphology of block copolymer micelles, three main parameters [48] have to be considered:

- i the stretching of the core-forming chains ;
- ii the core-corona interfacial energy ;
- iii the repulsion among coronal chains.

Since the diameter of the worm-like micelles is similar to the diameter of the spherical micelles observed in Figure 5.9, a change in the stretching of the PS core-forming block can be excluded. There is no reason to believe that parameters (ii) and (iii) will be modified by an increased length of PSS. However, one can assume the impossibility for very long PSS chains to wrap around a single spherical PS core. The original PS cores could thus merge into worm-like structures in order

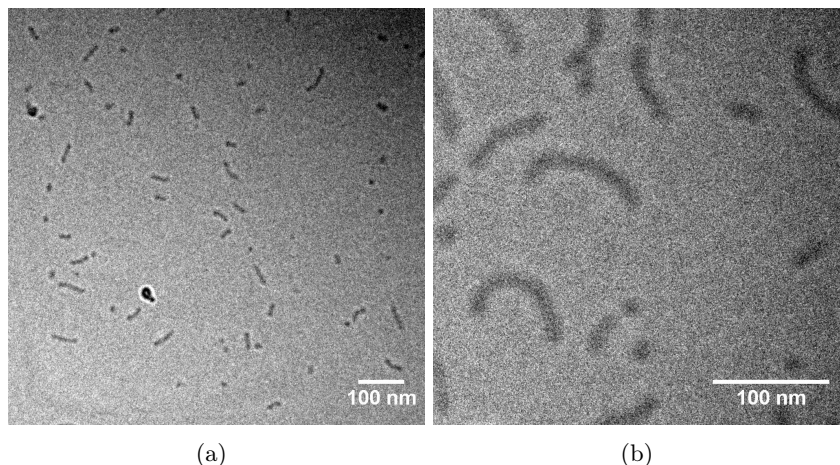


Figure 5.11: Typical (cryo)-TEM pictures obtained after transfer in water of PS₂₀-[Ru]-PEO₇₀/PSS₁₄₁₆ (a) and PS₂₀-[Ru]-PEO₇₀/PSS₄₀₀₅ (b) complexes.

to facilitate the wrapping of the PSS chains as depicted in Figure 5.10. The morphological transition from spherical to worm-like micelles could be thus attributed only to steric constraints originating from the PSS chains. Those worm-like micelles are quite flexible, probably because of the rather short PS block (only 20 units). This flexibility is further confirmed by the DLS data since the same R_h was obtained at all angles and a purely diffusive behavior was proven (see Figure 5.7). Moreover, the increase of the average contour length of the worm-like micelles (a factor 2.75 between 40 and 110) scales as the increase of the DP of PSS (a factor 2.83 between 1416 and 4005), proving an interesting correlation between the evolution of the worm-like micellar size and the DP of the PSS. Taking this correlation into account, we have thus performed a rough estimation of the PS₂₀-[Ru]-PEO₇₀ chains aggregation number (Z) in the micelles on the basis of the TEM pictures. This was done by considering a density of 1.05 g/cm^3 for amorphous PS [49], and assuming that the sizes measured by TEM correspond essentially to the core of the micelles. The calculations gave an aggregation number of 650 for the spherical micelles, and of 1610 and 4430 for the worm-like micelles

(approximated by a cylinder) obtained for the PS₂₀-[Ru]-PEO₇₀/PSS₁₄₁₆ and PS₂₀-[Ru]-PEO₇₀/PSS₄₀₀₅ complexes, respectively. These values are in good agreement with data found in literature [50, 51] and help to rationalize the other results. Below the transition, i.e., for PSS with a DP up to 607, spherical micelles with an aggregation number of 650 in PS₂₀-[Ru]-PEO₇₀ chains are obtained, and are thus composed of several PS₂₀-[Ru]-PEO₇₀/PSS complexes.

This regime holds until the aggregation number matches the DP of the PSS (Z of 650 compared to a DP of 607). Above the transition, i.e., for PSS with a DP larger than 607, worm-like micelles composed of a single PS₂₀-[Ru]-PEO₇₀/PSS complex are obtained. The aggregation numbers determined for the two samples in this regime are indeed in rather good agreement with the DP of the PSS chains (Z = 1610 for PSS₁₄₁₆, Z = 4430 for PSS₄₀₀₅). The morphological transition from spherical to worm-like micelles could be attributed to steric constraints originating from the PSS chains, i.e., to the impossibility for very long PS₂₀-[Ru]-PEO₇₀/PSS complexes to fold into a spherical PS core. Finally, the spherical and worm-like micelles originating from PS₂₀-[Ru]-PEO₇₀/PSS complexes were found to be stable in aqueous solutions for period over 6 months and did not show further aggregation. This confirms once again the beneficial role of PSS chains on the colloidal stabilization of the system.

5.4 Conclusions

In this chapter, the formation of copolymer brushes using an original supramolecular approach has been studied. This strategy is based on the complexation of a charged supramolecular block copolymers (PS₂₀-[Ru]-PEO₇₀) with a polyelectrolyte backbone (PSS) in a DMF/water (95/5) solution, leading to PS₂₀-[Ru]-PEO₇₀/PSS complexes. The characteristic size of these complexes can be further tuned by varying the length of the PSS chains and the PS₂₀-[Ru]-PEO₇₀/SS molar ratio. In all cases, the formation of flexible amphiphilic brushes with a random coil conformation has been evidenced. In a further step, the amphiphilic character of these complexes has been used to create micellar systems in water. Micellization was induced by adding water to the initial amphiphilic brushes,

followed by a dialysis step against water to completely remove DMF. This results in the collapse of the PS blocks into micellar cores. The formation of these micelles has been evidenced by DLS and TEM techniques. For the smaller DP of the PSS chains (up to 607), well-defined spherical micelles were formed, whereas for the larger DP, a transition to worm-like morphologies occurred. This phenomenon was evidenced by cryo-TEM observation. Although an effect on the core-corona interfacial energy is not excluded, steric constraints introduced by the polymeric counterion are thought to be at the origin of this morphological transition. This contribution broaden the field of metallo-supramolecular polymer chemistry by providing a novel and easy strategy to obtain brushes exhibiting interesting self-assembly properties in water.

Experimental part

Chemicals were purchased from Aldrich, Fluka, Polymersource Inc., Polymer Science Inc. and Shearwater. The synthesis and characterization of PS₂₀-[Ru]-PEO₇₀ are described in details elsewhere [42]. PSS were bought from Fluka as standards for GPC with a PDI from 1.1 to 1.2.

Preparation of the complexes: Sodium polystyrene sulfonate (PSS) was dissolved in a DMF/water mixture (85/15) at a concentration of 0.28 g/L, and stirred at room temperature during half an hour. A solution of PS₂₀-[Ru]-PEO₇₀ in pure DMF was prepared at a concentration of 2 g/L. To 1 mL of this solution, 500 μ L of the PSS solution were added dropwise to obtain a stoichiometric ratio between the SS units and the positive charges on the PS₂₀-[Ru]-PEO₇₀ copolymer, and the mixture was stirred at room temperature for 4 hours. The final concentration (of PS₂₀-[Ru]-PEO₇₀) was set to 1 g/L by dilution with pure DMF.

Preparation of the micelles: Micelles were prepared by adding water to trigger micellization. Starting from 1 mL of the solution of complexes, 500 μ L of water were added dropwise (10x50 μ L), followed by the addition of an equal volume of water in one shot to “freeze” the micelles. [52] Subsequently, the DMF/water solution was dialyzed against water for 24 hours replacing the water at least three times (Spectra-Por dialysis bags, cutoff 6000-8000 Da). The final concentration of the copolymer in pure water was set to 0.3 g/L.

Cryo transmission electronic microscopy measurements: Measurements were performed on a FEI Tecnai 20, type Sphera TEM operating at 200 kV (LaB6 filament). Images were recorded with a bottom mounted Gatan CCD camera. A Gatan cryo holder operating at -174 °C was used for the cryo TEM measurements. TEM grids, both 200 mesh carbon coated copper grids and R2/2 Quantifoil Jena grids were purchased from SPI. Prior to blotting the grids made hydrophilic by surface plasma treatment using a Cressington 208 carbon coater operating at 5 mA for 40 seconds. For conventional sample preparation 3 μ L aliquots were applied to a 200 mesh carbon coated copper grid and subsequently excess liquid was quickly manually blotted away with filter paper. Cryo TEM specimens were prepared within the environmental chamber (22 °C, relative humidity 100 %) of an automated vitrification robot (FEI Vitrobot Mark III). Excess liquid was blotted away (-2 mm. offset, 2 s) with filter paper within the environmental chamber of the Vitrobot. The grids were subsequently shot through a shutter into melting ethane placed just outside the environmental chamber. Vitrified specimens were stored under liquid nitrogen before imaging.

Transmission electronic microscopy measurements: Transmission electron microscopy (TEM) was performed on a LEO 922 microscope, operating at 200 *kV* accelerating voltage in bright field mode. The images were formed by unscattered electrons only. Samples for TEM experiments were prepared by spin-coating a drop of the solution of micelles onto a carbon-coated TEM grid. The grids were allowed to dry in a vacuum chamber during 24 hours. Finally, the samples were exposed to RuO₄ vapors during several minutes before measurement [53].

Dynamic light scattering: The hydrodynamic radius, R_h , of the micellar complexes were measured by dynamic light scattering (DLS). The experimental autocorrelation function, $g(t)$, is commonly expressed in the form of a cumulant expansion (eq 6.1):

$$g(t) = \exp \left(-\tilde{A}_1 t + \left(\frac{\tilde{A}_2}{2!} \right) t^2 - \left(\frac{\tilde{A}_3}{3!} \right) t^3 + \dots \right) \quad (5.1)$$

where Γ_i is the *i*th cumulant and $\Gamma_1 = Dq^2$ where D is the translational diffusion coefficient and q is the absolute value of the scattering vector. The polydispersity index (PDI) of the objects was estimated from the ratio. The diffusion coefficient extrapolated to zero concentration is related to the hydrodynamic radius R_h by the Stokes-Einstein equation (eq 6.2):

$$R_h = \frac{k_b T}{6\pi\eta D} \quad (5.2)$$

where k_b is the Boltzmann constant and η the viscosity of the solvent. DLS measurements were performed on a Malvern CGS-3 apparatus equipped with a He-Ne laser with a wavelength λ of 632.8 *nm*. The temperature was controlled at 298 *K*, and the measurements were done at several angles. The experimental data have been also analyzed by the CONTIN method which is based on an inverse-Laplace transformation of the data and which gives access to a size distribution histogram for the analyzed micellar solutions.

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METAL-LIGAND COMPLEXES IN THE CORONA OF BLOCK COPOLYMER MICELLES

Abstract

A terpyridine end-capped poly(tert-butylacrylate)-block-poly(styrene) (I-PtBA-b-PS) copolymer has been synthesized by nitroxide mediated radical polymerization using a terpyridine-functionalized initiator. Micellization of this copolymer was achieved in ethanol, a selective solvent for the PtBA block. The formed micelles consist of a PS core and a PtBA corona. Terpyridine ligands are located at the extremity of the PtBA chains and are available for complexation with metal ions. The effect of the addition of various metal ions to this system was studied in the dilute regime by dynamic light scattering. Whenever the concentration of the micelles is sufficiently low, addition of metal ions only results in the intramicellar complexation of terpyridine ended PtBA coronal chains. Since terpyridine can either form mono-complexes or bis-complexes with metal ions, different situations have been observed depending on the metal-to-ligand ratio and to the nature of the metal ions. Finally, the possibility to use these metal-ligand complexes to add an additional poly(ethylene oxide) layer on the initial micelles has been demonstrated. This new approach opens a pathway to tune the size, conformation and functionality of coronal chains in block copolymer micelles.

6.1 Introduction

Supramolecular copolymers have become of increasing interest over the last years in the context of new materials with tunable properties [1, 2]. In particular, metallo-supramolecular polymers in which metal-ligand complexes are used as assembling entities have known important progresses, allowing a better control over the synthetic strategies to prepare varied architectures, and providing a better understanding of the parameters governing their self-assembly [3]. Metallo-supramolecular polymers can be classified according to their structure, i.e. polycondensation-type supramolecular polymers vs. supramolecular block copolymers.

In polycondensation-type polymers, each monomer or macromonomer is linked to its neighbour by metal-ligand complexes. This approach requires the use of monomers or macromonomers bearing at least two binding sites that could be further condensed through supramolecular interactions [4].

In supramolecular block copolymers, metal-ligand linkers are introduced at specific locations in block copolymer architectures [5]. This should lead to systems combining the characteristic features of block copolymers (*e.g.* microphase separation between immiscible constituent blocks) to the ones of supramolecular polymers (*e.g.* reversibility and tunability of the strength of the supramolecular bonds). The supramolecular linkers can be used to either bridge together different homopolymer blocks, or to link together different block copolymers. The first approach leads to diblock copolymers containing a supramolecular linker between the constituent blocks [6]. The second strategy is based on the use of block copolymers containing a linking group specifically introduced at a defined locus of the copolymer chain (generally at the chain end or the block junction). These linking groups can further promote the formation of a supramolecular structure, *e.g.*, star-like structures, by bridging two or more copolymer chains together [7] (see figure 6.1).

In this chapter, we report on the use of metallo-supramolecular interactions to tune the size of micelles by changing the conformation of the coronal chains. This new strategy consists in starting from a diblock copolymer of poly(*tert*-butyl acrylate) (PtBA) and poly(styrene) (PS) end-functionalized with a terpyridine moiety (scheme 6.1) to form mi-

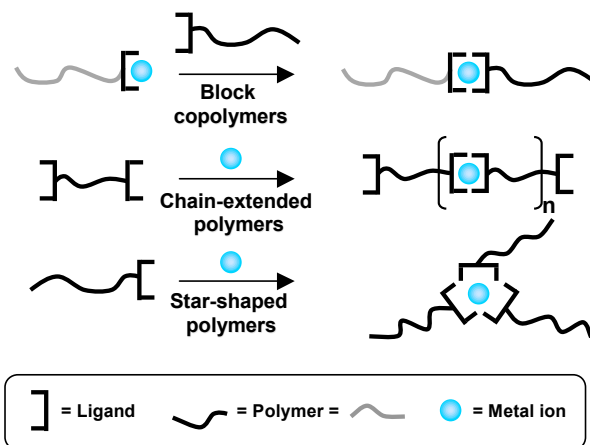
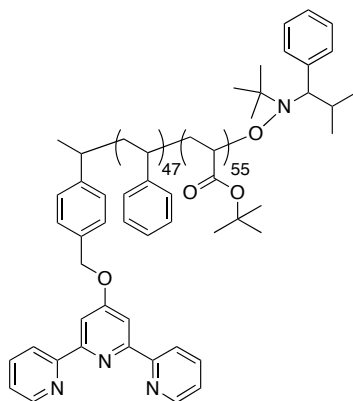


Figure 6.1: Metal ion induced self-assembly of polymers with metal coordinating end-groups resulting in block copolymers, chain-extended polymers or star-shaped polymers. From Ref. [7]

celles in ethanol, a selective solvent of the PtBA. These micelles are thus made of a PS core and a PtBA corona with terpyridine ligands located at the extremity of the PtBA chains. The second step is the addition of metal ions to the micelles in order to induce the formation of complexes with the terpyridine terminal groups. Three metal ions will be considered, i.e., Zn^{2+} , Ni^{2+} and Fe^{2+} , since there are known to form metal ion/terpyridine complexes with quite different binding constants [7–11].

Depending on the metal-to-ligand ratio and on the type of metal salt, formation of *bis*-terpyridine or *mono*-terpyridine complexes are expected. This should lead to the formation of metallo-supramolecular block copolymers hierarchically combining the self-organization [12] of covalent block copolymers into micelles to the one of metallo-supramolecular polymers in the micellar corona. To the best of our knowledge, such a combination have not been reported so far. Dynamic light scattering and transmission electronic microscopy will be further used to characterize these systems.



Scheme 6.1: Chemical structure of the terpyridine end-functionalized poly(styrene)-*b*-poly(*t*-butylacrylate) used in this chapter.

6.2 Self-assembly behavior in ethanol

A poly(styrene)-*b*-poly(*t*-butylacrylate) diblock copolymer chains bearing a terpyridine ligand at the poly(*t*-butylacrylate) chain-end (PS₄₇-*b*-PtBA₅₅-) has been synthesized by nitroxide mediated radical polymerization (NMP) [13]. The polydispersity index of this copolymer was 1.2 according to size exclusion chromatography. Micellization of this copolymer is achieved by direct dissolution of the PS₄₇-*b*-PtBA₅₅- copolymer in ethanol, a selective solvent for the PtBA block. This results in spherical micelles (Figure 6.2) with a radius of 13 *nm* in the dried state as evidenced by transmission electronic microscopy (TEM).

Since TEM specimens have been stained with ruthenium tetroxide which selectively reacts with poly(styrene) block [14], one could assume that PS micellar cores are essentially observed in these TEM experiments. Information about the size of the whole micelles in solution can however be obtained by dynamic light scattering (DLS). DLS measurements indicated the formation of micelles with a hydrodynamic radius, R_h , of 22 *nm* and a polydispersity index (PDI) of 0.03 in agreement with the formation of monodisperse well-defined micelles (Figure 6.3). No angular dependence of the scattering signal was detected, in agreement with the formation of spherical micelles. Moreover, the size distribution

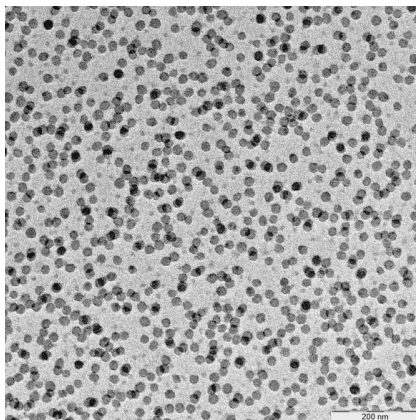


Figure 6.2: TEM picture of micelles formed by the PS₄₇-*b*-PtBA₅₅-[copolymer in ethanol (RuO₄ staining).

histogram obtained by the CONTIN method indicated that only one population of micelles was present in solution.

6.3 Addition of a metal salt

Because of the chemical structure of the PS₄₇-*b*-PtBA₅₅-[copolymer, terpyridine ligands are located at the extremity of coronal chains of micelles. These terpyridine can be further used for complexation with metal ions, enabling the formation of metal-ligand complexes within the micellar corona. In order to avoid intermicellar crosslinking and the possible formation of gel-like structures, the micellar concentration was kept low in the following experiments (3 g/L). Moreover, CONTIN size distribution histograms were systematically recorded after each addition of metal salts in order to rule out the formation of aggregated species. Three metal ions have been considered, i.e. Zn²⁺, Ni²⁺ and Fe²⁺. Whenever the metal ion/terpyridine molar ratio is set to 1/2, the formation of *bis*-terpyridine-metal ion complexes in the micellar corona is expected as depicted in Figure 6.4. This could eventually result in the formation of flower-like micelles.

Since the micelles are made of a glassy PS core and are thus charac-

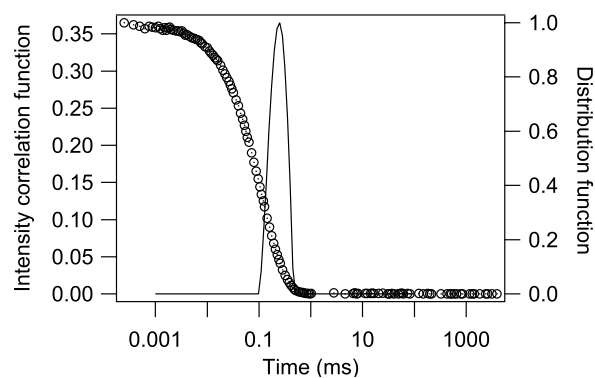


Figure 6.3: Intensity correlation function and Contin size distribution of micelles formed by the $\text{PS}_{47}\text{-}b\text{-PtBA}_{55}\text{-I}$ copolymer in ethanol.

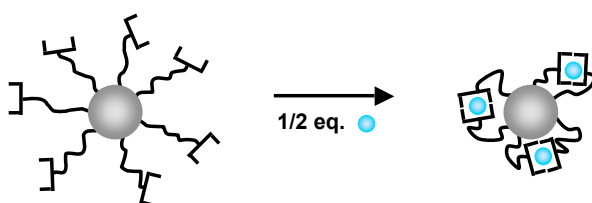


Figure 6.4: Effect of the addition of a metal salt to the initial micelles formed in ethanol. (PS block in grey, PtBA chains in black, metal ions as small dots)

terized by an extremely slow unimers-micelles equilibration rate [15], no further changes in aggregation number of the micelles is expected during the addition of metal salts at the experiments time scale (DLS measurements were typically performed a day after the addition of metal salt). Therefore, changes in R_h measured after the addition of metal salts are thought to exclusively translate modifications occurring into the micellar corona. The looping of coronal chains should result in a decrease of the overall R_h of the micelles.

These hypothesis were essentially confirmed by DLS measurements. The R_h of the PS₄₇-*b*-PtBA₅₅-[micelles was found to decrease after addition of metal ions (Table 6.1).

The extent of this decrease depended on the metal ion used. The largest decrease was observed for Ni²⁺ ions and the smallest for Zn²⁺ ions. The R_h measured are now close to the dimension of the micelles as measured by TEM. This means that the addition of metal ions induces a rather strong contraction of the PtBA coronal chains. Nevertheless the Ni²⁺-containing micelles are stable over weeks and do not display any secondary aggregation, as confirmed by DLS. The looped PtBA coronal chains should still enable a good micellar stability. That metal-terpyridine complexes have indeed been formed is confirmed by the UV/Vis spectra (Figure 6.5), showing the metal-to-ligand charge transfer bands characteristic of the different metal-ion complexes.

	0 eq.	0.5 eq.	1 eq.	5 eq.
Zn ²⁺		14 (0.12)	17 (0.12)	22 (0.16)
Ni ²⁺	22 (0.11)	11 (0.16)	12 (0.09)	14 (0.04)
Fe ²⁺		13 (0.14)	14 (0.07)	18 (0.10)

Table 6.1: Hydrodynamic radii R_h (in *nm*) of PS₄₇-*b*-PtBA₅₅-[micelles in the presence of various amounts (in eq. compared to the terpyridine ligands) of metal salts. (Numbers in parentheses corresponds to the PDI as determined by the CUMULANT routine)

In a second step, another 0.5 eq. of metal ion was added to the micelles in order to reach a final metal ion/terpyridine molar ratio of 1/1.

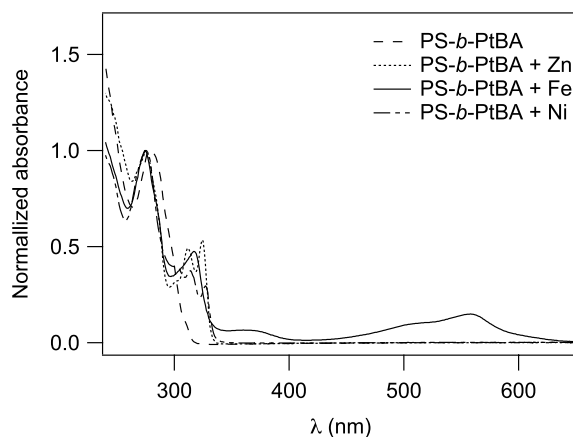


Figure 6.5: UV/Vis spectra of micelles of $\text{PS}_{47}\text{-}b\text{-PtBA}_{55}\text{-[}$ in ethanol with 0.5 eq. of the different metal ions (Zn^{II} , Fe^{II} and Ni^{II}). The spectrum of the copolymer micelles without metal ions is also shown as reference

This may trigger to the formation of *mono*-complexes (Figure 6.6) leading to the disappearance of the PtBA loops and hence to an expansion of the corona.

The results obtained by DLS (Table 6.1) showed no change in the micellar dimension for the Ni^{2+} and Fe^{2+} -containing samples while the R_h increased from 14 to 17 nm in case of the Zn^{2+} sample. A metal ion/terpyridine molar ratio of 1/1 was also achieved by directly adding the proper amount of metal ions to the initial $\text{PS}_{47}\text{-}b\text{-PtBA}_{55}\text{-[}$ micelles. Same results as the ones obtained from the two-fold addition of 1/2 eq. of metal salts were obtained. These results indicate that flower-like micelles containing *bis*-terpyridine metal complexes are essentially observed for Ni^{2+} and Fe^{2+} although the metal ion/terpyridine molar ratio points towards *mono*-complexes. In case of Zn^{2+} , the formation of *mono*-complexes is observed when the metal ion/terpyridine molar ratio is 1/1. To favor the formation of *mono*-complexes still further, a large excess of metal ions (final metal ion/terpyridine molar ratio of at least 5/1) was added (Table 6.1). Under these conditions, the Ni^{2+} -containing sample

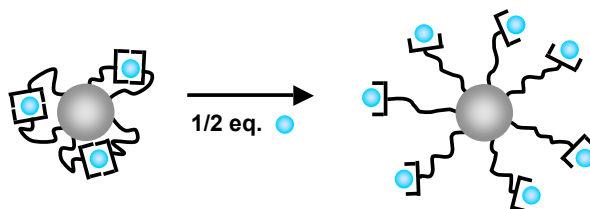


Figure 6.6: Effect of the addition of a metal salt to the previously flower-like micelles formed in ethanol. (PS block in grey, PtBA chains in black, metal ions as small dots)

still keeps the flower-like configuration since no increase in the size of the micelle is observed. The Fe^{2+} -containing sample shows an increase to a R_h of 18 nm due to the disappearance of looped PtBA chains concomitant with the replacement of *bis*-complexes by *mono*-complexes. In the case of Zn^{2+} , the R_h of the micelles further increases to reach 22 nm corresponding to the size of the initial micelles. This suggests that at 1 eq. of Zn^{2+} not all *bis*-complexes were opened into *mono*-complexes, and that a larger excess is needed to fully open all the *bis*-complexes. These experimental observations are in agreement with the corresponding stability constants of the complexes from terpyridine and Ni^{2+} , Fe^{2+} and Zn^{2+} [8–11]. Indeed, Ni^{2+} forms the most stable complexes and the Zn^{2+} the least stable, with the Fe^{2+} in between. The Zn^{2+} /terpyridine complexes are thus the most sensitive to an increase in the metal ion concentration, and the Ni^{2+} /terpyridine complexes the least sensitive ones.

In all these experiments, a linear dependence of the inverse relaxation time versus the scattering vector was observed (see e.g. Figure 6.7), signaling a translational diffusive motion in agreement with the formation of spherical micelles. Moreover, the CONTIN analysis of the DLS data confirmed that no aggregates of micelles were formed during these experiments. Unfortunately, UV-Vis spectroscopy is useless in these experiments due to the overlap of the characteristic MLCT bands of *mono*- and *bis*-terpyridine metal complexes based on Zn^{2+} , Ni^{2+} and Fe^{2+} .

Since the shifts of the ^1H -NMR signals associated to the terpyridine

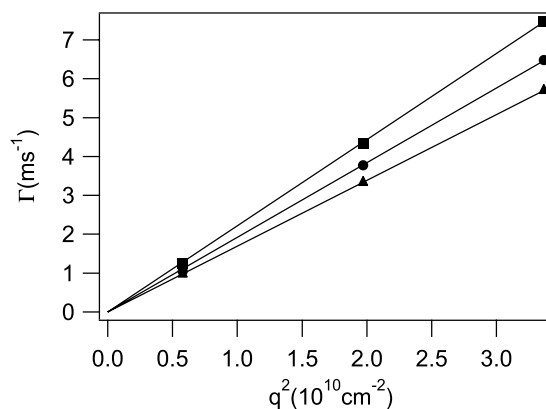


Figure 6.7: Translational diffusion behavior in case of micelles loaded with different amounts of Zn salt. (*black-filled triangles*: no metal salt, *black-filled dots*: 1 eq. of ZnCl_2 , *black-filled squares*: 0.5 eq. of ZnCl_2)

ligands differs from *mono*- to *bis*-complexes (see for example Ref. [16]), ^1H -NMR has been used to shed lights on the observations obtained from DLS measurements. Because Zn^{2+} -based complexes showed the more drastic changes in the DLS experiments, and moreover form diamagnetic complexes with terpyridine ligands, they are the most suitable candidates for this study [17, 18]. Since it has been proven [19] that the complexation behavior of terpyridine with Zn^{2+} is strongly dependent on the interplay between the metal-terpyridine interaction, the coordination ability of the counter ion and the nature of the solvent, the samples were prepared by following the same procedure as for the micelles. A PtBA homopolymer, of similar molecular weight than the PtBA block of the copolymer, bearing a terpyridine chain-end was dissolved in d^6 -EtOD, and different amounts of ZnCl_2 , dissolved also in d^6 -EtOD, were then added. The recorded spectra are shown in Figure 6.8. The signals of the protons H_6 (*) and $\text{H}_{3'}$ (#) are highlighted, since they are sensitive to the coordination mode of the terpyridine.

In a *bis*-complex, H_6 is positioned directly above the central pyridine unit of the second terpyridine, and experiences shielding by the aromatic ring current. Therefore the signal is shifted to high field by

0.8 ppm compared to a free terpyridine [20]. On the other hand, the H_{3'} signal appears as a sharp singlet and is shifted downfield by 0.7 ppm. These displacement are indeed the ones observed on the NMR spectrum recorded on the sample containing 0.5 eq. of Zn²⁺ ions, evidencing the formation of *bis*-complex. In a *mono*-complex, both the H₆ and H_{3'} signals are slightly shifted downfield compared to a free terpyridine [20], which is the situation observed for the addition of 1 eq. of Zn²⁺ ions. These ¹H-NMR results essentially validate the conclusions drawn earlier from DLS measurements. The signal broadening at a metal/ligand ratio of 1/2 observed in Figure 6.8 is probably due to exchange phenomena between different species, occurring at a rate similar to the NMR timescale, which is in the millisecond range. During the whole titration all compounds remained homogeneously dissolved so that aggregation or precipitation can be ruled out as a reason for the observed line broadening. At a ratio of 1/1, the signals remain sharp indicating an exchange kinetics which is significantly slower than the NMR timescale.

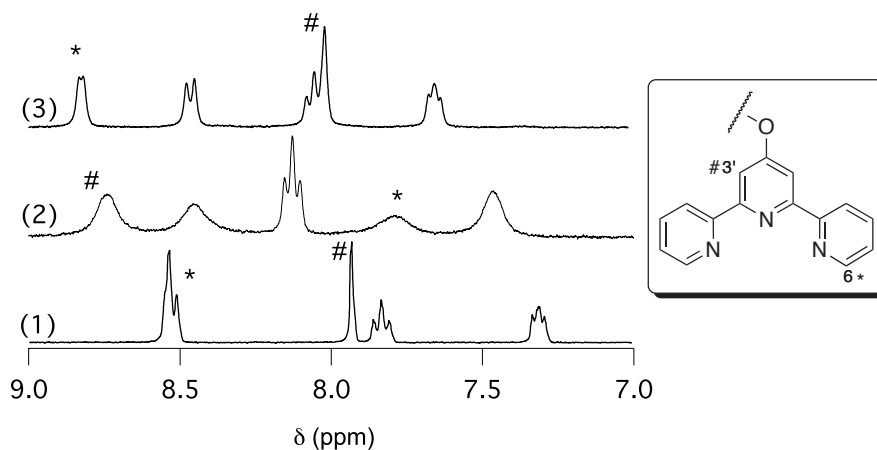


Figure 6.8: Metal to ligand titration followed by ¹H-NMR: (1) before any addition, (2) after addition of 0.5 eq. of Zn²⁺, (3) after addition of 1 eq. of Zn²⁺. The * and # symbols highlighted the position of H₆ and H_{3'} respectively

6.4 Towards the formation of core-shell corona micelles

In addition to tuning the micellar size by changing the conformation of the coronal chains, our strategy can also be used to build slightly more complex objects, going from the core-shell initial system to a core-shell-corona system. This is done by complexing a third terpyridine-functionalized polymer block on the PS₄₇-*b*-PtBA₅₅-[micelles decorated with metal ions. An equimolar amount, with respect to the copolymer chains, of a terpyridine end-functionalized poly(ethylene oxide), PEO₁₂₅-[, has been added to the PS₄₇-*b*-PtBA₅₅-[micelles previously loaded with 1 eq. of Fe²⁺ ions, and should thus yield PS₄₇-*b*-PtBA₅₅-[Fe]-PEO₁₂₅ micelles. The iron salt was chosen because it offers the best compromise between the stability and dynamic character of the terpyridine complexes. Those micelles were then characterized by DLS which showed a R_h of 56 nm with a narrow PDI, and a single population in the CONTIN histogram (Table 6.2). This evidences thus the formation of well defined micelles with a PS core and a corona of PtBA₅₅-[Fe]-PEO₁₂₅. To further prove that the additional PEO layer has been grafted to the initial micelles, the PS₄₇-*b*-PtBA₅₅-[Fe]-PEO₁₂₅ micelles were transferred into water, a selective solvent for the PEO block. This was done by first adding a volume of water, by steps of 50 μ L, equal to half the ethanol volume in order to trigger the micellization. The ethanol/water solution was then dialyzed against water for 24 hours replacing the water at least three times (Spectra-Por dialysis bags) to remove the ethanol. The final concentration of the micelles in pure water was set to 1 g/L. Stable micelles with a R_h of 37 nm have been detected in pure water by DLS (Table 6.2). The decrease in R_h of the PS₄₇-*b*-PtBA₅₅-[Fe]-PEO₁₂₅ micelles in pure water compared to ethanol is due to the collapse of the PtBA block which is not soluble in water. Micelles with a PS core, a PtBA shell and a corona of PEO are thus obtained (see Figure 6.8), proving the success of the transfer in water and thereby the efficiency of the grafting of the additional PEO layer through formation of Fe²⁺/terpyridine complexes. This latter point was additionally ascertained by adding the same PEO₁₂₅-[to the PS₄₇-*b*-PtBA₅₅-[micelles without metal ions. In this case, the transfer into pure water failed, leading to precipitation of

the $\text{PS}_{47}\text{-}b\text{-PtBA}_{55}\text{-[Fe}^{2+}]$ micelles.

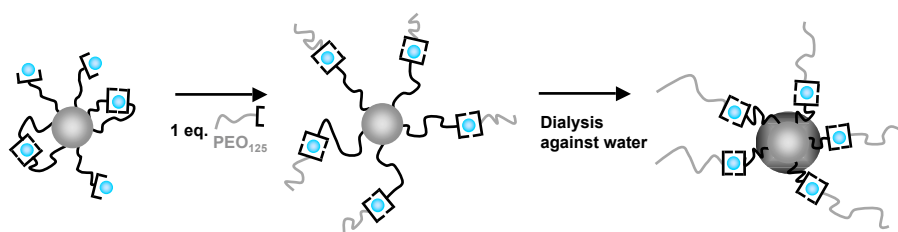


Figure 6.9: Effect of the addition of a PEO_{125} block on $\text{PS}_{47}\text{-}b\text{-PtBA}_{55}\text{-[Fe}^{2+}]$ micelles loaded with 1 eq. of Fe^{2+} and collapse of the PtBA layer after transfer of the micelles into water. (PS block in grey, PtBA block in black, PEO block in grey, metal ions as small dots).

	Fe^{2+} (1 eq.)
Ethanol	56 (0.12)
Water	37 (0.11)

Table 6.2: Hydrodynamic radii R_h (in nm) of $\text{PS}_{47}\text{-}b\text{-PtBA}_{55}\text{-[Fe}^{2+}]$ micelles after addition of PEO_{125} . (Numbers in parentheses corresponds to the PDI as determined by the Cumulant method)

6.5 Conclusions

We have demonstrated that the addition of metal ions to micelles formed by the $\text{PS}_{47}\text{-}b\text{-PtBA}_{55}\text{-[}$ copolymer in ethanol, and consisting of a PS core and PtBA coronal chains with terpyridine ligands at their extremity, allows to tune their hydrodynamic radius by changing the conformation of the coronal chains. This approach leads to the formation of metallo-supramolecular block copolymers hierarchically combining the characteristic features of covalent block copolymer micelles and metallo-supramolecular polymers. Finally, our approach allows the addition of a third layer in the micellar structure by complexing a terpyridine functionalized third block onto the initial micelles. We believe that this new approach significantly broaden the scope of utilization of metal-ligands complexes in self-assembled micellar systems.

Experimental part

The terpyridine functionalized diblock PS₄₇-*b*-PtBA₅₅-[is synthesized by nitroxide-mediated radical polymerization according to a procedure already described. [13] The polymerization degrees of the poly(styrene) (PS) and of the poly(*t*-butylacrylate) (PtBA) are of 47 and 55, respectively. The α -terpyridine- ω -methyl-poly(ethylene oxide) with a degree of polymerization of 125 (PEO₁₂₅) is prepared as described in ref. [5].

Micelle preparation: The PS₄₇-*b*-PtBA₅₅-[copolymer is dissolved directly in ethanol at a concentration of 3 g/L. The solution is allowed to stand during several days before any measurements. Half an equimolar, or an equimolar amount (relative to the amount of available terpyridine groups) of the appropriate metal chloride salt (NiCl₂, FeCl₂, ZnCl₂) in ethanol is then added, and the solution is stirred for 24 hours. In order to study the transfer of these objects in water, an equimolar amount, with respect to terpyridine groups, of a terpyridine end-functionalized poly(ethylene oxide) is added (PEO₁₂₅). The solution is stirred for 24 hours. Then a volume equal to half the ethanol volume is added by steps of 50 μ L in order to trigger the micellization in water. Finally, the ethanol/water solution is dialyzed against water for 24 hours replacing the water at least three times (Spectra-Por dialysis bags). The final concentration of the micelles in pure water is set to 1 g/L.

Transmission electronic microscopy measurements: Transmission electron microscopy (TEM) was performed on a LEO 922 microscope, operating at 200 kV accelerating voltage in bright field mode. The images were formed by unscattered electrons only. Samples for TEM experiments were prepared by spin-coating a drop of the solution of micelles onto a carbon-coated TEM grid. The grids were allowed to dry in a vacuum chamber during 24 hours. Finally, the samples were exposed to RuO₄ vapors during several minutes before measurement [14].

Dynamic light scattering: The hydrodynamic radius, R_h , of the micellar complexes were measured by dynamic light scattering (DLS). The experimental autocorrelation function, $g(t)$, is commonly expressed in the form of a cumulant expansion (eq 6.1):

$$g(t) = \exp \left(-\tilde{A}_1 t + \left(\frac{\tilde{A}_2}{2!} \right) t^2 - \left(\frac{\tilde{A}_3}{3!} \right) t^3 + \dots \right) \quad (6.1)$$

where Γ_i is the *i*th cumulant and $\Gamma_1 = Dq^2$ where D is the translational diffusion coefficient and q is the absolute value of the scattering vector. The polydispersity index (PDI) of the objects was estimated from the ratio. The diffusion coefficient extrapolated to zero concentration is related to the hydro-

dynamic radius R_h by the Stokes-Einstein equation (eq 6.2):

$$R_h = \frac{k_b T}{6\pi\eta D} \quad (6.2)$$

where k_b is the Boltzmann constant and η the viscosity of the solvent. DLS measurements were performed on a Malvern CGS-3 apparatus equipped with a He-Ne laser with a wavelength λ of 632.8 nm. The temperature was controlled at 298 K, and the measurements were done at several angles. The experimental data have been also analyzed by the CONTIN method which is based on an inverse-Laplace transformation of the data and which gives access to a size distribution histogram for the analyzed micellar solutions.

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STIMULI-RESPONSIVE MICELLAR GELS BASED ON METAL-LIGAND INTERACTIONS

Abstract

*Micellar gels have been obtained by adding metal ions to micelles bearing terpyridine ligands at the extremity of the coronal chains. The micelles, prepared by direct dissolution in ethanol of a PS-*b*-PtBA-[di-block copolymer bearing a terpyridine end-group, consist of a PS core and PtBA-[coronal chains since ethanol is a selective solvent for PtBA. These initial micelles have been characterized by dynamic and static light scattering in the dilute regime and were found to be spherical and extremely well defined. The gels are obtained upon addition of 0.5 eq. of metal ions (Zn^{2+} , Ni^{2+} , Fe^{2+}) to a concentrated solution of the PS-*b*-PtBA-[micelles. The gelification phenomenon is attributed to intermicellar bridges resulting from the formation of bis-terpyridine metal ion complexes. Rheological measurements revealed that the characteristic behavior of those gels critically depends on the added metal ions, in relation with the strength of the accordingly formed bis-terpyridine metal ion complexes. This approach offers an unprecedented control over gel properties and interesting stimuli-responsive properties that pave the way towards self-healing materials.*

7.1 Introduction

Block copolymer micelles are ideal model systems for exploring soft material behavior due to their easily tunable properties (such as interactions, size, softness). Indeed, block copolymer micelles can be seen as typical intermediate structures [1–3], sitting between the colloidal and polymeric limits. If many short chains stick out of the micellar corona (i.e. crew-cut micelles) the colloidal nature prevails, whereas for very long coronal chains (i.e. star-like micelles) the polymeric response is dominant. Moreover, micelles can be assembled into a network, ultimately leading to the formation of a macroscopic gel. Such materials can be considered as hierarchically-organized systems since they combine at a first level the self-organization of block copolymer chains into micellar structures, with the gel formation as a second level assembly.

Assembly of micelles leading to gels has been mainly investigated for polyoxyalkylene-type ABA copolymers (Pluronics) in water, although micellar gels in apolar solvents have been also largely considered [4]. Recently, ABC triblock terpolymers have also been exploited for micellar gel formation [5–10]. However, in all the previous examples reported in the literature, the onset of the gelation process is related to the concentration at which the coronal chains of the micelles start to overlap, resulting in entanglements.

In this study, we introduce a novel class of block copolymer micelles bearing “sticky” groups at the extremity of coronal chains. More precisely, our strategy is based on the use of metal-ligand complexes as reversible and tunable intermicellar crosslinkers. The idea of using “sticky” groups to induce gel formation has indeed been previously proposed in the case of telechelic associative polymers [11, 12], ABA triblocks in microemulsions [13] and end-functionalized diblock copolymers [14, 15]. Very recently, Ligoure and coworkers reported on micellar gels obtained from wormlike micelles bridged by telechelic polymers [16]. A similar approach has been also conducted by the group of Lodge [17, 18]. Finally, to the best of our knowledge, nothing has been reported yet on micelles bridged by metal-ligand interactions.

It has been previously demonstrated that metal ligand complexes are interesting tools to build networks and gels. A first type of strat-

egy relies on using polymers bearing multiple metal-complexing units as pendant groups [19–23]. The first examples have already been reported in the 1990s. Through the complexation of bipyridine moieties, redox and thermoreversible hydrogels were obtained. By connecting a polymerizable group to terpyridine ligands, copolymers bearing pendant terpyridine moieties were synthesized by random copolymerization. More recently, copolymers of this type could also be prepared in a controlled fashion using RAFT polymerization. The addition of metal ions to such copolymers led to cross-linking through complex formation. The viscosity was dependant on the terpyridine content in the copolymer and on the nature of the metal ion used. At higher concentrations, gel formation was observed. Another type of approach, using the ligand 1,6-*bis*(10-methylbenzimidazolyl)-4-hydroxypyridine, was presented by Rowan et al. for the preparation of photoactive mechanoresponsive gels [24, 25]. They synthesized a ditopic unit that can form 2:1 metal complexes with transition-metal ions and 3:1 complexes with lanthanide ions. The latter complexes act as branching points and are responsible for gelation upon introduction of a small percentage of lanthanide ions to a coordination polymer. Because the lanthanide complexes are less stable, the branching points of the gel open upon heating, or if mechanic stress is exerted by shaking, inducing a liquefaction of the gel. When the sample is cooled or kept at rest, the gel is reformed.

Prompted by these very interesting previous reports, we decided to merge the concepts of block copolymer micellar gels and supramolecular gels and networks based on metal ligand complexes. To this aim, we have developed diblock copolymer micelles whose coronal chains bear a terpyridine ligand at their extremity. In dilute solution, we have previously shown (see Chapter 6) that addition of metal ions resulted in the formation of intramicellar *mono*- or *bis*-terpyridine metal complexes that strongly influenced micellar size. By raising micellar concentration, we observe intermicellar *bis*-terpyridine metal complexes after addition of metal ions, ultimately leading to micellar gels.

7.2 Characterization of the self-assembly behavior in diluted solution

For this work, a $\text{PS}_{80}\text{-}b\text{-PtBA}_{200}\text{-[}$ diblock copolymer has been synthesized by NMP using the terpyridine functionalized alkoxyamine as initiator. The $\text{PS}_{80}\text{-}b\text{-PtBA}_{200}\text{-[}$ copolymer is dissolved directly in ethanol, inducing micellization since ethanol is a selective solvent for the PtBA block. The solution, where the micellar concentration is set at 12 wt %, is allowed to stir several days before any measurements in order to reach the equilibrium. As in the previous chapter, terpyridine ligands are located at the extremity of the coronal chains of the micelles. However, in this case, longer PtBA blocks and much higher concentration of micelles are used in order to favour intermicellar interactions upon the addition of metal ions. These terpyridines can be further used for complexation with metal ions, enabling the formation of metal-ligand complexes between micelles (see Figure 7.1). Three metal ions have been considered, i.e. Zn^{2+} , Ni^{2+} and Fe^{2+} . Whenever the metal ion/terpyridine molar ratio is set to 1/2, the formation of *bis*-terpyridine-metal ion complexes is expected, leading to the formation of micellar gels.

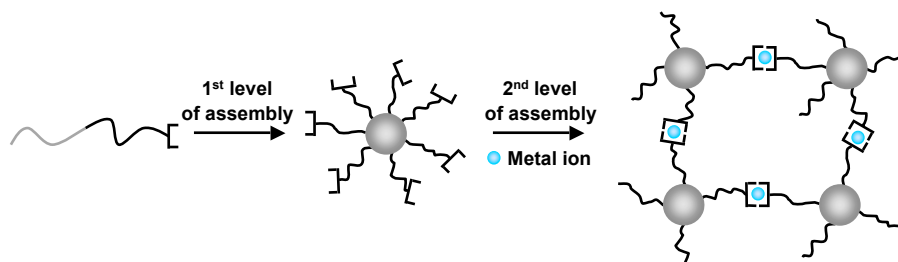


Figure 7.1: Two levels of self-assembly leading to the formation of a network.

Firstly, the characteristic features of the micelles formed by the $\text{PS}_{80}\text{-}b\text{-PtBA}_{200}\text{-[}$ diblock copolymer have been investigated by dynamic light scattering (DLS) on ethanol solutions of different concentrations (from 1 g/L to 10 g/L), at various angles (from 40° to 140°). Indeed, light scattering measurements have to be performed in more diluted solutions

than those used for gel formation, in order to prevent intermicellar interactions.

The analysis of the normalized intensity autocorrelation function $g(q, t)$, where q is the scattering vector ($q = [4\pi n_0 \sin(\theta/2)]/\lambda$) and t the time, was carried out following the method of cumulants [26], fitted with *mono*-exponential decay functions. Once the first cumulant Γ is determined, the concentration and angular dependence can be expressed as:

$$\Gamma/q^2 = D_z(1 + k_D c + \dots)(1 + CR_g^2 q^2 + \dots) \quad (7.1)$$

where D_z is the z -average diffusion coefficient, C is a parameter characteristic of the molecular architecture of the different species, k_D is the effective interaction parameter.

$D_z(c)$ was determined from the evolution of Γ versus q^2 (cf. Figure 7.2) at eight different scattering angles using the cumulant method by extrapolation to 0° scattering angle. Fitting these data gives a linear correlation with $r^2 = 0.9985$, indicating that only translational diffusion occurs. Then $D_z(c)$ was plotted against the concentration and the “true” z -average diffusion coefficient was determined by extrapolating $D_z(c)$ to $c \rightarrow 0$ (Figure 7.2). Finally, with the accordingly determined diffusion coefficient, the z -average hydrodynamic radius R_h can be calculated from the Stokes-Einstein equation:

$$R_h = \frac{k_b T}{6\pi\eta D_z} \quad (7.2)$$

where η is the solvent viscosity. The accordingly determined hydrodynamic radius was found to be $R_h = 21 \text{ nm}$. Dynamic light scattering data were also analyzed using the CONTIN method [27] to determine the distribution of hydrodynamic sizes. The autocorrelation functions $g(q, t)$ and the particle size distribution obtained by CONTIN analysis of DLS data are shown in Figure 7.3 at three angles (60° , 90° and 130°). This graph shows a unimodal and narrow distribution, independent of the scattering angle.

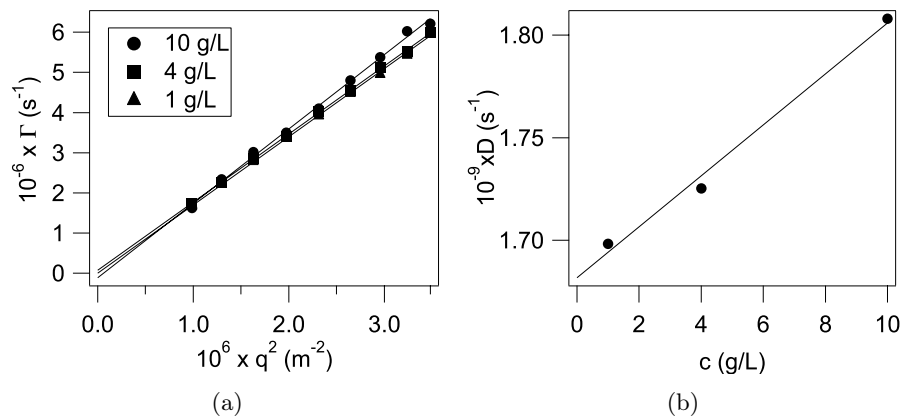


Figure 7.2: (a) Dependence of the first cumulant frequency (Γ) with the square magnitude of the scattering vector (q^2) at three different concentrations (b) dependence of the z -average diffusion coefficient with the concentration.

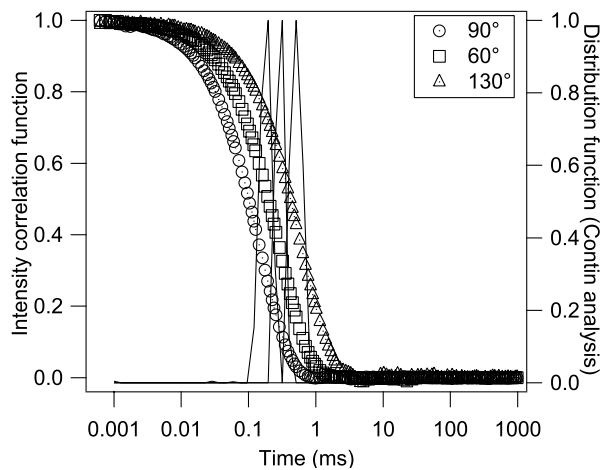


Figure 7.3: Intensity autocorrelation functions and CONTIN analysis of PS₈₀-*b*-PtBA₂₀₀- micelles in ethanol at three different scattering angles.

In addition to DLS, static light scattering experiments (SLS) were performed in ethanol with concentration ranging from 1 to 10 g/L. The analysis of the scattering intensities using a Zimm plot (Figure 7.4) yields the weight averaged molar mass, $M_{w,app}$, the z -averaged radius of gyration, $\langle R_g \rangle$ and the second virial coefficient A_2 [28]. SLS yields a $\langle R_g \rangle = 15$ nm. Comparing this value to the hydrodynamic radius R_h previously determined ($R_h = 20$ nm), a ratio $R_g/R_h = 0.75$ (the so-called ρ -parameter) is found, which is close to the values expected for a uniform sphere (0.774) [29,30]. The static and dynamic light scattering results are summarized in Table 7.1. An estimation of the aggregation number of the micelle, N_{agg} , is obtained by dividing the apparent molecular weight of the micelle by the molecular weight of the corresponding diblock copolymer. The value of N_{agg} is included in Table 7.1, and is in agreement with typical values found in literature for block copolymer micelles [31,32].

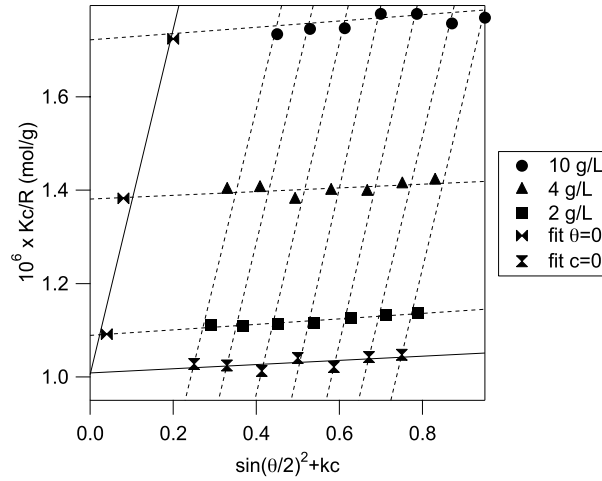


Figure 7.4: Zimm plot of PS₈₀-*b*-PtBA₂₀₀- micelles in ethanol at 25 °C.

T (°C)	R_h (nm)	$10^{-5} \cdot M_{w,app}$ (g/mol)	$\langle R_g \rangle$ (nm)	$10^{-8} \cdot A_2$ (mol.L/g ²)	N_{agg}	R_g/R_h
25	20	9.50	15	3.50	28	0.75

Table 7.1: Characteristic parameters for PS₈₀-*b*-PtBA₂₀₀-[micelles in diluted solutions deduced from DLS and SLS experiments.

7.3 Rheological characterization in more concentrated solution

In collaboration with the group of Prof. C. Bailly, rheological characterizations were performed on concentrated micellar solutions in ethanol (12 wt. %) by Dr. F. Stadler with a TA Instruments ARES using a cone and plate geometry. The measurements were carried out at 18 °C in an ethanol saturated atmosphere to minimize evaporation of the solvent. The experimental section provides further details about the experiments described in this section.

Figure 7.5 shows the storage and loss moduli G' and G'' obtained at a frequency ω of 10 s⁻¹ (=1.6 Hz) and a small deformation. Depending on the metal ion used the G' and G'' values change notably. For the sample without any added metal ion a Newtonian behavior is basically detected (the viscosity is independent of strain and frequency). The storage modulus of this sample is very low, being barely detectable and thus a very large experimental uncertainty is associated with it.

The sample containing Zn²⁺ ions (Zn²⁺/terpyridine molar ratio of 1/2) has a somewhat higher modulus (factor 5) than the sample without ions and shows a very weak gelation at low frequencies and low strains, but it can still be considered to show essentially a Newtonian behavior. The sample where Ni²⁺ metal ions have been added (Ni²⁺/terpyridine molar ratio of 1/2) has a much higher modulus and shows a significant elasticity, expressed by the storage modulus G' being essentially as large as the loss modulus G'' . This phenomenon ($G' = G''$) is usually associated with a gel-like structure.

In comparison to the unloaded and the Zn²⁺ loaded samples, the Ni²⁺

containing sample exhibits a distinct behavior. Unlike the two samples previously described, this sample withstands the tube inversion test, i.e. the solution sticks to the bottom of the tube, even if the tube is upside down. This translates in a 400-times increase of G' . The similarity of the values of $G'(\omega)$ and $G''(\omega)$ is valid over the whole range of frequencies, in agreement with the typical behavior for gels and rubbers.

Finally, the sample loaded with Fe^{2+} metal ions exhibits a loss modulus G'' significantly smaller than the storage modulus G' , in agreement with a rubber behavior. However, this “rubber” is about 1000 times softer than usual rubbers, thus we can characterize this Fe^{2+} loaded sample as an “ultrasoft” rubber. Moreover, $G'(\omega)$ and $G''(\omega)$ for this sample are approximately constant over a wide range of frequencies.

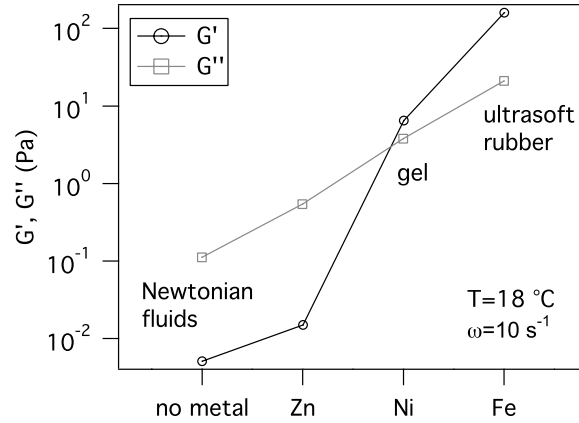


Figure 7.5: Storage G' and loss modulus G'' at $\omega = 10 \text{ s}^{-1}$ and RT for the different samples (12 wt. %) investigated in this study.

The sample response to shear deformation depends strongly on the deformation, which can induce structural changes (Fig. 7.6). At a deformation γ_0 of 100 % (see $t = 600 - 800 \text{ s}$ in Fig. 7.6), storage G' and loss G'' moduli are reduced by about 30 %. After switching back to 10 % deformation, the two moduli go back to their original values after about 10 s, which is very close to an instantaneous switchback. On the other hand, at a higher deformation of 1000 % (see $t \approx 1450 \text{ s}$), a significant

decrease of the two moduli is observed. Moreover a peak in G'' is noticed at the onset of the high deformation. After this instantaneous recovery G' and to smaller extent G'' increase slowly finally reaching the original state about 4000 s after the high strain.

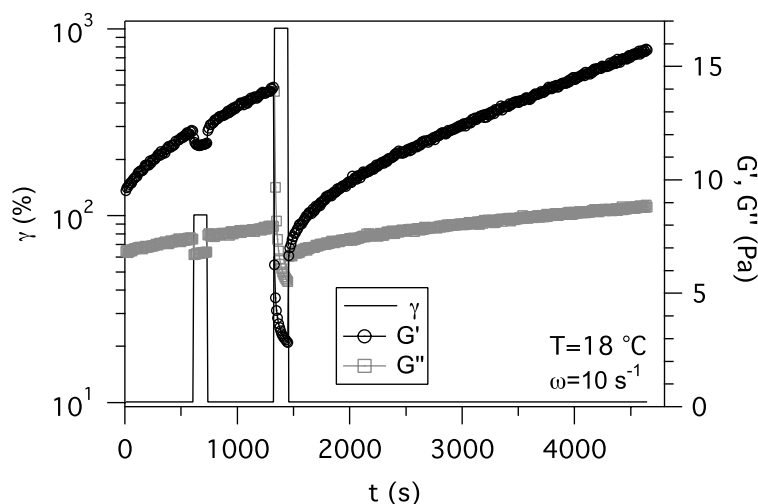


Figure 7.6: Time and strain dependence of the Fe^{2+} loaded sample.

To better visualize these results, a so-called strain sweep has been performed corresponding to a measurement of the moduli $G'(\gamma_0)$ and $G''(\gamma_0)$ as a function of the deformation γ_0 (Fig. 7.7). $G'(\gamma_0)$ and $G''(\gamma_0)$ are constant at $\gamma_0 < 50$ %, followed by a peak in $G'(\gamma_0)$. This behavior (including $G'(\gamma_0) > G''(\gamma_0)$) is characteristic of highly elastic rubbery materials. When the γ_0 value reaches 200 %, $G''(\gamma_0)$ increases distinctly reaching the level of $G'(\gamma_0)$. This behavior is associated with a gel, characterized by $G' = G''$ and is independent of frequency (not shown). At deformation γ_0 larger than 400 %, $G'(\gamma_0)$ and $G''(\gamma_0)$ decrease, leading to an increasingly dominant $G''(\gamma_0)$. This behavior is typically observed for viscoelastic polymer melts and solutions.

The different stability of the Fe^{2+} , Ni^{2+} , and Zn^{2+} *bis*-terpyridine complexes lead to different rheological behavior. The sample without any ions behaves basically like an unstructured Newtonian fluid. In the sample loaded with 0.5 equivalent of Zn^{2+} with respect to the terpyridine,

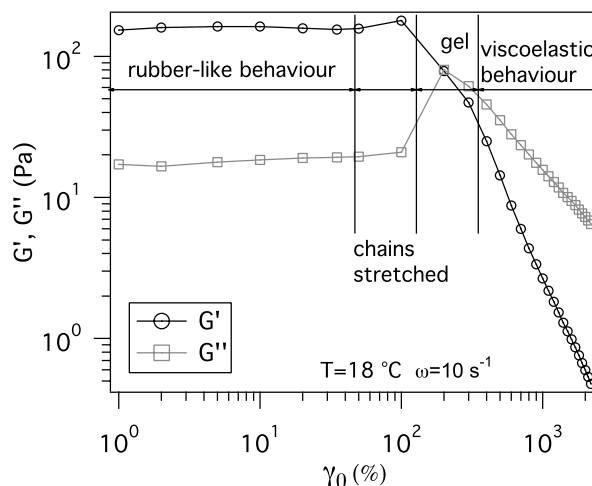


Figure 7.7: Strain sweep recorded on the Ni^{2+} loaded sample.

some structuration is evidenced at low frequencies, which is extremely weak and shear sensitive. Indeed, the *bis*-terpyridine Zn^{2+} complexes exhibit the lowest stability constant of the considered metal ion series, and thus when a very weak shear is applied, the structure is lost due to mechanical stress ($>2 \text{ Pa}$). On the other hand, the stronger *bis*-terpyridine Ni^{2+} complexes lead to a much more significant interaction pattern. At a deformation γ_0 of 300 % (which is at the transition between gel-like and viscoelastic behavior in Fig. 7.7) the sample is able to absorb up to 550 Pa stress. At small deformations this material behaves like a network, which is understandable, as the micelles are cross-linked by the *bis*-terpyridine Ni^{2+} complexes located at the end of the coronal chains. Once a certain stress is exceeded the complexes start to break, leading thus to the increase of $G''(\gamma_0)$ and to the decrease of the elastic modulus $G'(\gamma_0)$. In this gel regime, the network structure is weakened probably because of the presence of opened complexes beside *bis*-terpyridine Ni^{2+} complexes. This leads to the parallelism of $G''(\omega, \gamma_0)$ and $G'(\omega, \gamma_0)$. At larger strains, the network is mechanically broken apart, leading to single micelles or small clusters of micelles behaving like a normal polymer melt, since the stress is too high to form a network.

The different time dependencies of the recovery of the moduli after high deformation (Fig. 7.6) can be also explained. At a deformation γ_0 of 100 % the material is deformed elastically, i.e. the structure remains unaltered, and thus the original behavior at small strains is more or less instantaneously recovered. At high strains ($\gamma_0 = 1000$ %), however, the material has suffered significant structural degradation and thus recovering the original state takes a long time. A thixotropic behavior is thus observed

7.4 Conclusions

In this work, the formation of well-defined $\text{PS}_{80}\text{-}b\text{-PtBA}_{200}$ -[diblock copolymer micelles in ethanol has been firstly extensively investigated by dynamic and static light experiment. We have then induced the formation of a network of micelles bridged together by *bis*-terpyridine metal complexes upon addition of metal ions. Three metal ions have been considered, i.e. Zn^{2+} , Ni^{2+} and Fe^{2+} , and the concentration of the micellar solution was set to 12 wt. %. Considering a metal/terpyridine molar ratio of 1/2, we have observed an increase of the viscosity of the initial solution, leading in the case of Ni^{2+} and Fe^{2+} to the formation of micellar gels. A series of rheological experiments have been thus performed to provide a deeper insight into these promising materials. The samples loaded with Ni^{2+} and Fe^{2+} exhibit a gel and a “soft-rubber” behaviors, respectively. Structural changes have been observed when the samples are submitted to shear deformation, and a thixotropic behavior has been observed.

Experimental part

The terpyridine functionalized diblock $\text{PS}_{80}\text{-}b\text{-PtBA}_{200}\text{-[}$ is synthesized by nitroxide-mediated radical polymerization according to a procedure already described (see Experimental section, Chapter 3).

Micelle preparation: The $\text{PS}_{80}\text{-}b\text{-PtBA}_{200}\text{-[}$ copolymer is dissolved directly in ethanol at a concentration of 120 g/L . The solution is allowed to stand during several days before any measurements. Half an equimolar (relative to the amount of available terpyridine groups) of the appropriate metal chloride salt (NiCl_2 , FeCl_2 , ZnCl_2) in ethanol is then added under vigorous stirring.

Dynamic light scattering: DLS and SLS measurements were performed on a Malvern CGS-3 apparatus equipped with a He-Ne laser with a wavelength λ of 632.8 nm . The temperature was controlled at 298 K , and the measurements were done at several angles.

Rheological experiments: The rheological characterization was performed with a TA Instruments ARES using a $25\text{ mm}/0.02\text{ rad}$ cone and plate geometry. The measurements were carried out at RT ($\approx 18\text{ }^\circ\text{C}$) in an ethanol saturated atmosphere to minimize evaporation of the solvent. Three different kinds of tests were performed in oscillation. The first kind is a time sweep, where data were continuously acquired at a constant deformation γ_0 and oscillation frequency ω . This test was used to check the changes of the material properties as a function of time. The strain dependence was checked with a strain sweep, a test at a constant oscillation frequency but a continuously increasing strain up to a strain amplitude γ_0 of 2300% , representing the maximum strain possible with the current setup. The last setup is the frequency sweep, where the deformation γ_0 was kept constant under variation of the frequency ω . An alternative approach for obtaining a strain sweep was also used: the acquisition of several frequency sweeps under variation of the strain amplitude γ_0 .

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SELF-ASSEMBLY OF
METALLO-SUPRAMOLECULAR BLOCK
COPOLYMERS IN THIN FILMS

Abstract

The self-assembly of a metallo-supramolecular block copolymer PS-[Ru]-PEO, where -[Ru]- is a bis-2,2':6',2''-terpyridine-ruthenium(II) complex, in thin films was investigated. Metallo-supramolecular copolymers exhibit a different behavior compared to their covalent counterpart. The presence of the charged complex at the junction of the two blocks has a strong impact on the self-assembly, effecting the orientation of the cylinders and ordering process. PEO cylinders oriented normal to the film surface are obtained directly regardless of the experimental conditions over a wide range of thicknesses. Exposure to polar solvent vapors can be used to improve the lateral ordering of the cylindrical microdomains.

8.1 Introduction

In recent years, supramolecular polymer chemistry, applying the principles of supramolecular chemistry to the synthesis and self-organization of macromolecules, has gained increasing interest. The first approach developed, perhaps the most common one, is the preparation of polycondensation-type supramolecular polymers where each monomer or macromonomer is linked by noncovalent interactions [1–7]. More recently, a second approach has been developed where supramolecular linkers are introduced at specific locations in the block copolymer architecture, leading to well-defined supramolecular block copolymers [2, 8]. These systems combine the characteristic features of block copolymers (e.g., microphase separation between immiscible constituent blocks) with those of supramolecular systems (e.g., reversibility, and tunability of the strength of the supramolecular bonds). Hydrogen bonds [2, 3, 9] and metal-ligand coordination bonds [8] have been exploited to prepare supramolecular block copolymers, but examples based on the latter interaction, so-called metallo-supramolecular block copolymers, are more numerous due to the stronger binding strength compared to hydrogen binding systems. Metallo-supramolecular block copolymers offer several advantages over their covalent counterparts. The reversibility of the supramolecular bond enables the design of smart “switchable” materials with tailor-made properties. Moreover, the presence of a metal complex in the copolymer structure introduces additional electrochemical, photochemical, and redox properties [4, 5, 7]. These novel copolymers are thus good candidates for the formation of nanostructured materials. In addition to these interesting properties, studies on the self-assembly behavior of these copolymers in different media revealed a strong influence of the metal-ligand complex on the resultant structures. For example, a 13 member library of $\text{PS}_x\text{-[Ru]-PEO}_y$ block copolymers was prepared and their micellization in water was studied (see Chapter 4). Characterization of the micelles revealed that the core size did not scale linearly with the degree of polymerization (DP) of the PS block, as expected from the theory of classical covalent copolymers. It was proven that this unusual behavior is due 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, with the core diameter scaling linearly with $DP^{3/5}$. The influence of the metal-ligand complex manifests itself also in the melt [10, 11]. A small-angle X-ray scattering (SAXS) investigation on a PS_{20} -[Ru]-PEO₇₀ revealed that, contrary to its covalent counterpart PS_{22} -*b*-PEO₇₀, a microphase separation occurred for the metallo-supramolecular copolymer. When hexafluorophosphate (PF_6^-) is used as the counterion, the morphology observed is spherical, not the expected lamellar morphology considering the composition of the copolymer. This is due to the aggregation of the terpyridine-ruthenium(II) complexes and of the counterions, forming spherical aggregates. If the more bulky tetraphenylborate (BPh_4^-) is used as counterion, a highly ordered lamellar melt is obtained after annealing at 55 °C for 40 *h*.

All these observations prompted us to study the self-assembly in thin films of metallo-supramolecular block copolymers in more detail. In this chapter we report on the preparation of films of a PS-[Ru]-PEO copolymer under different conditions and their characterization by scanning force microscopy (SFM) to determine the influence of the metal-ligand complex on the self-assembly behavior in thin films.

8.2 Formation of thin films starting from PS_{300} -[Ru^{II}]-PEO₂₂₅

The PS_{300} -[Ru]-PEO₂₂₅ metallo-supramolecular block copolymer considered in this study has been prepared following a sequential two-step self-assembly process (see Chapter 3, Section 3.3 for further details). The PS_{300} -[Ru]-PEO₂₂₅ copolymer has a PEO volume fraction of 0.24 and should self-assemble into a morphology consisting of PEO cylindrical microdomains in a PS matrix. Fustin et al. have previously reported that such metallo-supramolecular block copolymers are good candidates to form nanoporous thin films with cylindrical pores, which were obtained in two steps [12]. In the first step, cylindrical microdomains of PEO oriented normal to the substrate were obtained by spin-coating a

solution of the copolymer in a non-selective solvent without the need of further treatment. In the second step, the metal-ligand complexes were opened by oxidizing the Ru^{II} into Ru^{III} . An oxidation of Ru^{II} into Ru^{III} is accompanied by a transformation of the initial *bis*-complexes into *mono*-complexes. This releases the minor block and creates the nanopores. The removal of the PEO was evidenced by SFM, X-ray photoelectron spectroscopy and X-ray reflectivity.

Here, the self-assembly in thin films of the $\text{PS}_{300}\text{-[Ru]-PEO}_{225}$ metallo-supramolecular block copolymer is studied in more detail. Films were spin-coated from solutions using different non-selective solvents (benzene, toluene, THF). Figure 8.1 shows a phase contrast SFM image of a thin film of this copolymer spin-coated from a THF solution. Arrays of nanoscopic cylindrical domains of PEO are seen at the surface of the film, suggesting their orientation normal to the substrate. The average center-to-center distance of the cylindrical microdomains, λ_{C-C} , is 39 nm. Similar results were obtained from solutions in other solvents (toluene or benzene). This behavior is completely different from that observed for a covalent $\text{PS-}b\text{-PEO}$ block copolymer. In that case, the orientation of the PEO cylinders is strongly dependent on the spin-coating conditions [13–17].

According to the solvent used and relative humidity, cylindrical microdomains oriented parallel to or normal to the surface or a mixed orientation can be obtained. Best results were obtained when benzene is used as solvent [15, 17]. For the $\text{PS}_{300}\text{-[Ru]-PEO}_{225}$ copolymer, cylindrical microdomains oriented normal to the surface are obtained independently of the preparation conditions. This different behavior between metallo-supramolecular and covalent block copolymers arises from the presence of the charged metal-ligand complex at the junction between the PS and PEO blocks. Interestingly, the $\text{PS}_{300}\text{-[Ru]-PEO}_{225}$ copolymer behaves like an ABC triblock copolymer, where the metal-ligand complex and the associated counterions act as a middle block that is strongly incompatible with the other blocks and that has a strong affinity to the substrate. This was also observed in a previous study on the melt morphology of a PS-[Ru]-PEO copolymer [10, 11]. The enhanced incompatibility of the blocks, compared to the covalent $\text{PS-}b\text{-PEO}$ block copolymer, and the preferential segregation of the metal complex to the

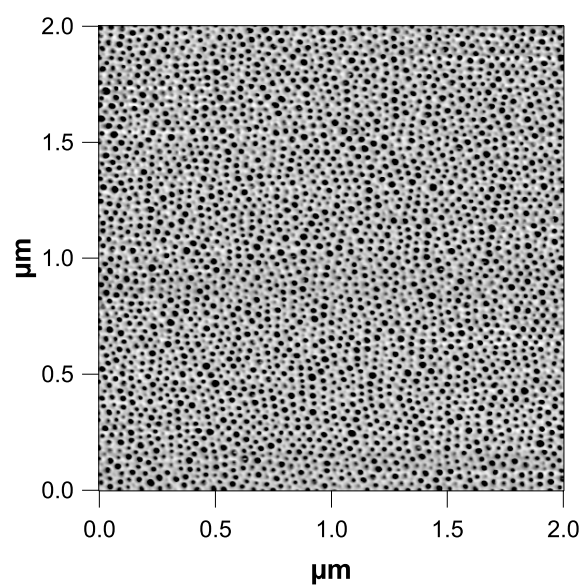


Figure 8.1: SFM phase image of a 100 *nm* thick film of PS₃₀₀-[Ru]-PEO₂₂₅ spin-coated from a THF solution.

substrate interface are, more than likely, responsible for the orientation of the cylindrical microdomains normal to the film surface. A similar behavior was recently observed when the PEO sequence of a PS-*b*-PEO block copolymer is doped with salts prior to the self-assembly in thin films [13]. It was found that the complexation of the PEO with an added salt enhanced the immiscibility of the blocks and the mediation of interfacial interactions by the added salt produced a strong orientation of the PEO cylindrical microdomains normal to the film surface. In addition, those studies reported that the orientation was less sensitive to the preparation conditions.

Films of different thicknesses have been prepared to examine the propagation of the orientation of the microdomain orientation from the interface into the film. The film thickness was varied between 50 and 250 *nm* and in all cases the cylindrical microdomains were found to orient normal to the film surface after spin-coating. To insure that the cylindrical domains spanned across the entire thickness of the film, a 250 *nm* film was prepared on a silicon substrate covered with a 400 *nm* thick silicon oxide layer. The film was floated onto the surface of a dilute hydrofluoric acid solution (5 wt. %) and transferred to a water bath. Using a clean silicon slide the copolymer film was then transferred upside down onto the slide such that the bottom of the original film was now on the top. The SFM image of this sample (Figure 8.2) shows that the cylindrical microdomains are present at the bottom of the film, suggesting that the microdomain orientation propagates through the entire film.

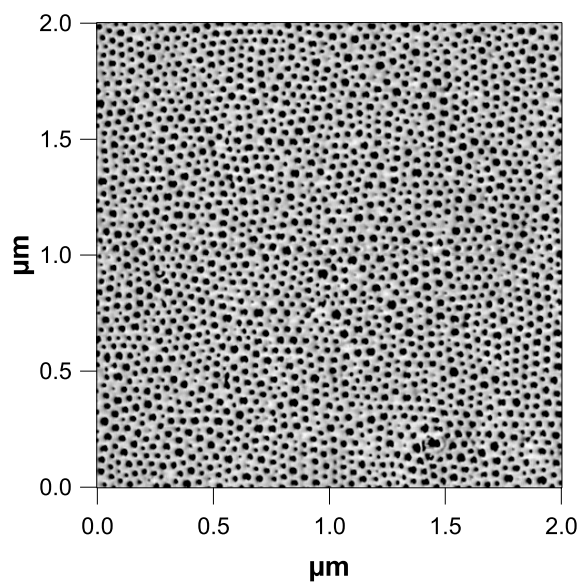


Figure 8.2: SFM phase image of a 250 *nm* thick film of PS₃₀₀-[Ru]-PEO₂₂₅ spin-coated from a THF solution that was floated and flipped to show the bottom of the original film.

8.3 Improvement of the lateral ordering of the cylinders upon solvent annealing

The behavior of the metallo-supramolecular copolymer films upon solvent annealing has also been investigated. It has been reported that long-range, well-ordered, structures can be obtained from covalent PS-*b*-PEO copolymers when the films are annealed in benzene vapor for several hours [16]. The metallo-supramolecular copolymer was, therefore, exposed to benzene vapors for 24 hours. A typical SFM phase image recorded on such a film is shown in Figure 8.3.

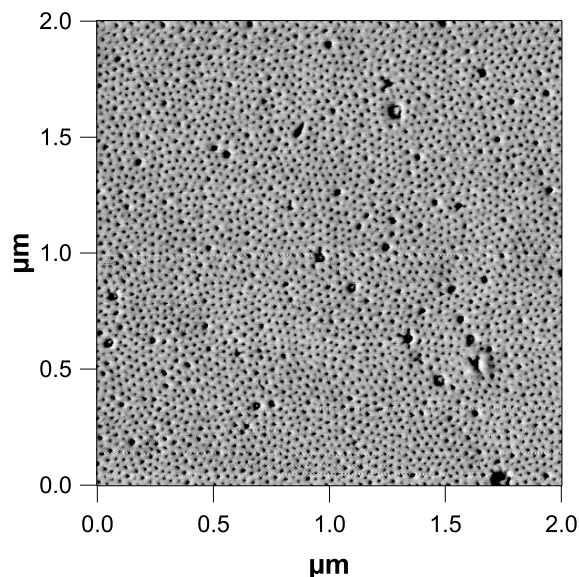


Figure 8.3: SFM phase image of a film of PS₃₀₀-[Ru]-PEO₂₂₅ spin-coated from a benzene solution and annealed 24 *h* in benzene vapor.

The annealing did not improve the lateral ordering of the microdomains but, rather, generated many defects, not present in the initial film. Different annealing times were attempted with similar results. The appearance of these defects may arise from the poor solubility of the metal-ligand complexes in benzene or from a strong affinity of the metal-ligand complex to the substrate interface. When the film swells upon expo-

sure to solvent vapors, the polymer chains gain mobility and are able to rearrange, but the insolubility of the complexes and the affinity of the complex to the substrate may cause them to aggregate, limit the chain mobility and produce defects in the film. Consequently, the film was exposed to a more polar solvent, i.e., THF. Figure 8.4 shows an SFM image of a film of the metallo-supramolecular copolymer annealed for 24 hours in THF vapors. In this case, several domains of nicely ordered cylinders are observed, while the average center-to-center distance of the cylindrical domains, λ_{C-C} , increased to 44 nm upon annealing. This suggests that the use of a solvent polar prevents the aggregation of the metal-ligand complexes and mediates interfacial interactions sufficiently to enable the lateral ordering of the cylindrical microdomains.

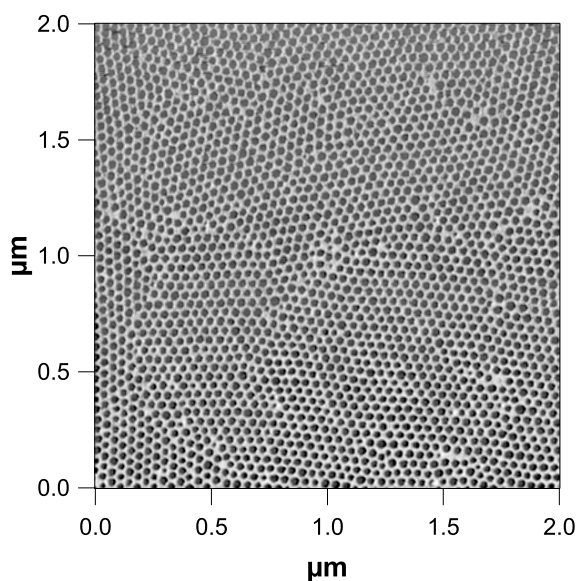


Figure 8.4: SFM phase image of a film of PS₃₀₀-[Ru]-PEO₂₂₅ spin-coated from a THF solution and annealed 24 h in THF vapor.

8.4 Conclusions

Metallo-supramolecular block copolymers exhibit a different behavior upon self-assembly in thin films compared to their covalent (“classical”) counterparts. This difference is due to the presence of the charged complex at the junction of the two blocks, acting as a third highly immiscible block that effects the orientation of the cylindrical microdomains and the lateral ordering. Cylindrical microdomains of PEO oriented normal to the film surface that span the entire film thickness are obtained directly after spin coating, independently of the preparation conditions. Exposure to a polar solvent vapor can be used to improve the lateral ordering of the cylindrical domains.

Experimental part

Materials: The terpyridine-functionalized PEO and PS were synthesized as reported on Chapter 3 by grafting a chloroterpyridine to the OH end group of commercial PEO, and by nitroxide mediated radical polymerization using a initiator functionalized with a terpyridine, respectively. The PS-[Ru]-PEO metallo-supramolecular copolymer was synthesized following an optimization of the procedure previously reported (see Section 3.3) The investigated sample will be designated by the acronym PS₃₀₀-[RuCl₃], the number in subscript being the average degree of polymerization of each block.

Synthesis of PS₃₀₀-[RuCl₃ *mono*-complex: Terpyridine-terminated poly(styrene), PS₃₀₀ and a eight fold-excess of RuCl₃.xH₂O were charged into a Schlenk flask with a mixture of EtOH:THF (1:1). The reaction medium was deoxygenated by purging argon during one hour and then heated at 85 °C under argon for 24 hours and allowed to cool to room temperature. The final mixture was then partitioned between chloroform and water. The water layer was washed three times with CHCl₃, and the combined organic phases were dried over MgSO₄, and condensed in vacuo. ¹H-NMR was checked to verify the absence of the terpyridine signals due to the paramagnetic nature of the pure *mono*-complex. The resulting solid was reprecipitated from THF into methanol:water (2:1) (2 times), and placed in an oven overnight at 40 °C. Yields were between 80-90 %.

Synthesis of PS₃₀₀-[Ru]-PEO₂₂₅ *bis*-complex: A solution of terpyridine functionalized PEO₂₂₅-[(200 mg, 1.88*10⁻⁵ mol) and PS₃₀₀-[RuCl₃ (470 mg, 1.57*10⁻⁵ mol) in a mixture of THF:EtOH (3:2) (20 mL) was heated under argon at 80 °C for 60 minutes. A few drops of *N*-ethylmorpholine were added after one hour and stirring at 80 °C was continued during 24 hours. Then an excess of solid NH₄PF₆ (51 mg, 2.80*10⁻⁴ mol) was added and the solution was allowed to cool to room temperature. Stirring was continued during one hour, and subsequently, the solvents were removed in vacuo. The residue was extracted with CHCl₃ and water (0.01 M NH₄PF₆). The organic layers were dried over MgSO₄ and concentrated in vacuo. The compound was further precipitated into hexane starting from THF. The precipitate was filtered and water was added. The aqueous suspension was stirred at room temperature during two days to remove unreacted PEO, then filtered off. In a last step, diethylether was added and stirred at room temperature during two days to remove unreacted PS. Finally, the product was filtered, and solubilized in a minimum amount of THF and reprecipitated in hexane to yield the PS₃₀₀-[Ru]-PEO₂₂₅ copolymer (30 %). ¹H-NMR (CDCl₃): δ= 8.41 (m, 2H; H_{3,3'} PEO), 8.34-8.22 (m, 6H; H_{3,3'} PS, H_{3,5'} PS&PEO), 7.83 (m, 4H; H_{4,4'} PS&PEO), 7.47 (m, 2H; *H*-PhCH₂Otpy), 7.36 (m, 6H; H_{5,5'} PS&PEO, *H*-PhCH₂Otpy), 7.21-6.28 (m, 1511H; H_{PS} backbone aromatics, H_{6,6'} PS&PEO), 5.58 (m, 2H; tpyOCH₂ PS), 4.77 (m, 2H; tpyOCH₂ PEO), 4.11-3.30 (m, 864H, H_{PEO} backbone), 2.20-

1.20 (m, 922H; H_{PS} backbone aliphatics).

Film Formation: Silicon substrates were cleaned by a piranha solution and carefully rinsed with ultra-pure water. Solutions of the copolymer in different solvents were then spin coated onto these substrates. The spinning speed and/or the solution concentration were used to control the film thickness.

Instrumentation: Atomic force microscopy images were obtained using a Digital Instruments Nanoscope IV scanning force microscope in tapping mode using NCL type cantilevers (Si, 48 *N/m*, 330 *kHz*, Nanosensors).

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CONCLUSIONS AND PERSPECTIVES

THIS work was devoted to the study of metallo-supramolecular polymers, and some applications suited to this type of peculiar architectures. Indeed, the assembly of polymer blocks using metal-ligand interactions is a promising strategy, as illustrated by the growing number of scientific papers recently published in this field.

The introduction summarizes recent progresses achieved to date in the area of metallo-supramolecular block copolymers where the linear architectures based on 2,2':6',2'' terpyridine ligands are distinguished from star-like architectures based mainly on 2,2'-bipyridine ligands.

In the Chapter 3 of this PhD-thesis, we have extensively described the synthesis of well-defined metallo-supramolecular polymers. The synthesis of a modified universal alkoxyamine, bearing the terpyridine functionality was the first step leading to the formation of terpyridine end-functionalized polymers by NMP. Terpyridine end-functionalized poly(styrene), poly(*tert*-butylacrylate) and poly(2-dimethylamino ethyl acrylate) have been thus synthesized using this methodology. Moreover, this controlled radical polymerization process has been further extended to the formation of classical diblock copolymers. On the other hand, end-group modification on the polymer chain-end has been a valuable strategy to introduce the terpyridine ligand for polymers with a lower molecular weight. Then, these terpyridine end-functionalized polymers have been further linked together by a two step self-assembly process, driven by the high stability of terpyridine-ruthenium(III) complexes. The im-

provement of the synthesis as well as the purification process have been realized, leading to the formation of a library of diblock copolymers, with *bis*-terpyridine(II)-ruthenium complexes located at the junction between the two blocks. Furthermore, as an extent of the previously formed metallo-supramolecular block copolymers, we have developed a new type of easily reversible diblock copolymers based on heteroleptic *bis*-complexes of cobalt(III)-terpyridine. Starting from an initial study performed on model ligands, we have successfully extended it to polymers.

Chapter 4 was dedicated to the influence of the *bis*-terpyridine(II) ruthenium complexes on the self-assembly behavior in water. Starting from the synthesized library of 12 different PS-[Ru]-PEO block copolymers, we have systematically characterized by AFM and TEM, the star-like micelles obtained in water. Our results revealed that the core size does not scale linearly with the DP of the PS block as expected from the theory of classical covalent copolymers. Since mainly two core sizes were observed, one around 10 nm for DP of 70 and below, and one around 20 nm for DP of 200 and above, we have attributed this unusual behavior to the electrostatic repulsions between the charged *bis*-terpyridine ruthenium complexes present at the core/corona interface. We have confirmed this initial assumption by preparing micelles in the presence of salt to screen out the electrostatic repulsions. In this case, a “classical” behavior was observed as predicted by the theory.

The following chapters were devoted to various applications taking advantage of the metallo-supramolecular strategy. In Chapter 5, we have studied the formation of copolymer brushes, based on the complexation of a charged supramolecular block copolymers (PS₂₀-[Ru]-PEO₇₀) with a polyelectrolyte backbone (PSS) in a DMF/water (95/5) solution. We have demonstrated that these peculiar complexes adopted a random-coil conformation and that their characteristic size could be further tuned by varying the length of the PSS chains and the PS₂₀-[Ru]-PEO₇₀/SS molar ratio. Then, the amphiphilic character of these flexible brushes has been further exploited to create micellar systems in water. DLS, TEM and cryo-TEM techniques have been used to characterize these structures. For the PSS chains with the smaller DP, well-defined spherical micelles were formed, whereas for the larger DP, a transition to worm-like mor-

phologies occurred. This strategy paves the way to amphiphilic brushes exhibiting interesting self-assembly properties in water.

In Chapter 6, we have studied the addition of metal ions to micelles formed by the PS₄₇-*b*-PtBA₅₅-[copolymer in ethanol, and consisting of a PS core and PtBA coronal chains with terpyridine ligands at their extremity. This approach leads to the formation of self-assembled structures hierarchically combining the characteristic features of covalent block copolymer micelles and metallo-supramolecular polymers. Upon addition of metal ions to diluted micellar solutions, *intra*-micellar *bis*-terpyridine metal ion complexes were created leading to the formation of flower-like micelles. Moreover, we have further exploited this strategy with the successful addition of a third layer to the micellar structure by complexing a terpyridine-functionalized PEO onto the initial micelles.

In Chapter 7, we have considered micelles formed by a PS-*b*-PtBA-[copolymer in more concentrated ethanol solution. In these conditions, addition of metal ions triggers intermicellar *bis*-terpyridine metal-ion complexes, ultimately leading to a network of connected micelles. As in the previous chapter, three metal ions have been considered, i.e. Zn²⁺, Ni²⁺ and Fe²⁺. Whenever the metal ion/terpyridine molar ratio was set to 1/2, an increase of the viscosity of the initial solution was observed, leading in the case of Ni²⁺ and Fe²⁺ to the formation of micellar gels. Rheological tests have been thus realized to provide a deeper insight into these promising materials. Reversible structural changes have been observed when the samples are submitted to shear deformation, and a thixotropic behavior has been observed.

Finally, in the last chapter (Chapter 8), we have concentrated our efforts on thin films formed with metallo-supramolecular block copolymers. Indeed, it has been previously shown that metallo-supramolecular block copolymers are valuable tools for the formation of nanoporous thin films. However, they exhibit a different behavior upon self-assembly in thin films compared to their covalent counterparts. We have thus studied the self-assembly of metallo-supramolecular block copolymers in thin-film under different conditions to determine the influence of the metal-ligand complex. We have shown that the presence of the charged complex at the junction of the two blocks, acts as a third highly immiscible block triggering the orientation of the cylindrical microdomains and the lateral

ordering, independently of the preparation conditions.

In this work, we have demonstrated the possibility to use metallo-supramolecular block copolymers as promising systems for various applications. Chapter 3 ends with the synthesis of copolymers containing *bis*-terpyridine cobalt(III) complexes at the block junction. Such systems show enhanced reversibility properties and should be investigated in more details. However, the synthesis of these copolymers is not yet fully optimized and some efforts have to be performed. Indeed, terpyridine-cobalt(III) metallo-supramolecular diblock copolymers could be used as suitable building blocks for the synthesis of nanoporous thin films, since terpyridine-cobalt(III) complexes can be opened in milder conditions than for the ruthenium ones.

We also demonstrated in more details that metal-ligand interactions can be used also for linking together well-defined nano-objects obtained from the self-assembly of covalent block copolymers, ultimately leading in concentrated solutions to the formation of micellar gels. Preliminary rheological experiments have been performed exhibiting unique properties. The structure of those micellar gels has to be further elucidated by SAXS and small-angle neutron scattering (SANS) in order to gain a maximum insight in the dynamic structure and behavior and to determine structure-property relationships. In this respect, it should be very interesting to investigate also in the future the influence of various micellar characteristic features on the final properties of the gels such as the size, softness or rigidity of the micellar core and the length of the coronal chains.

Furthermore, since NMP has been shown to be a valuable technique to synthesize various polymer blocks end-functionalized with a terpyridine, it could be interesting to combine stimuli-responsive polymer blocks (e.g. polymer blocks exhibiting LCST behavior), such as poly(dimethylaminoethyl(meth)acrylate) or poly(*N*-isopropylacrylamide) with stimuli-responsive metal-ligand units. Materials with unprecedented control over their properties could be thus envisaged. Indeed, if a pH sensitive coronal block is used for example, the swelling of the gel can be controlled by changing the protonation degree of the coronal block. The same pH stimulus, but in a different range, can also be used to trigger the opening of the metal-ligand complexes, and thus the gel to sol

transition.

Finally, another type of approach using the ligand 1,6-bis(10-methylbenzimidazolyl)-4-hydroxypyridine could be envisaged for the preparation of photoactive mechanoresponsive gels. The interest of this ligand lies in his ability to form well-defined *tris*-complexes with lanthanide ions (see Figure 9.1). As demonstrated by the group of Rowan, these complexes act as branching points and are responsible for gelation upon introduction of a small percentage of lanthanide ions to a coordination polymer. Because the lanthanide complexes are less stable, the branching points of the gel open upon heating, or if mechanic stress is exerted by shaking, inducing a liquefaction of the gel. When the sample is cooled or kept at rest, the gel is reformed.

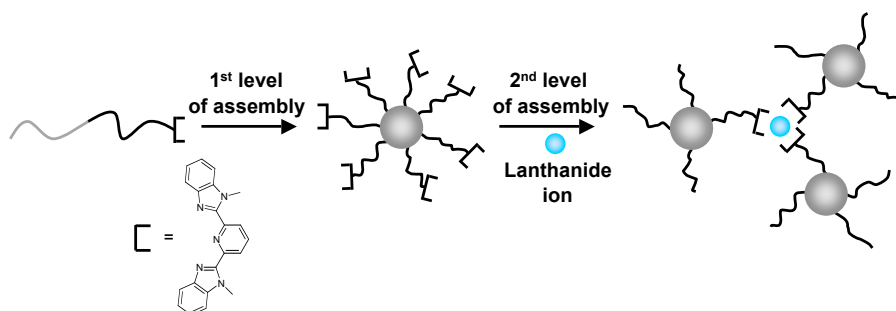


Figure 9.1: Schematic pathway of the formation of a supramolecular network using well defined *tris*-complexes with lanthanide ions.

CURRICULUM VITAE

Pierre Guillet was born in Saint-Nazaire (France) in 1979. He obtained his MSc in chemistry from the National Chemistry Engineering School (ENSIACET), Toulouse, France in June 2003. In March 2004, he started his Ph.D. program at the Université catholique de Louvain, Belgium, under the supervision of Professor J.-F. Gohy. His research topic involves the synthesis and characterization of metallo-supramolecular amphiphilic copolymers, and their self-assembly in solution. The result of his research are presented in this thesis.

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