

Université catholique de Louvain
Ecole Polytechnique de Louvain
Institute of Condensed Matter and Nanosciences
Division of Bio- and Soft Matter



Understanding the effect of constraint release on the dynamics of entangled polymers

Maksim E. Shivokhin
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JURY MEMBERS:

Prof. C. Bailly (UCL), supervisor
Prof. Jacques Devaux (UCL), chairman
Prof. Evelyne Van Ruymbeke (UCL)
Prof. Roland Keunings (UCL)
Prof. Giovanni Ianniruberto (Università degli Studi di Napoli, Italy)
Prof. Wim Briels (University of Twente, The Netherlands)

DEDICATION

I dedicate this thesis to my wife, Elena Markova, and my parents, Evgeny Shivokhin and Elena Shivokhina. Without their patience, understanding, support, and most of all love, the completion of this work would not have been possible.

Also, I dedicate this thesis to my daughter, Sophia Shivokhina, whose birth has brought wonderful fun, great motivation and bright inspiration into my life.

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ABSTRACT OF THE THESIS.

In this thesis we mainly investigate multi-chain effects on the dynamics of entangled polymers. We have developed a systematic methodology for testing different relaxation mechanisms. For this purpose we have used a stochastic single chain slip-spring model which quantitatively predicts chain dynamics at long time scales. In this model all relaxation mechanisms are naturally integrated. In order to test different assumptions related to respective contributions of different relaxation mechanisms we used a set of simplified slip-spring “toy” models, where different relaxation modes are systematically deactivated, analyzed and later reassembled in a controlled way. For testing existing constraint release (CR) theories we have analyzed different mixtures of linear and simple branched polymers. Some key findings of this work are summarized below:

- The effect of adding short linear chains on the stress relaxation dynamics of long star-branched polymers has first been investigated. We have found that the effective friction of stars diffusing in the fat tube is larger than its bare friction. Additional friction originates from the blinking nature of entanglements with shorter chains. We have investigated the dependence of this extra friction on blend composition and proposed an analytical equation for predicting its effect on the terminal relaxation zone dominated solely by relaxation of star chains.
- Based on these findings, we have investigated the effect of topological constraints with various mobilities on orientational relaxation of a probe chain. First, we have recognized that the stress relaxation dynamics of the chain originate from a combination of CR dynamics and sliding dynamics of the chain, where for “type-A polymers” the global relaxation effect of the sliding dynamics can be measured by dielectric spectroscopy and simulated as chain end-to-end vector autocorrelation function. After validating the standard slip-spring model by simultaneous comparison with published rheological and dielectric data of nearly monodisperse and binary melts of linear polyisoprene (PI) we have systematically analyzed the CR effect from each component of the binary blend on relaxation of the end-to-end vector. We find that the longest relaxation time of the end-to-end vector of a probe chain is in fact affected by the dynamics of all topological constraints with a lifetime shorter than its own reptation time in

the skinny tube. Furthermore, we have proposed an analytical equation for predicting the longest relaxation times of the probe chain in any monodisperse and binary environment of topological constraints. This equation includes only one adjustable parameter related to the chain segment jumping amplitude in the event of constraint release. We have verified the derived equations by comparison with the simulation data.

- Further, we have addressed some difficulties related to different approaches combining relaxation mechanisms in tube models. As suggested in the hierarchical algorithm we have separated the total stress relaxation of a star in three time zones according to the dominant relaxation mechanism. Next, we have verified that arm-retraction is not interrupted and only slightly influenced by CR from short chains in the time zone dominated by CR motion of the skinny tube. Finally, by recognizing that up to the fat tube zone all relaxation mechanisms are independent and simultaneously contribute to the total stress relaxation, we have proposed simple multiplicative law for combining all relaxation zones as done in the time marching algorithm.
- Finally, with respect to the industrially relevant polystyrene (PS) systems we have demonstrated that: materials with bimodal molar mass distribution demonstrate more pronounced strain rate dependence of the extensional properties with respect to the monomodal. Enhancement of strain hardening (achieved by adding small- M_w miscible diluents) often leads to trade-off with respect to the failure behavior characteristics.

This Ph.D. has been integrated in the now completed DYNACOP (DYNAmics of Architecturally COMplex Polymers) network, which was 7th Framework Marie Curie Initial Training Network. DYNACOP involved ten universities and two industrial companies across Europe. The scientific objective of DYNACOP was to obtain a fundamental understanding of the flow behaviour and the dynamics of topologically complex macromolecular fluids and their role in processing.

The results of this thesis have been reported in several international conferences in the format of oral and poster presentations. Content of chapters 2 and 3 have been published in (Shivokhin, M.E.; Van Ruymbeke, E.; Bailly, C.; Kouloumasis, D.; Hadjichristidis,

N.; Likhtman, A.E. *Macromolecules* 2014, 47(7), 2451-2463). Results of chapters 4 and 5 are currently being prepared for publication.

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Chapter 1:

INTRODUCTION AND STATE OF THE ART

1.1 Overview

Rheology is the study of flow and deformation of (soft) matter. It can still be considered a relatively new science since the term *rheology* itself was only coined in 1920 by Eugene Bingham. It is a highly interdisciplinary area with theoretical as well as experimental aspects, increasingly characterized by a multiscale approach, starting from atomistic descriptions of matter all the way up to the macroscopic continuum. It is also unique among experimental fields of research by the huge number of orders of magnitudes it has to cover, on the time scale, spatial extension or levels of stress. Besides a fundamental scientific interest, rheology has also a very direct link to applications in daily life, be it in industrial context, biological systems, geology, etc.... In particular, in order to ensure reproducibility of polymer processing operations and to prevent flow instabilities, it is essential to understand the interrelation between the processing parameters and the rheological behavior of a melt. While rheology was initially studied from a pure continuum mechanics viewpoint and focused heavily on building “macroscopic” constitutive equations, it was progressively recognized that the rheological behavior of complex fluids in general, polymers in particular, is fundamentally a consequence of their molecular structure and therefore it would be fruitful to try to derive their rheology behavior from molecular (dynamics) considerations, e.g. the rheology of polymers either in solution or melt is controlled by the level of chain entanglements and the presence or not of entangled branches. The study of molecular rheology is concerned with developing fundamental relationships between molecular structure and the flowing characteristics of the melt.

Molecular structure and relaxation dynamics of polymers are reflected in their time-dependent viscoelastic properties. For instance, strain hardening behavior which is crucial in the production of fibers and foams is mostly pronounced for branched or high-molecular weight polymers due to their longer relaxation time as compared to

short linear chains. Another essential rheological feature of complex fluids, called shear thinning, is related to decreasing resistance to flow with increasing rate of shear. This is a very important property in polymer processing because it speeds up material flow and reduces heat generation and energy consumption during shear-dominated processing. Concerning the influence of molecular characteristics, the onset and degree of shear thinning vary significantly depending on molecular weight distribution. In particular, materials with broader molecular weight distribution tend to thin more at lower shear rates than those with narrower distribution at the same average molecular weight.

It is known that the structure of industrially relevant polymers is generally characterized by broad polydispersity of molecular weight ($PDI=2\dots5$) and often poorly controlled branching level. During processing in the molten state, materials experience a complex combination of shear and extension flows under a nonlinear regime of deformations. Many different mathematical models have been developed in order to understand and at least qualitatively predict rheological characteristics of industrial polymers based on their micro- and molecular structure. Most of these models are using molecular-based parameters. In order to determine the values of these parameters one should first synthesize model polymers with well-defined structure and secondly employ different experimental techniques in order to probe the influence of the molecular structure at different time-scales and at well controlled loading.

However, choosing an experiment which is sensitive to each of unknown parameters is not a trivial issue. For instance, the experimental signal measured by rheology is not always sufficient to test specific relaxation mechanisms and reach required levels of loading. Moreover, various relaxation modes combine in a single time-overlapping experimental response and it is often quite difficult to separate the contributions. Therefore, often a combination of different experimental techniques is required. However, the observation windows of different experimental techniques are not always overlapping and the level of experimental uncertainty for different experimental methods can vary significantly.

These limitations highlight the need for more universal tools which could serve as “ideal experiments”. Such tools can be found in the realm of numerical simulations. In order to provide insights on the molecular dependence of rheological behavior, the models used in the simulations need to be “molecularly informed”. While it is tempting at first to use a very detailed level of molecular description (e.g. MD) to capture a maximum of dynamic features, the resulting numerical complexity drastically limits the size and time-scale of tractable systems. Hence mesoscale descriptions are and will remain invaluable for linking molecular description to the resulting dynamics. Different levels of coarse graining can be considered, with the corresponding balances of detail and tractability. A very popular (because it is very effective) meso description of polymer flow is of course the tube model, initiated by Doi, Edwards and de Gennes (*de Gennes, 1971; Doi, Edwards, 1978*). It is at the onset a “single body” (a probe chain) and “mean field” (in the tube) approach that heavily relies on chemistry-dependent universal descriptors of the entanglement network topology and dynamics. Going from qualitative estimates (i.e. scaling laws) on simple systems to quantitative predictions on complex industrial polymers is a huge challenge for tube theory. One key difficulty concerns the handling of interrelated relaxations of multiple chains with complex structures (molecular weight and architecture) in the linear as well as nonlinear deformation regimes. This is the so-called “constraint release” issue. In order to improve the description of constraint release in tube models, it is important to ground this analysis in a deeper level description of the chains. This is where slip-link stochastic models come into play.

Hence in this thesis we use a mesoscale stochastic model (the so-called slip-spring model) developed by Likhtman (*Likhtman, 2005*) which is first validated by comparisons with rheological and dielectric data of well-defined model polymers. We then take advantage of the model to build a detailed analysis of constraint release in existing tube theories and draw conclusions on shortcomings and improvements.

In the next sections of this introductory chapter, we briefly introduce the Rouse model which represents the theoretical background for all other polymer dynamics models. This model is commonly used for predicting linear rheology of unentangled polymer

melts. For describing diffusion in entangled networks we will introduce the idea of Doi and Edwards about a tube restricting the motion of the Rouse chain and the resulting additional relaxation mechanisms. Next, we review the state of the art of different theories which have been developed to account for the effect of molecular environment on the diffusion of entangled chains. In particular, we will overview different approaches used to account for the constraint release in various implementations of the slip-link models. After summarizing this overview, we highlight detailed objectives of the study and present the structure of the thesis will be presented.

1.2 Molecular models

1.2.1 Rouse model.

The simplest molecular model capable of predicting the complete relaxation spectrum of unentangled flexible chains is that of Rouse (*Rouse, 1953*). This model ignores interactions between the beads mediated by the solvent, namely hydrodynamics interactions and many-chain effects are neglected. Thus this model can only be applied to the melts of unentangled chains or to entangled chains but only in the time-range limited by the stress equilibration time of a single entanglement strand.

In this model, the polymer chain is mapped as a system of N beads connected by $N-1$ springs. Every bead-spring segment is large enough to have Gaussian statistics and the smallest possible size to consider is that of Kuhn segment of length b . Every segment is characterized by a bead friction ζ and a spring constant $3k_B T/b^2$. Motion of the linear chain in the bath of temperature T is described by N coupled differential equations. Dynamics of end beads pulled only by one spring is described by a Langevin equation (*Ghosh, Colby, 2008*):

$$\zeta \frac{dR_0}{dt} = \frac{3k_B T}{b^2} (R_1 - R_0) + g_0(t)$$

Where, R_i – is the position of i^{th} bead; g_i – is a random velocity corresponding to Brownian kicks from the environment with particular distribution function (*Doi, 1996*).

All interior beads are connected by two springs to adjacent beads in the chain and their dynamics is described as

$$\zeta \frac{dR_i}{dt} = \frac{3k_B T}{b^2} (R_{i-1} - 2R_i + R_{i+1}) + g_i(t)$$

In total, dynamics of a linear chain with N beads is represented by 2 equations describing dynamics of end beads and $N-2$ equations corresponding to interior beads..

The solution of the Rouse model is obtained by diagonalizing the connectivity matrix A_{ij} , resulting in diagonal matrix of eigenvalues λ_p , where p is the mode index. The largest eigenvalue corresponds to the shortest relaxation time τ_0 ; the other relaxation times can be computed from the inverse relation between eigenvalue and relaxation time:

$$\frac{\tau_p}{\tau_0} = \frac{\lambda_{\max}}{\lambda_p} = \frac{N^2}{p^2}$$

Where the longest Rouse time has index $p=1$:

$$\tau_R = \tau_0 N^2 = \frac{\zeta b^2 N^2}{3\pi^2 k_B T}$$

The stress relaxation modulus is calculated as sum of exponential relaxations from these p modes:

$$G(t) = \frac{k_B T c}{N} \sum_{p=1}^N \exp\left(-\frac{2t}{\tau_p}\right)$$

Where the number of monomers per unit volume $c = NN_c/V$, with N_c the number of chains and V the volume.

The zero shear rate viscosity can be estimated as follows:

$$\eta_0 \cong \int_0^\infty G(t) dt .$$

1.2.2. Doi-Edwards tube model.

In this section we introduce an approach widely used to extend chain motions described by the Rouse model of unentangled chain to take into account topological constraints imposed by neighboring chains. Namely, we will talk about the tube model of de Gennes, Doi and Edwards (*de Gennes, 1971; Doi, Edwards, 1978*) and the corresponding relaxation mechanisms typical for entangled polymer networks.

In Figure 1.1 classical measurements of zero shear rate viscosity as function of chain molecular weight (M_w) (*Berry and Fox, 1968; Colby et al. 1987*) show a clear transition from the unentangled regime (at $M < M_c$; values of critical molecular weight M_c are given by (*Fetters, Lohse, Colby, 2006*) where $\eta_0 \sim M$, which can be well predicted by Rouse model, to a much stronger dependence above the critical molecular weight, where $\eta_0 \sim M^{3.4}$. The observed change in scaling behavior can be attributed to the interactions with other chains affecting probe chain dynamics. It is to predict this scaling in the entangled regime that the tube model has been introduced by (*Doi, Edwards, 1978*).

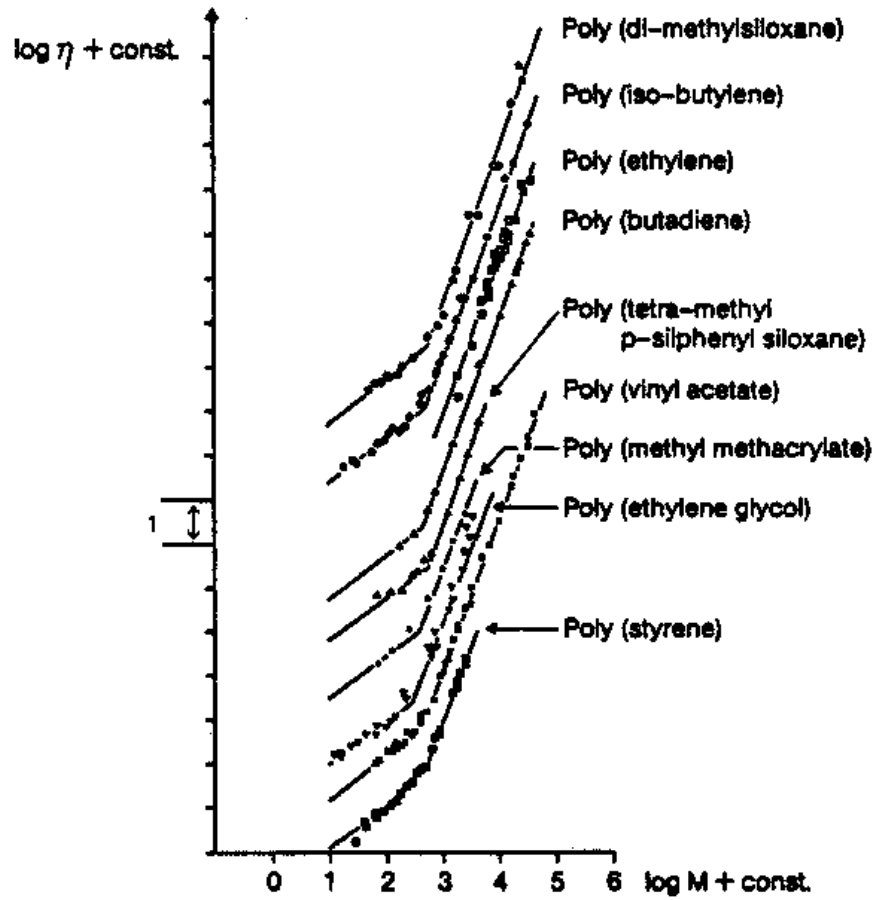


Figure 1.1: Relationship between molecular weight and zero-shear viscosity for several nearly monodisperse melts. For clarity the curves are shifted relative to each other along both the abscissa and ordinate. Adapted from Berry and Fox (Berry, Fox, *Adv. Polym. Sci.*, 1967).

According to this theory, topological constraints imposed by neighboring chains can be represented by a tube which allows the chain to freely diffuse along its own contour length but severely restricts any movements in the radial direction of the tube.

In order to make this picture quantitative some assumptions about tube topology (nature of the entanglement network) have to be made. For instance, the topology of the entanglement network is determined by a single length scale, either defined as the distance between entanglements or the tube diameter, a , that is independent from molecular weight and chain architecture. The exact nature of the tube and entanglements themselves is still not completely understood. There is much research currently in progress aiming to extract its quantitative value from atomistic and other

simulations (Everaers, 1999; Pattamaprom et al., 2000; Likhtman, McLeish 2002; Likhtman, Ponmurugan, 2014). However, much progress can still be achieved by considering a as an empirical quantity. The tube diameter can formally be defined as a correlation length of the primitive path. The latter is defined as the shortest trajectory from one chain end to the other that has the same topology as the original chain with respect to the entanglement network. The length of the primitive path can be computed as

$$L = \frac{Nb^2}{a}$$

At equilibrium, the primitive path is a Gaussian random walk with step length a and has the same end-to-end vector as original chain

$$Za^2 = Nb^2$$

Where Z is an average number of entanglements per chain, N the number of Kuhn segments and b is the Kuhn length. Hence $Z=N/N_e=M/M_e$, where M – is total molecular weight of the chain and M_e is average molecular weight between two entanglements.

The number of Kuhn segments per entanglement strand can be determined as follows

$$N_e = \frac{a^2}{b^2}$$

1.2.3. Reptation.

The tube model can be used for predicting linear rheology of entangled polymer melts. For this we assume that shortly after an applied small step shear strain, all chain conformations are restricted by the deformed tube and all applied stress is held by the entanglements forming this tube.

Next, the chain ends begin to explore new conformations by moving back and forth along the chain contour and thus progressively an increasing chain fraction relaxes from the end towards the center. In order to compute the time required for the chain to completely “forget” its original conformation by escaping from the tube one should solve a first passage problem. Doi and Edwards (1986) solved this problem using the

assumption that the primitive path length is fixed at its equilibrium value. This assumption reduces the issue to the first passage by one-dimensional diffusion of the center of mass of the chain. The center of mass diffusion constant is taken from the Rouse model

$$D_c = \frac{k_B T}{N \zeta}$$

The survival fraction of the tube can be computed as

$$\mu(t) = \sum_{p \text{ odd}} \frac{8}{\pi^2 p^2} \exp\left(-\frac{p^2 t}{\tau_d}\right)$$

Where τ_d is known as the reptation time that can be represented through molecular parameters as

$$\tau_d = \frac{\zeta N^3 b^4}{\pi^2 k_B T a^2} = 3Z \tau_R$$

Next, by introducing the proportionality coefficient G_N^0 relating the unrelaxed stress to the surviving tube fraction, the stress relaxation function of the chain can be computed

$$G(t) = G_N^0 \mu(t)$$

The proportionality coefficient G_N^0 is also known as the plateau modulus which can be represented through material parameters as

$$G_N^0 = \frac{4\rho RT}{5M_e}$$

Where ρ is the polymer melt density at temperature T .

With respect to crosslinked polymer networks, G_N^0 of polymer melts is lower by about 20%. This additional stress relaxation is due to longitudinal motions of entanglements along the backbone that facilitate stress equilibration along the chain. Experimentally G_N^0 can be obtained from the visual plateau of $G'(\omega)$, however this can be problematic for moderately entangled systems. For this reason it is more convenient to consider the entanglement modulus G_e corresponding to the high-frequency crossover of G' and G'' and determined as

$$G_e = \frac{\rho RT}{M_e}$$

Figure 1.2 shows the prediction of the reptation model compared to experimental data of $G'(\omega)$ and $G''(\omega)$ for nearly monodisperse well entangled linear chains.

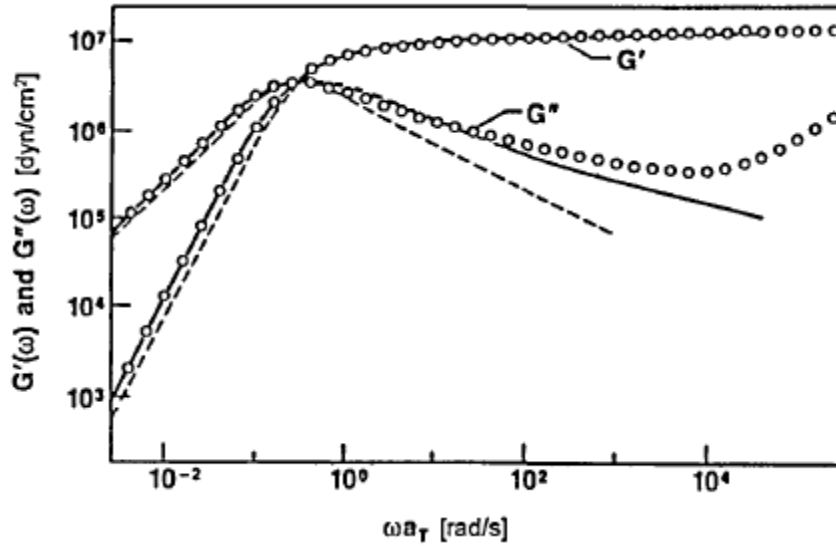


Figure 1.2: Comparison between the experimental linear moduli G' and G'' of nearly monodisperse polybutadiene of $M_w=360,000$ and the pure reptation model prediction (dashed lines) or the model with primitive path fluctuations (solid lines). Adapted from Pearson, D.S., *Rubber. Chem. Technol.*, 1987, 60, 439-496.

The qualitative predictions are encouraging, however, the predicted decrease of $G''(\omega)$ at frequencies above the terminal peak from pure reptation is too rapid with respect to the data. In addition the model predicts zero shear viscosity scaling as

$$\eta_0 \approx G_N^0 \tau_d \approx M^3$$

However, experimental data (see for example *Berry and Fox, 1968*) are closer to $\eta_0 \sim M^{3.4}$. This can be attributed to additional relaxation mechanisms not taken into account by the pure reptation model.

1.2.4. Primitive path fluctuations.

One of the most favored explanations to account for the observed discrepancies is based on an argument that the assumption of constant length of the primitive path is too crude.

The mechanism of primitive path fluctuations also referred to as contour length fluctuations (CLF) is well described by Dealy and Larson in (*Dealy, Larson, 2006*). As the tube diameter is much wider than the diameter of the chain itself it is thus easy to imagine that the chain is “wrinkled up” inside its tube and the degree of wrinkling is constantly fluctuating, driven by Brownian motion. When the chain is wrinkled more than usual it pushes chain ends inside the tube, thus vacating the ends of the tube. Later the chain “unwrinkles” a little and this pushes chain ends out but already in a new tube segment which does not hold the original stress. As one can imagine, CLF easily relaxes the less constrained segments of the primitive path close to the chain ends, as opposed to interior segments. Relaxation of deeper segments by CLF requires the chain to wrinkle too much by taking very entropically unfavorable conformations. Therefore star-shaped chains which are unable to reptate but relax purely by CLF are characterized by much longer relaxation and broadly distributed relaxation modes with respect to linear chains with the same span. However, for linear chains this mechanism effectively shortens length of the tube and thus accelerates the rate of relaxation relative to pure reptation.

In order to take into account this mechanism mathematically, one should include higher Rouse relaxation modes into the first passage problem. Many authors attempted to solve this problem (*Doi, 1981; Doi, 1983; des Cloizeaux, 1990; Milner, McLeish, 1998*) but no rigorous solution has been derived. The model of *Likhtman, McLeish, 2002* often referred to as “state of the art” has obtained an analytical solution of the relaxation function taking into account effect of CLF but with the help of unknown coefficients. The authors next use a stochastic simulation of the first passage of a Rouse chain stretched at the ends by constant force $3k_B T/a$ in order to obtain the unknown coefficients. When including the effect of moving neighboring chains referred to as constraint release (CR), this theory gives the correct scaling of zero shear viscosity and also quantitatively predicts the experimental signal of $G'(\omega)$ and $G''(\omega)$ for linear monodisperse chains.

1.2.5. Many-chain effects.

According to the Doi-Edwards tube model, the relaxation of a chain by reptation and primitive path fluctuations is considered to be constrained by a fixed tube. However, as one can readily imagine, the tube is formed by entanglements with other chains which are undergoing relaxation by the same mechanisms as the probe chain. Therefore, by extending the tube picture to account for the effect of molecular environment we are bound to introduce the idea of tube motion.

The mechanism of constraint release can be represented in two different but related ways. First, the concept of tube rearrangement refers to the reorganization of the tube due to the motion of surrounding chains without changing the diameter of the tube (*Graessley, 1982; Klein, 1978; Daoud, de Gennes, 1979; Klein, 1986*). Second, as proposed by Marrucci in (*Marrucci, 1985*), we can consider the idea of tube dilation or dynamic dilution according to which the relaxed portion of chains can be treated as effective solvent for still unrelaxed chains, leading to reduction of entanglement density, and thus tube diameter is constantly increasing with time.

In the next section we overview different theories proposed to account for constraint release in molecular systems characterized by different distributions of molecular weight and various well-defined molecular topologies.

1.2.6. Methods for combining stress relaxation mechanisms.

After introducing all general relaxation mechanisms typical of tube models, it should be noted that there is a variety of opinions on how the relaxation mechanisms should be combined. We will review two main approaches. The so called hierarchical approach which is utilized in the hierarchical model (*Larson, 2001; Park et al., 2005; Park, Larson, 2005*) and in so-called BoB model (*branch-on-branch algorithm*) from (*Das et al., 2006*) considers that the total relaxation spectrum is separated in identifiable time-

regimes according to a dominant relaxation mechanism in that time domain. Moreover, sometimes one dominant relaxation mechanism can be delayed (or frozen) until another is expended. For instance, the contour length fluctuations of long chains in a binary linear/linear (*Park, Larson, 2004*) or star/linear (*Milner et al., 1998*) blend are not allowed during the CR Rouse motion of the tube, so this process is frozen for the corresponding time. Another implementation of this algorithm allows however arm retractions during tube motion, either in the so-called skinny tube (*Das et al., 2006*) or in the fat tube (*Larson, 2001*).

On the other hand, according to the so-called time marching algorithm (TMA) (*Van Ruymbeke et al., 2005*) all relaxation mechanisms are considered to be happening in parallel and their respective contributions are determined at every time-step based on survival probabilities from the respective relaxation mechanisms. The very important advantage of this model with respect to the hierarchical algorithms is that it can be easily applied to any number of blend components (*Van Ruymbeke et al., 2010*) and different molecular topologies: stars (*Shchetnikava et al., 2014*), combs (*Ahmadi et al., 2011*), H-polymers (*Van Ruymbeke et al., 2006*), Cayley-tree polymers (*Van Ruymbeke et al., 2010; Van Ruymbeke et al., 2007*), pom-pom polymers (*Van Ruymbeke et al., 2007*). The total stress relaxation modulus is computed as a product of all respective probabilities thus introducing an assumption that the corresponding relaxation mechanisms act independently.

1.3. General objectives of the thesis

At this point we would like to highlight the general objective of this thesis which will be further detailed after we overview and summarize all currently developed theories for dealing with constraint release.

In this study we are not relying on any specific implementation of the tube model but rather focus on a fundamental understanding of constraint release effects. For this

purpose we will need a more detailed stochastic model which includes all relaxation mechanisms combined in a natural way and interpret the obtained results in the frame of the tube picture in order to understand the present limitations of tube theory and find directions to improvements.

1.4. Constraint release theories.

1.4.1 Double reptation

Before discussing CR theories based on tube motion as the means to facilitate chain relaxation, we will firstly introduce the simplest approach to implement multi-chain effects into Doi-Edwards tube theory, called double reptation.

The idea is simple: given that residual stress at a given time after a step deformation is proportional to the surviving initial tube fraction, the stress can be released in a segment either by the diffusion of the probe chain end vacating this tube segment or by the motion of a neighboring chain end releasing the corresponding entanglement. . Assuming that every entanglement is produced as a topological constraint between only two chains, a test chain and a matrix chain, it can be concluded that the tube survival probability must be proportional to the product of survival probabilities of two chains forming an entanglement. Since probabilities of these two events are the same, then

$$G(t) = G_N^0 P^2(t)$$

The advantage of this model is that, apart from its simplicity it predicts quite well the terminal relaxation zone of polydisperse systems. This is due to the fact that a broad distribution of molecular weight smears out discrepancies which are due to neglecting intermediate relaxation modes.

Apart from a good fit of the terminal relaxation zone, this model fails to predict relaxation at early and intermediate time scales. In references (*Pattamapron et al., 2000; Pattamapron, Larson, 2001*) the authors introduce the so called *dual constraint model*. This model improves prediction w.r.t. the double reptation theory at high

frequency by including Rouse relaxation inside the tube. Moreover, it improves the prediction at intermediate times by accounting for short-time fluctuation modes.

1.4.2. Tube reorganization models.

Discrepancies of double reptation for binary mixtures are related to the assumption of instant relaxation of the corresponding tube segment upon release of each entanglement. However in reality this assumption can approximately be verified only for very small fraction of “fast blinking” entanglements. On the other hand, for the majority of entanglements, the disappearance of one entanglement is immediately followed by re-entanglement with the same or another chain before the stress can be completely released. According to Graessley in (Graessley, 1982) this process can be modeled by a local bond-flip model of freely jointed rods, each having the constant length a and being constrained by a slip-link of the finite lifetime t_w (see Figure 1.3).

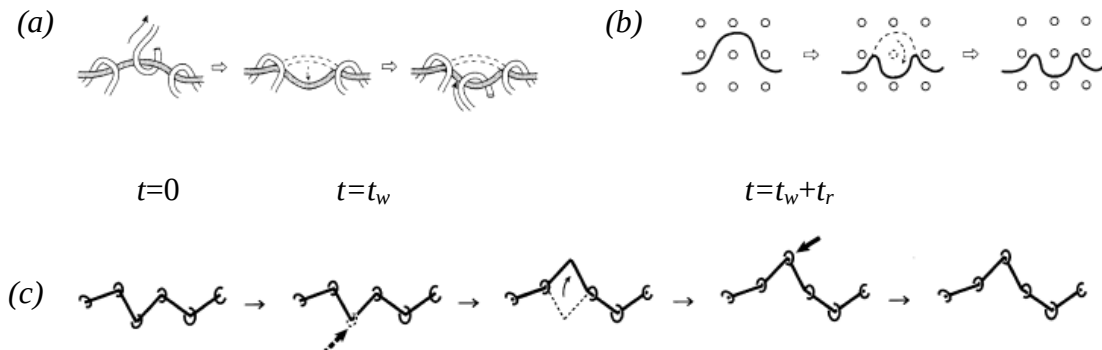


Figure 1.3: Schematic illustration for (a, b) the constraint release process. When a matrix chain shown by unfilled circles in (b) is relaxed the test chain acquires a freedom to change its configuration in a lateral direction. After this jump, either the same or other matrix chain approaches and reforms the constraint for this segment. In the bond-flip model demonstrated in (c) the slip-link indicated with the dashed arrow is removed at $t=t_w$ (entanglements lifetime) and reappears again later at time $t=t_w+t_r$ at a different position shown by the thick solid arrow. During the time t_r freed chain segment jumps on amplitude a , correspondent to length of the freely jointed rods. Adapted from H. Watanabe / *Prog. Polym. Sci.* 24 (1999) 1253–1403

Regardless of probability distribution of these jumps, the slow dynamics of the model coincide with that of the Rouse model (Graessley, 1982; Doi, Edwards, 1986). It must be noted that it is assumed that equilibrium length of the primitive path is preserved at each jump. Eliminating this assumption could result in changes of the primitive path

length followed by induced stress equilibration along its backbone. This additional relaxation contribution was analyzed in (Van Ruymbeke *et al.*, 2012).

In the “simplest” monodisperse case of linear chains characterized by a simplified spectrum of relaxation times $\tau_{d,L} \sim Z_L^3$, CR tube motion can be modelled by Rouse dynamics. The jumping tube is represented by a bead-spring Rouse chain having a number of randomly distributed beads equivalent to the total number of entanglements. The size of the elementary segments of this chain is as that of the tube diameter. The friction of these beads is proportional to the longest relaxation times of the neighboring chains (Rubinstein *et al.*, 1987).

However, a tube motion relaxation spectrum with a single CR rate cannot provide quantitatively accurate results even for monodisperse linear chains. In order to account for all CR modes, Rubinstein and Colby in (Rubinstein, Colby, 1988) proposed a self-consistent theory which determines the exact distributions of CR rates (tube segment mobilities) by applying an inverse Laplace transformation to the tube survival function of the surrounding chains $\mu(t)$ including reptation and CLF modes.

Later Viovy in (Viovy *et al.*, 1991) extended the theory of tube reorganization for the case of binary linear melts (two well separated terminal relaxation times) by introducing an additional relaxation mechanism. In this theory constraints imposed by the environment are represented by the so-called “thin” or “skinny” tube including entanglements with chains of all molecular weights. Besides, if long chains are self-entangled then CR Rouse motion of the thin tube with diameter a is limited by the length scale of the “fat” tube including entanglements with long chains only, whose diameter equals $a_{FT} = a/\phi^{1/2}$ with ϕ the fraction of long chains. Beyond this length scale, reorganization of the thin tube occurs via CR reptation mechanism (see Figure 1.4).

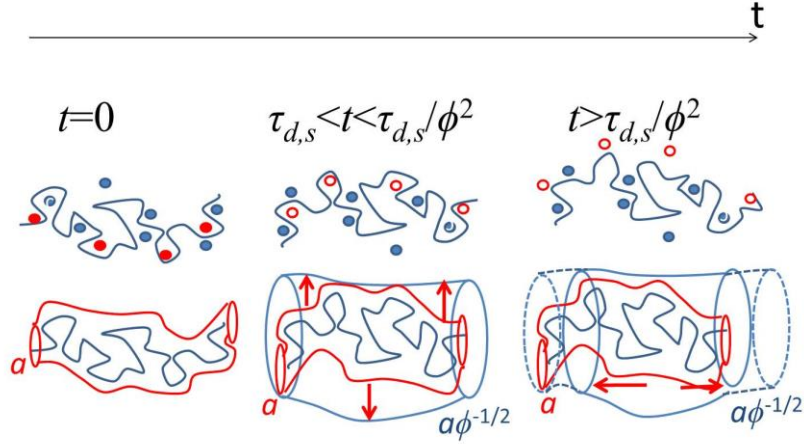


Figure 1.4: Schematic representation of the tube rearrangement picture in the ideal bidisperse blend according to Viovy et al., 1991. At $t < \tau_{d,s}/\phi^2$, the probe chain is constrained by the short and long chains (red and blue filled circles) or equivalently by the thin tube of diameter a . The stress relaxation occurs by chain reptating along the thin tube (thick red lines). At $\tau_{d,s} < t < \tau_{d,s}/\phi^2$ relaxed short chains are shown by empty red circles. The probe chain is still constrained by the short and long chains and is exploring fat tube of diameter a/ϕ^2 (think blue lines) in its lateral direction by CR Rouse motion of the thin tube. At $t > \tau_{d,s}/\phi^2$ the probe chain is still constrained by the short and long chains while escaping from the fat tube of diameter a/ϕ^2 by CR reptation of the thin tube. Sections of the fat tube shown by the dashed blue lines are vacated by the thin tube.

The scaling of the longest relaxation time of long chains in a binary blend system depends on the relation between the number of entanglements of short and long chains, Z_s , Z_L , and the fraction of long chains ϕ . In the limit where long chains are sufficiently diluted by short chains, i.e. when entanglements between long chains can be neglected, the long chains can relax either by chain reptation along the thin tube with longest relaxation time $\tau_{d,L} = 3Z_L^3\tau_e$ or by CR Rouse motion of the thin tube with fundamental time $\tau_{d,s} = 3Z_s^3\tau_e$, at which jumps with amplitude a occur. The longest relaxation of CR Rouse motion is determined as

$$\tau_{CRR} = Z_L^2\tau_{d,s} = 3Z_L^2Z_s^3\tau_e$$

where τ_e is the Rouse equilibration time of the chain entanglement segment.

Using the so called Struglinsky-Graessley criterion (*Struglinski and Graessley, 1985*) the dominant relaxation mechanism in the terminal zone can be determined by estimating value of ratio $r_{SG} = \tau_{d,L}/\tau_{CRR}$. At small values of this parameter the terminal relaxation is by long chain reptation in the thin tube, whereas at larger values the relaxation is dominated by CR Rouse motion of the thin tube (*Read et al., 2012*).

On the other hand, if long chains are self-entangled and thus fat tube can be formed, then there could be three possible relaxation mechanisms dominating terminal relaxation of the long chain. The “Viovy diagram” in Figure 1.5 conveniently visualizes the transition between different dominant relaxation mechanisms of the long chains by plotting r_{SG} vs Z_{FT} , where $Z_{FT}=Z_L\phi$ is the number of entanglements along the fat tube.

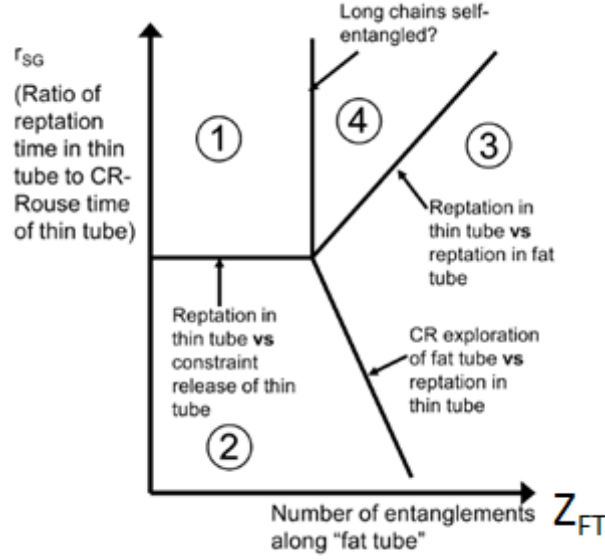


Figure 1.5: Schematic of the “Viovy diagram”, representing different regimes of relaxation in an idealized binary blend. The regimes are: (1) Relaxation and termination by CR Rouse motion of the tube. (2) Relaxation by CR Rouse and termination by reptation in the thin tube. (3) Relaxation of mutually entangled long chains, terminated by reptation in the thin tube. (4) Relaxation of mutually entangled long chains, terminated by reptation along the fat tube and mediated by CR of the thin tube. Axes are logarithmic. Adapted from (D.J.Read et al., J.Rheol, 2012).

One line of this diagram is obtained by comparing timescales of long chain reptation in the thin tube $\tau_{d,L}$ and reptation of the thin tube along the fat tube estimated as

$$\tau_{CR,rept} = 3Z_{FT}^3 \tau_{e,FT} = 9Z_L^3 Z_s^3 \tau_e \phi_L$$

Another important timescale is that required for the thin tube to explore a fat tube segment by CR Rouse motion.

$$\tau_{e,FT} = \tau_{d,s} n^2 = \frac{3Z_s^3 \tau_e}{\phi^2}$$

Where $n=1/\phi$ – is average number of thin tube segments per fat tube segment.

Then by setting $\tau_{d,L}=\tau_{CR, rept}$ and $\tau_{d,L}=\tau_{e,FT}$ we get two corresponding lines in the Viovy diagram

$$r_{SG} = \frac{\tau_{CR, rept}}{\tau_{CRR}} = 3Z_{FT}$$

$$r_{SG} = \frac{\tau_{e,FT}}{\tau_{CRR}} = \frac{1}{Z_{FT}^2}$$

It must be noted, that there are a few important failings in this theory.

- For the binary melt, this theory claims the existence of only two discrete tube diameters: a and $a/\phi^{1/2}$ for the case of self-entangled long chains or a and $R=N^{1/2}b$ for the case when long chains are not self-entangled. Despite this discontinuity of tube diameters, stress relaxation is a continuous function of time (Viovy *et al.*, 1991).
- Upon dilution of long chains with small amounts of short chains, reptation along the thin tube remains the fastest relaxation time of long chain. This result contradicts experimental observations of (Park, Larson, 2006) demonstrating a speeding up of the longest relaxation time of the long chains after adding different fractions of short chains. Moreover, in (S.Wang *et al.*, 2003), dependence of terminal time on molecular weight of the short chains has been observed.
- The theory neglects broadly distributed relaxation modes of CLF and thus assigns an exact long chain fraction to the entanglements forming the fat tube. This issue has been addressed in ref (Read *et al.*, 2012).

While the theory of Viovy predicts tube dilation only in the case when the short chains are unentangled, the dilation theory of Doi, 1987 assumes that the tube diameter of long chains can change if short chains of any molecular weight are added to the melt of long chains. In accordance with the experimental data this assumption allows to observe the speeding up of terminal relaxation in binary blends.

1.4.3. Doi's tube dilation.

The CR theory of *Doi et al, 1987* combines Rouse-like dynamics of the tube with constant diameter a (referred to as tube rearrangement) with tube dilation (enlargement of the effective tube diameter) and argues that contributions of both mechanisms are different.

The authors analyze the behavior of a polymer blend in the entire molecular parameter space (M_L, M_s, ϕ) and divide the space into regimes.

As already mentioned, according to Doi's CR picture, tube dilation is only controlled by the fact that long chains are mixed with a fraction of shorter chains.

The effective diameter of the dilated tube a' is estimated as the intersection between the mean square displacement (MSD) of the freely moving chain segment and that of the tube governed by CR Rouse dynamics.

Doi indicates three cases of tube dilation, defined as: no dilation (ND), free dilation (FD) and restricted dilation (RD). These cases are concerned with molecular weight dependence of longest the relaxation time, $\tau_{d,L}'$, defined with respect to the molecular parameters space:

$$\text{ND} : M_s^3 / M_e^2 M_L > 1 : a' = a ; \tau_{d,L}' \simeq \tau_{d,L} \propto M_L^3$$

$$\text{RD} : M_s^3 / M_e^2 M_L < \phi : a' = a / \phi^{0.5} ; \tau_{d,L}' \simeq \tau_{d,s} Z_L^2$$

$$\text{FD} : 1 > M_s^3 / M_e^2 M_L > \phi : a < a' < a / \phi^{0.5} ; \tau_{d,L}' \simeq \phi \tau_{d,L}$$

In the restricted dilation regime, the tube fully dilates to have the maximum diameter $a' = a / \phi^{0.5}$ and further dilation is restricted by the mutual entanglements of the long

chains. In the free dilation regime, the tube partially dilates to have $a' < a/\phi^{0.5}$ and the dilation up to this a' is free from the effect of the long-long entanglements.

The behavior of the relaxation modulus in this theory is determined from the assumption of independence between two types of relaxation modes (*Graessley, 1982*). The first type is related to the escape of the chain from the tube due to the motion of the polymer itself. It includes all relaxation modes available to the single chain in the tube such as reptation and CLF. However CLF modes are neglected in this theory. The second mode is related to the CR motion of the tube itself. Thus, the expression for the stress relaxation function is given as:

$$G(t) = G_N^0 \mu(t) R(t)$$

Where $\mu(t)$ is the probability that the reptating chain at time t remains confined by the original tube with diameter a , whereas $R(t)$ is the relaxation contribution due to the CR tube motion (tube rearrangement).

The key result of this theory is that in contrast to *Viovy et al., 1991* constraint release in a binary blend is also accompanied by tube dilation. The condition of tube dilation is controlled by the Graessley criterion (*Struglinski, Graessley, 1985*) extended to account for blend composition. In agreement with numerous experimental data, this theory predicts an acceleration of terminal relaxation upon mixing with shorter chains. However, the assumption that the effect of short chains completely vanishes at times longer than $\tau_{d,s}/\phi^2$ and thus allows the long chains to freely diffuse inside the dilated tube has to be further analyzed.

1.4.4. Marrucci's dynamic tube dilation (DTD).

In contrast to *Doi et al., 1987* who assume that tube dilation may occur only upon mixing long chains with chains of lower molecular weight, the central idea of the dynamic tube dilution (DTD) theory is that tube diameter increases progressively with

time due to the dilution effect from fast relaxing chains (see Figure 1.6). This theory was originally developed for monodisperse linear chains by Marrucci (*Marrucci 1985*) as an approximation of the tube rearrangement effect on the viscoelastic properties. Further extension of this theory to monodisperse star polymers (*Ball, McLeish, 1989*), star/linear blends (*Milner et al., 1998*) star/star blends (*Blottiere et al., 1998*), H-polymers (*McLeish et al, 1999*), combs (*Daniels et al., 2001*) and some cases of binary blends of linears with well separated M_w has demonstrated quantitative predictions of the viscoelastic relaxation. Because of the relative simplicity of its mathematical implementation and despite being widely criticized, this CR theory has been adopted by most advanced tube models. In this section we briefly introduce the theory of DTD and review some significant points of criticism.

Marrucci assumes that a fraction $1-\mu(t)$ of the original entanglements has been removed at time t and thus an effective tube diameter can be estimated as

$$a(t) = a(0)\mu(t / \tau_d)^{-d/2}$$

Where τ_d is the disengagement or reptation time of the chain and d is so-called dilution exponent close to unity, whose exact value depends on the yet un-resolved precise nature of entanglements. Depending on the model and considered molecular structure d can be equal to either 1 (*Bhattacharjee et al. 2002; Larson, 2001; Park, Larson, 2003*) or 1.3 (*Auhl et al., 2009; Watanabe et al. 2004*). On the other hand, in (*Van Ruymbeke et al., 2012*) it is shown that $d=1$ is more appropriate at short times, whereas at longer times $d=4/3$ gives better description of the experiment.

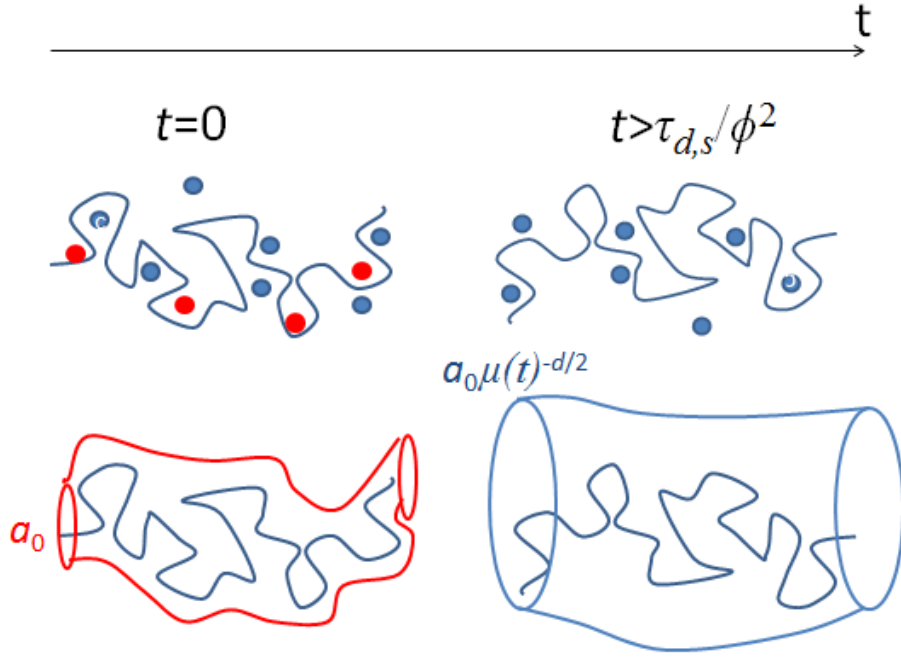


Figure 1.6: Schematic representation of the DTD picture. Red and blue circles represent short and long chains, respectively. At $t < \tau_{d,s}/\phi^2$ the probe chain is reptating in the thin tube with diameter a_0 formed by entanglements with short and long chains. All entanglements with short chains are becoming ineffective after the fat tube with current diameter $a_0 \mu(t)^{-d/2}$ has been explored by Rouse-like motion of the thin tube at $t > \tau_{d,s}/\phi^2$ by performing jumps on amplitude a_0 with frequency inverse to the lifetime of probe/short entanglements, $1/\tau_{d,s}$. Following motion of the chain is constrained only by the fat tube.

Rubinstein et al. in (Rubinstein et al., 1987) have shown that the expression proposed by Marrucci is equivalent to the prediction of the tube rearrangement model (Rouse tube dynamics) but only for the case of intermediate timescales in a binary blend of linear chains with well separated molecular weights.

In the Doi-Edwards expression for stress relaxation, the tube diameter enters both the plateau modulus as $G_N^0 \sim \phi/N_e \sim \phi/a^2$, where N_e – is average number of Kuhn segments per entanglement strand, and the reptation time $\tau_d = L^2/\pi^2 D_{tot}$ through $L = Nb^2/a$, where the bare chain diffusion coefficient $D_{tot} = k_B T/N\zeta$ is independent of a .

According to Marrucci's theory, the relaxation contribution due to the tube rearrangement can be simply calculated as

$$R(t) = \mu^d$$

Then by substituting $R(t)$ in the Graessley expression for $G(t)$ (Graessley, 1982) Marrucci has deduced

$$G(t) = G_N^0 \mu(t)^{1+d}$$

On the other hand, with respect to the effect of dilution on the reptation time of long chains, both Viovy, 1985 and Rubinstein *et al.*, 1987 argue that since every relaxed constraint is immediately replaced by the new one, the contour length for chain reptation remains unchanged thereby leaving the reptation time unaffected and equal to that in the thin tube.

DTD in star polymers.

McLeish in (Ball, McLeish, 1989) followed by (Milner, McLeish, 1997) and finally (McLeish, 2003) have extended application of this theory to star polymers which naturally have a broad distribution of exponentially separated relaxation times and thus being good candidates for applying DTD. In (Ball, McLeish, 1989) the authors extend the theory of (Pearson, Helfand, 1984) for star relaxation in a fixed network. They introduce a dilution function $\Phi(x) = 1-x$ into the effective entropic potential $U_{eff}(x)$ for retraction of the chain end to a fractional distance $x=0..1$.

$$\frac{\partial U_{eff}(x)}{\partial x} = \frac{\partial U(x, Z[\Phi(x)]^d)}{\partial x}$$

Despite providing quantitative agreement with experimental data, the theory still relies on adjustable modulus and time-scale factors. In particular, some discrepancy in the terminal relaxation zone could be masked by taking a slightly larger values of N_e with respect to the diluted value, $N_{e,0}/\phi^d$. Alternatively, in order to overcome the observed discrepancy, McLeish in (McLeish, 2003) argues that although the chain is indeed retracting in the dilated tube with a lowered potential, it does so with the penalty of higher drag, which is not accounted for in (Ball, McLeish, 1998). By further developing this idea, McLeish concludes that the introduction of the renormalized diffusion constant results in a crossover to different dynamics during the last 1/3 of star-arm

retraction. This different dynamics can be accounted for by arresting tube dilation for the last 1/3 of the star-arm (see Figure 1.7). Similar conclusions have been made by (Shanbhag *et al.*, 2001) who also suggests a new physics for describing relaxation of entanglements close to the branch point in order to explain failure of DTD in the terminal relaxation zone. According to his picture, at long times, the dynamics is dominated by rare events in which the innermost and long living entanglements are slowly diffusing towards the chain end where they are met and “killed” by the retracting chain end itself.

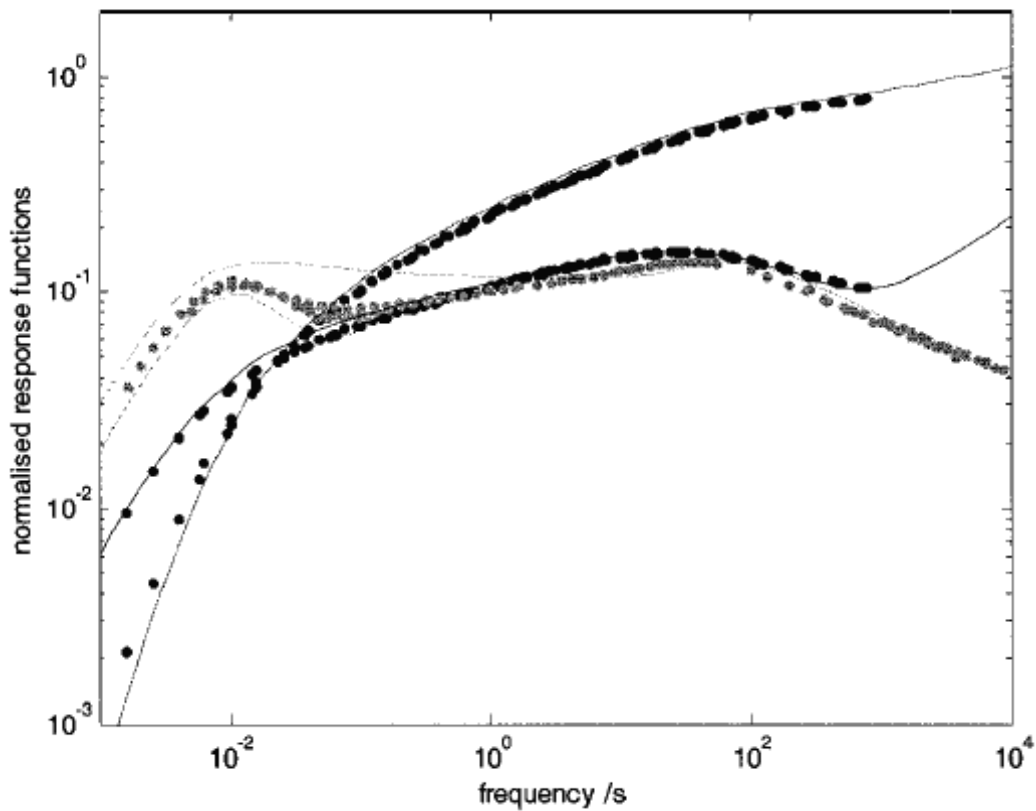


Figure 1.7: Normalized viscoelastic storage and loss modulus and dielectric loss permittivity on 6-arm PI star melt with $M_{arm}/M_e=16$. Solid black curves and upper dashed line are predictions of viscoelastic (G' , G'') and dielectric (ϵ'') moduli by DTD theory of Milner, McLeish, 1997. Lower dashed curve is prediction of ϵ'' by the same theory with arrested dynamic dilation at last 1/3 of the star arm. Adapted from McLeish, 2003.

Another argument against the DTD picture applied to star-shaped polymers is given by (Frischknecht, Milner, 2000). The authors analyze self-diffusion and viscoelastic terminal time of star-shaped polymers. By plotting the product of the self-diffusion

coefficient and zero shear viscosity $D_{self}\eta_0$ as function of the number of entanglements per star-arm, Z_{arm} , they show that although the magnitude of the product corresponds to retractions in the dilated tube, the scaling of the product indicates that CR hops take place in the thin tube.

Alternatively, H. Watanabe and co-workers employ dielectric spectroscopy of type-A dielectrically active polymers having dipoles parallel to the chain's backbone (Figure 1.8) for estimating the survival fraction of the dilated tube, $\mu(t)$, without relying on any model. By combining these measurements with the rheology they test the validity of the DTD picture.

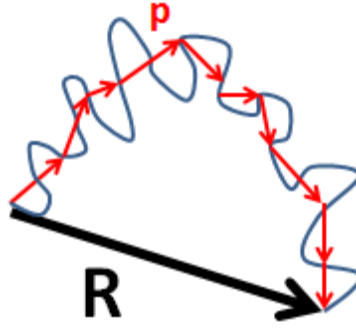


Figure 1.8: Schematic representation of the end-to-end vector $R(t)=\sum p_i(t)$ as sum of type-A dipoles parallel along the backbone. The dielectric relaxation function is computed as auto-correlation function of R : $\Phi(t)=\langle R(t)R(0) \rangle$.

1.4.5. Watanabe's full and partial DTD.

In this section we describe approach used by Watanabe and his group in order to test Marrucci's DTD picture (referred to as full-DTD in (Watanabe *et al.*, 2004) and later) using rheo-dielectric measurements of type-A dielectrically active polymers.

According to Watanabe, every constraint release event is followed by two different but related molecular pictures. The first picture is equivalent to the tube rearrangement picture of (Graessley, 1982; Klein, 1978; Daoud, de Gennes, 1979; Klein, 1986) which results in large-scale motion of the chain resulting from an accumulation of local CR-hops of the probe chain with constant amplitude a . The second picture results in time-dependent dilation of the tube diameter, $a_{f-DTD}(t)=a/\mu(t)^{d/2}$, where the relaxed chain

fraction serves as a solvent for still oriented segments. In order to take advantage of the dilated tube diameter, the chain should have enough time to explore the new diameter by CR Rouse motion. However, if the rate of the tube diameter enlargement is too fast to allow equilibration by Rouse CR motion of the thin tube, then the full-DTD picture fails at corresponding time-scales (see Figure 1.9).

From the failure of the full-DTD picture under these circumstances, it can be concluded that not all relaxed chains can be “used” as solvent for unrelaxed segment. Therefore, a modification of the full-DTD theory has to be introduced and referred to as partial-DTD (Watanabe *et al.*, 2004).

The criterion for validity of the full-DTD picture states that full-DTD only holds in the time-range, where the number of segments assumed to be equilibrated in this picture, $\beta_{f-DTD}(t) = \mu(t)^{-d}$ ($d=1.3$) does not exceed number of CR-equilibrated entanglement segments, $\beta_{CR}(t)$. Otherwise it fails.

This criterion introduces an additional parameter $\beta^*(t)$ defined as

$$\beta^*(t) = \begin{cases} \beta_{CR}(t) & \text{for } \beta_{f-DTD}(t) > \beta_{CR}(t) \\ \beta_{f-DTD}(t) & \text{for } \beta_{f-DTD}(t) < \beta_{CR}(t) \end{cases},$$

The number of CR equilibrated entanglement segments is computed as $\beta_{CR}(t) = \frac{1}{\psi_{CR}(t)}$,

with a hypothetical CR stress decay function determined as

$$\psi_{CR}(t) = \frac{1}{Z} \sum_{p=1}^Z \exp\left(-\frac{t}{\tau_{CR,p}}\right),$$

where $\tau_{CR,p}$ is the characteristic time of p^{th} CR mode.

In Figure 1.9, the experimental data for two sets of binary linear blends with a small fraction of high- M_w component are compared with the relaxation functions predicted by

the full-DTD and partial-DTD pictures. In this figure, the stress relaxation functions corresponding to the partial and full DTD pictures are computed as

$$G_{p-DTD}(t) = \frac{\mu(t)}{\beta^*(t)}$$

$$G_{f-DTD}(t) = \mu(t)^{1+d}$$

In the case of a binary blend, the total survival fraction, $\mu(t) = (1 - \phi_L)\mu_s(t) + \phi_L\mu_L(t)$, with ϕ_L of long chains is estimated experimentally from dielectric spectroscopy.

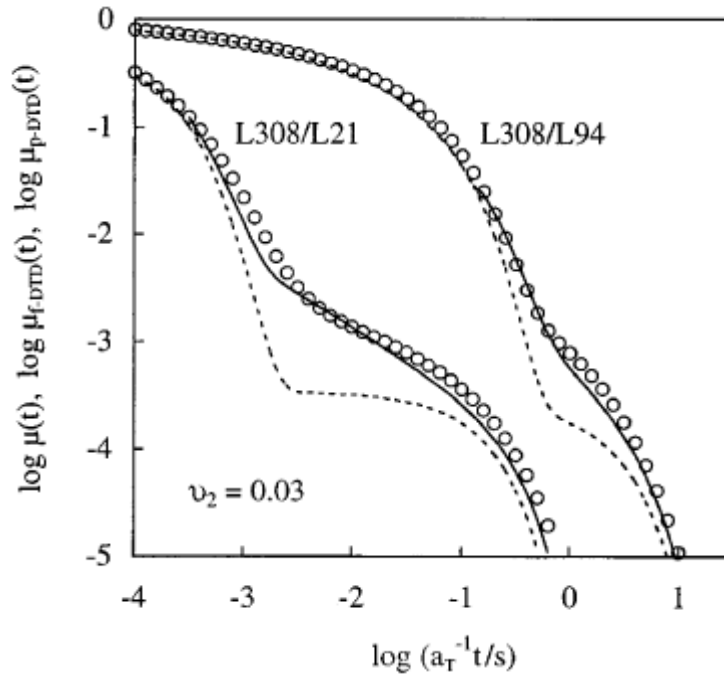


Figure 1.9: Comparison of the normalized viscoelastic relaxation function (circles) of the binary blends of (3wt.% of PI 308 kg/mol in the matrix of PI 21kg/mol and 94kg/mol) with the relaxation functions $G_{f-DTD}(t)$ (dotted line) and $G_{p-DTD}(t)$ (solid line). Both functions are calculated from the dielectric data on the basis of the full-DTD and the partial-DTD pictures. The solid lines coincide with the dotted lines in the time-range which is not shown. Adapted from Watanabe et al., *Macromol.*, 2004, 37, 1937. (In notations of Watanabe the computed and experimental normalized viscoelastic relaxation functions are denoted as $\mu(t)$, $\mu_{f-DTD}(t)$, $\mu_{p-DTD}(t)$, respectively).

The comparisons shown in Figure 1.9 demonstrate severe failure of the full-DTD picture in the intermediate time range, whereas prediction of the partial-DTD coincides with the experimental data.

The same comparison made for other molecular architectures demonstrate that full-DTD picture works well for monodisperse linear chains (*Matsumiya et al., 2000; Watanabe et al., 2002; Watanabe, 2001; Watanabe, 2001*) but fails for monodisperse stars in the terminal time range (*Watanabe et al., 2000; Matsumiya, Watanabe, 2001; Watanabe et al., 2002; Watanabe, 2001*). It was also shown that the DTD theory of Milner-McLeish (*Milner and McLeish, 1997*) is not able to simultaneously predict the viscoelastic and dielectric data of monodisperse stars with the same set of parameters.

On the other hand, stress relaxation predicted by the partial-DTD picture is shown to be close to the experimental data for the monodisperse stars (*Watanabe et al., 2006*). However, a satisfactory match is only possible after introducing an additional correction to $\mu(t)$ due to the fluctuations of the arm at the edge of the surviving fraction of the dilated tube. Otherwise a pronounced discrepancy in the terminal relaxation zone is observed.

Comparison with rheological or dielectric data is often not sufficient for testing different CR theories applied in tube models. There is a need to complement the analysis by more detailed stochastic models that can be used to extract different physical observables at different length and time-scales. In the next section we introduce existing stochastic mesoscale models used for simulating equilibrium dynamics of entangled polymer melts. The focus will be made on the analysis of different CR pictures applied in these models.

1.5. Overview of the slip-link models.

The concept of the slip-link model as an alternative to the tube model has existed for almost as long as the tube model itself, since Doi and Edwards in 1978 (*Doi, Edwards, 1978*) introduced it to motivate the use of a certain equation relating stress with chain conformation in their tube model. It is based on the idea of substituting the tube by virtual slip-links which allow the chain to diffuse along its length by reptation but

restrict its motion in the lateral direction in the same way as topological constraints applied by entanglements. As for tube models, there are numerous implementations of the slip-link idea developed by different research groups. One of the key differences between them, which is in line with the main objective of this study, is the way they handle CR.

Nair-Schieber model (NS).

In order to account for CR, Nair and Schieber (*Nair, Schieber, 2006*) tested an approach based on Rouse-like dynamics of the slip-links. Following the self-consistent approach of Rubinstein and Colby (*Rubinstein, Colby, 1988*) for determining diffusivity of entanglements, they mimicked renewal of constraints by Rouse-like fluctuations of the slip-link coordinates while the total number of entanglements was kept constant.

Discrete Slip-link model (DSM).

In the discrete version of the NS model referred to as DSM (*Schieber et al., 2003*) an alternative method of introducing CR is proposed (*Khaliulin, Schieber, 2009*). In contrast to the NS model, the number of Kuhn steps per entanglement strand can be changed between neighboring strands, driven by Brownian forces and free energy differences. The constraint release dynamics allow randomly distributed slip-links to be destroyed if a slip-link is abandoned by the last Kuhn segment of the chain. This is followed by new slip-link being created at random positions along the chain. Thus the number of entanglements in this implementation is fluctuating. Upon creation, every entanglement is assigned a specific lifetime determined self-consistently in agreement with the sliding dynamics of paired imaginary chains in analogy with (*Rubinstein, Colby, 1988*). The authors prove that in the case of monodisperse melts this CR implementation is equivalent to the more computationally expensive approach of Doi and Takimoto (*Doi, Takimoto, 2003*). DSM (*Pilyugina et al., Macromol., 2012*) has been successfully applied to simultaneously predict rheology and dielectric relaxation of binary linear blends and monodisperse star-shaped polymers, however it fails to

correctly predict dielectric relaxation of binary blends with small fractions of long chains.

Doi-Takimoto model (DT).

The model of Doi-Takimoto (DT) includes CR by coupling entanglements on different chains. Whenever an entanglement is destroyed or created on a given chain by sliding dynamics, a coupled entanglement on another randomly chosen chain is destroyed or created by CR. The Doi-Takimoto pairing algorithm is keeping a correspondence between different chains by “virtually” coupling them via slip-links. However, there is an ambiguity between coordinates of randomly selected partners. This ambiguity can not be resolved within single chain models since there is no coupling in real space.

Primitive chain network model (PCN)

The primitive chain network model (PCN) of Masubuchi (*Masubuchi, 2001*) resolves this ambiguity. In this multi-chain model, each slip-link is shared between two chains in real space. As in most of other slip-link models an entanglement is considered as the interaction of two “partner” chains. The sliding dynamics of the chain determines the fluctuating number of monomers between any two neighboring slip-links.. The entanglement is suppressed when the average number of beads at the end segment of one partner chain becomes smaller than some predefined minimum number, n . Alternatively, a new entanglement is created if the current number of beads at the chain end becomes larger than n . Loss of an entanglement at the end of one chain also results in the loss of an entanglement at any random position of a partner chain.

When constructing a new slip-link at the end of a chain, a list of possible candidates located within a given radius from this end is generated. Then one of them is chosen and a new slip-link is added in the middle of the selected subchain.

In ref. (*Masubuchi et al., 2008*) the authors have tested different realizations of constraint release by comparing their predictions of stress relaxation in binary linear blends which is the best test for the CR. Namely, they tested the DT model, the NS model and the PCN model. Obtained results indicate that the pairing algorithm utilized in DT and PCN gives better agreement with published data than the NS model. The discrepancy was mostly pronounced at intermediate frequencies where predicted by NS model values of G' and G'' were significantly overestimated, whereas at low frequencies G' was underestimated. Observed discrepancies were shown to be sensitive to the difference between the lengths of the short and long chains. This is indicating that the discrepancies are directly related to the different descriptions of CR. This conclusion was later confirmed by Schieber in (*Khaliulin, Schieber, 2009*).

In the next section I describe the slip-spring model of Likhtman (*Likhtman, 2005*). While other slip-link models are coarse-grained at the level of the distance between entanglements and focus only on the slip-link positions, average number of beads between them and total number of entanglements, the slip-spring model is less coarse-grained and it explicitly simulates motions of all beads along the chains. This allows to compute all physical observables at the smaller time and length-scales than other slip-link models. As a result, the stress relaxation modulus can be computed in the higher frequency range of G^* including fast Rouse modes.

1.6. The slip-spring model.

The slip-spring stochastic single chain model developed by Likhtman in ref. (*Likhtman, 2005*) is based on a Rouse bead-spring chain with effects of neighboring chains introduced via slip-links (see Figure 1.10). These slip-links are connected to a fixed anchoring points via virtual springs, representing the confinement potential of neighboring chains. Due to the movement of other chains the slip-links can slide along the backbone of the chain.

Constraint release.

Constraint release in the slip-spring model is introduced in a way consistent with the “coupling of entanglements” algorithm of Doi-Takimoto (Doi, Takimoto, 2003) and Hua-Schieber (Hua, Schieber, 1998). The pairing between chains is introduced via slip-links. Constraint release occurs when a slip-link on one chain slides over its end. This destroys the corresponding slip-link on both partners thereby allowing freed chain segments to freely move in 3D space. Next, in order to maintain the average density of slip-links, a new slip-link connecting two random partners immediately appears at some random position of one chain and at the end of another chain thereby constraining dynamics of the corresponding chain segments. In the frame of this study all simulations using this model assume all entanglements to be binary interactions, i.e. when a slip-link slides over a chain end, only two partner chains are losing the corresponding entanglement. This assumption corresponds to dilution exponent $d=1$, which is used in most slip-link models although its validity is not totally obvious (Rubinstein, Colby, 1990).

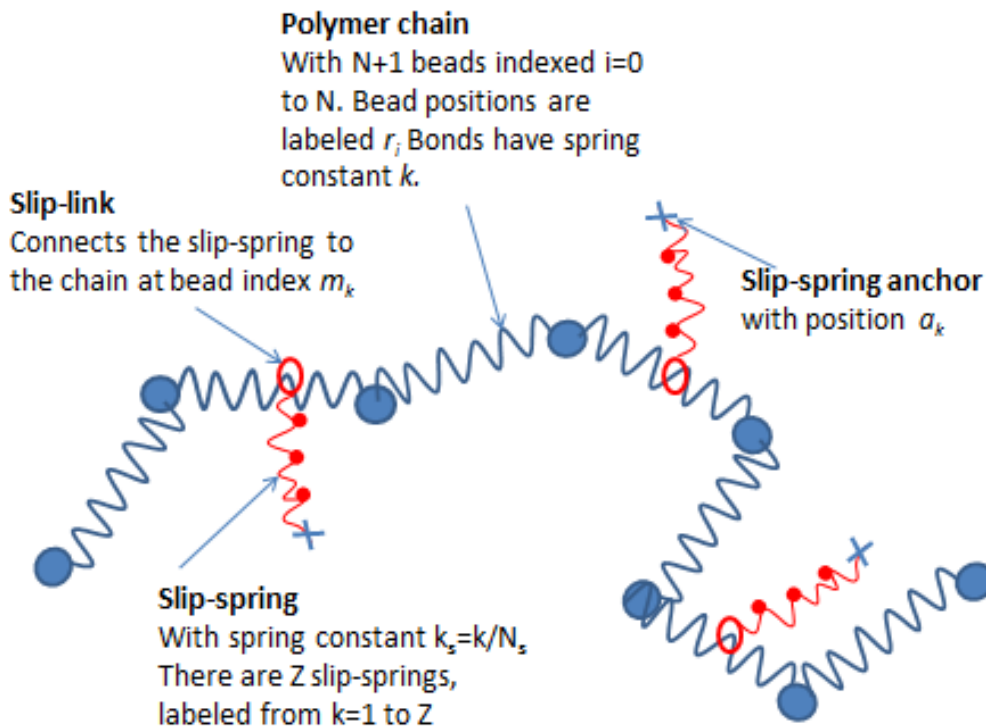


Figure 1.10: Diagram of the slip-spring model

Parameters.

In this model (see figure 1.10), the positions of beads are labelled as r_i , where i is the bead index and there are $N+1$ beads connected by N springs. There are on average N_e beads between two slip-links and Z slip-links per chains. The anchoring point of the j^{th} slip-link is denoted as a_j .

Positions of the anchoring points a_j are distributed around s_j (positions of corresponding slip-links) according to Boltzmann weight $P(x_a) \sim \exp((-3k_B T/2N_s b^2)(s_j - a_j)^2)$. Thus any dynamics of this system which preserves the Boltzmann distribution will obey unperturbed Gaussian statistics at all length scales. This was tested in ref (Likhtman, 2005) by comparison of the predicted structure factor and of the 2nd and 4th moments of the distance between different monomers with the theoretical values for the Gaussian chain.

The strength of the slip-springs is determined by the effective number of beads N_s . In references (Likhtman, 2005 ; Ramirez et al., 2007) it was shown that particular values of N_e and N_s at constant N_s/N_e ratio have very small effect and primarily only on the shape of transition between the plateau and the Rouse zones. In contrast, the ratio between N_e and N_s affects the plateau modulus and terminal properties. There are two possible extremes: $N_s \gg N_e$ corresponding to many soft slip-links. This is equivalent to the classical tube picture, however, in this condition the constraint release algorithm implemented in the slip-spring model would result in the wrong scaling of the plateau modulus. In order to fix this issue one would need to assign for every slip-link at least two other partner chains. Thus, upon disentanglement of any chain the corresponding number of slip-links would be deleted.

Alternatively, the binary assumption for every entanglement can be used if $N_s \ll N_e$. The optimal choice of parameters used in most of the simulations in ref. (Likhtman, 2005) is $N_e=4$ and $N_s=0.5$. In this limit, increasing the number of monomers by λ , scaling time by λ^2 and length of the monomers by $\lambda^{-1/2}$ does not change the result.

The model has three fitting parameters: chemistry sensitive unit mass M_0 defined as molecular weight represented by one bead; elementary time τ_0 and stress of the model G_0 . The stress of the model is calculated in units of $G_0 = \rho RT/M_0$ with ρ , R and T being

the polymer density, universal gas constant and absolute temperature, respectively. G_0 should not be confused with the plateau modulus G_N^0 .

In our simulations we use at least 10 chains per one component of polymer mixture and we average obtained results over at least 5 simulations. In order to validate that this provides statistically large sample we have run simulations with 10, 100 and 1000 chains of polymers of different molecular weight and topology (linear and stars) with 5 simulations per sample. The obtained results show that independently on the total number of beads and chain topology simulations with number of chains above 10 do not show any significant influence on the result.

Slip.

In this model, the chain is reptating by sliding through slip-links. The slip-links can occupy any coordinate along the chain, $x_j=[0...N]$. Moreover we assume that slip-links travel along the straight line between two neighboring beads and their 3D positions are determined as

$$s_j(x_j, \{r\}) = r_{\text{trunc}(x_j)} + (x_j - \text{trunc}(x_j))(r_{\text{trunc}(x_j)+1} - r_{\text{trunc}(x_j)})$$

Where $\text{trunc}(x_j)$ denotes the closest integer to x_j (*Likhtman, 2012*).

In contrast with other slip-link models where this motion is frictionless, in the slip-spring model there is an additional friction coefficient associated with the slip motion. Besides, there is an additional parameter defining how slip-links behave when they approach each other. Throughout this study we assume that there is an effective repulsion between two neighboring slip-links and therefore they can not approach each other closer than on two beads. This assumption makes the chain feel more entangled with respect to the case when slip-links can freely cross each other or occupy the same bead. However, which option is closer to the real behavior of polymer chains remains an open question and deserves detailed analysis, which is beyond the scope of this work.

Energy.

The slip-spring model is based on a bead-spring Rouse chain with energy

$$U^C = \frac{1}{2} k \sum_{i=0}^{N-1} (r_{i+1} - r_i)^2,$$

where the spring stiffness k is determined as

$$k = \frac{3k_B T}{b^2}$$

and the length of the unit segment is taken as $b=1$.

The energy of the slip-spring is given as

$$U_j^s = \frac{k}{2N_s} (a_j - s_j(x_j, \{r\}))^2.$$

Thus, the energy of the entire system is given as

$$U = \frac{k}{2} \sum_{i=0}^{N-1} (r_{i+1} - r_i)^2 + \frac{k}{2N_s} \sum_{j=0}^{Z-1} (a_j - s_j(x_j, \{r\}))^2$$

The dynamics of the chain is described by the stochastic equation of motion:

$$\begin{aligned} \zeta \frac{dr_i}{dt} = & k(r_{i+1} - 2r_i + r_{i-1}) + f_i(t) + \\ & \frac{k}{N_s} \sum_{j: \text{trunc}(x_j)=i} (1 - (x_j - \text{trunc}(x_j))) (a_j - s_j) + \\ & \frac{k}{N_s} \sum_{j: \text{trunc}(x_j)=i-1} (x_j - \text{trunc}(x_j)) (a_j - s_j) \end{aligned}$$

The first two terms represent the equation of motion for a Rouse chain (described earlier in this chapter), the third term represents the force due to all slip-links on the segment $(r_{i+1}-r_i)$ and the final term is the force due to all slip-links on the segment (r_i-r_{i-1}) .

Next, we formulate the stochastic equation of motion for the slip-links, satisfying Boltzmann distribution for all variables.

$$\zeta_s \frac{dx_j}{dt} = \frac{k}{N_s} (r_{\text{trunc}(x_j)+1} - r_{\text{trunc}(x_j)}) (a_j - s_j) + g_j(t),$$

In two last equations $f_i(t)$ and $g_j(t)$ represent random forces with zero mean satisfying the fluctuation-dissipation theorem; ζ_s is another model parameter representing additional artificial friction of the slip-link motion along the chain. The value of this friction coefficient can not be zero because it will result in zero escape time of the slip-links from the chain. By contrast, nonzero ζ_s results in exponential dependence of this escape time from the potential of the slip-springs and only linear dependence on ζ_s . In ref. (Likhtman, 2005) it was shown that variations of ζ_s/ζ in the range of 0.01...0.1, where ζ ($=1$) is a single bead friction, only slightly affects on viscosity (within 30%). For most of the simulations in ref (Likhtman, 2005) the value of this parameter was fixed to $\zeta_s/\zeta=0.1$.

Computation of the stress.

In the slip-spring model the total stress is computed as a sum of chain and slip-spring stress.

$$\sigma_{tot}(t) = \sigma_{chain}(t) + \sigma_{ss}(t)$$

In the references (Ramirez et al., 2007; Likhtman, 2012) the authors argue that even though the slip-spring stress does not contribute to the instantaneous stress of the probe chain the cross-correlation term between chain stress and the stress of the slip-spring should be accounted for when computing the response of the chain to the deformation .

$$G(t) = G_0 \left(\langle \sigma_{chain}(t) \sigma_{chain}(0) \rangle + \langle \sigma_{chain}(t) \sigma_{ss}(0) \rangle \right)$$

In ref (Ramírez et al., 2007) the authors have demonstrated the importance of including the cross-correlation term in the relaxation function. In particular they illustrate the relative stress contribution of the cross-correlation term on the plateau modulus for a different values of N_e/N_s . For the case of $N_e/N_s=8$ used in most of the simulations presented in ref (Likhtman, 2005) the contribution is about 30%.

Further, the end-to-end vector autocorrelation function of the chain is computed as follows:

$$\Phi(t) = \frac{\langle R(t)R(0) \rangle}{\langle R_0^2 \rangle},$$

where R is the end-to-end vector of the chain.

For the case of blends, all terms of the equations for computing total $G(t)$ and $\Phi(t)$ must be weighted in accordance with the component's weight fractions.

1.7. Detailed objectives and structure of the thesis.

After Likhtman and McLeish in (Likhtman, McLeish, 2002) have developed an extension of the Doi-Edwards theory for monodisperse linear chains by taking into account in a rigorous way the effect of contour length fluctuations and CR, the problem of predicting linear viscoelasticity for the simplest entangled polymers can be considered solved. The next very important step on the way to the ultimate model for predicting linear rheology of complex industrially relevant systems, should be a fundamental understanding of “many-chain effects” paving the way to a full CR theory.

As can be concluded from the literature overview, the task to introduce the influence of a moving molecular environment on stress relaxation has been puzzling many researchers for over 30 years. This has resulted in the development of various theories with different levels of complexity but no clear universal picture has yet emerged. Moreover, there is an obvious lack of systematic methodology for detailed testing of CR theories and sometimes there is confusion due to absence of a common nomenclature for describing the same phenomena.

In this thesis we focus on advancing the understanding of CR mechanisms. For this purpose we analyze viscoelastic and dielectric relaxation data of probe chains in well-characterized simplified “model” environments of monodisperse, binary and ternary mixtures with star-shaped as well as linear architectures. Experimental data will be confronted with predictions of tube models. I will use the slip-spring model as a kind of

“idealized experiment” giving access to very detailed observables, which are impossible to obtain in real experiments.

For fulfilling this objective we aim to contribute to the following:

- Development of a systematic methodology for testing different “tube-based” relaxation mechanisms;
- Determination of the effective diffusion coefficient in entangled polymer mixtures;
- Understanding the balance and interrelation between different relaxation mechanisms in entangled melts.

Advancing in these directions will pave the way to substantial improvements of tube models and enhance their applicability to industrially relevant polymer systems.

This thesis is constructed as follows: in Chapter 2 we validate the slip-spring model by comparison with published rheology data on nearly monodisperse star-shaped polymers. To our knowledge this is the first time that this model is tested on star-branched polymers. Results of this validation will be used in Chapter 3, where we further validate the model by comparison with relaxation modulus of binary star/linear blends. In the same chapter we propose a methodology for extending tube theory for monodisperse stars to their blends with linear chains. This is achieved with the help of a detailed analysis of the effect of CR from linear chains on the viscoelastic relaxation of stars. The developed approach will be used in a systematic way in Chapter 4. In this chapter after validating the slip-spring model by simultaneous comparison with the viscoelastic and dielectric relaxation data of binary linear blends we propose a systematic approach for analyzing the effect of different CR environments on the relaxation of the end-to-end vector of a probe chain. The analyzed CR environment covers the entire parameter space of molecular weights and component fractions in binary and ternary mixtures. Finally, in Chapter 5 we will experimentally investigate industrially relevant PS systems with monomodal and bimodal distribution of molecular weights. In particular the CR effect of poorly entangled diluents will be analyzed with respect to shear and uniaxial

extension rheology. Finally we will make conclusions and highlight possible perspectives of this study.

Chapter 2:

SLIP-SPRING SIMULATIONS OF MONODISPERSE STARS.

Abstract

In this chapter we validate the slip-spring model by comparisons with published rheological data on nearly monodisperse star polymers with different molecular weights and two different chemical structures. We show that the obtained predictions are satisfactorily matching experimental data despite approximations related to prohibiting slip-links from passing through the branch point.

Part of this chapter is a result of a collaboration with A.E. Likhtman and has been published in M.E.Shivokhin et al., *Macromolecules* 2014, 47(7), 2451. We thank Prof. J.Roovers for kindly providing experimental data.

2.1. Introduction.

The key simulation tool of this thesis is the slip-spring model of Likhtman developed on the basis of the network model of Rubinstein and Panyukov (*Rubinstein, Panyukov, 1997*). In (*Likhtman, 2005*) this model has already been successfully validated for nearly monodisperse linear chains of different chemistries by comparing its predictions with experimental rheological data as well as with diffusion and neutron-spin echo data.

Up to date there are no published results on the use of this model for star-branched polymers. The main objective of this chapter is to validate linear rheology predictions of the slip-spring model for stars by comparison with published rheology data of nearly monodisperse star-shaped polymers. However, it should be noted that a detailed study of stress relaxation in monodisperse stars including branch point dynamics and possible rules for passing slip-links through the branch point is beyond the scope of this thesis.

The structure of this chapter is as follows. First, we shortly describe the implementation of the slip-spring model and its parameters. In the materials section we present the

characteristics of the nearly monodisperse star-shaped polymers whose rheology data will be used for validation of the model. This will be followed by the results and discussions section where we superimpose the experimental data with simulation results and discuss the quality of the predictions. And finally we will end this chapter by conclusions and perspectives.

2.2. Parameters of the slip-spring model

In the current implementation of the slip-spring model, slip-links are not permitted to cross the branch point; neighboring slip-links are not allowed to come closer than 2 beads from each other. As we will demonstrate, the effect of these assumptions on the quality of rheology predictions by the model is almost negligible. The CR algorithm used is equivalent to that used for linear chains as described in detail in the introduction chapter of this thesis.

The slip-spring simulation results are presented in dimensionless units, with thermal energy $k_B T=1$, size of the Kuhn segment, $b=1$ and effective friction coefficient of a Kuhn segment, $\zeta=1$ and slip-spring friction coefficient $\zeta_s=0.1$. The stress relaxation function is calculated from the Green-Kubo relationship, including chain stress auto-correlation and the cross-correlation between the chain stress and the stress carried out by the virtual springs (*Ramirez, et al. 2007; Likhtman, 2012*).

This model has three fitting parameters: chemistry sensitive unit mass M_0 defined as molecular weight represented by one bead; elementary time τ_0 and stress of the model G_0 . In Table 2.1 we summarize the fitted values of these parameters for both materials.

Regardless of molecular topology and molecular weight, we use $N_e=4$ as average number of beads between two slip-links and $N_s=0.5$ as virtual spring strength

Table 2.1: The fitted slip-spring parameters.

	M_0 , kg/mol	τ_0 , s	G_0 , MPa
PBd ($T_{ref}=27^\circ\text{C}$)	0.37	3.85e-6	8
PS ($T_{ref}=170^\circ\text{C}$)	3.7	1e-3	1.0

The stress of the model is calculated in units of $G_0=\rho RT/M_0$ with ρ , R and T being the polymer density, universal gas constant and absolute temperature, respectively. By using $\rho(\text{PBd})=900\text{kg/m}^3$, $\rho(\text{PS})=1050\text{kg/m}^3$, $T(\text{PS})=443\text{K}$, $T(\text{PBd})=300\text{K}$, $R=8.31\text{ m}^3\cdot\text{Pa}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and by substituting the fitted values of M_0 , it is possible to compute $G_0(\text{PBd})=6\text{MPa}$ and $G_0(\text{PS})=1\text{MPa}$, which is in good agreement with the fitted G_0 of both materials (see Table 2.1). This model stress G_0 should not be confused with the plateau modulus G_N^0 .

2.3. Materials.

Two sets of nearly monodisperse polystyrene (PS) and polybutadiene (PBd) 4-arm stars has been synthesized and measured by J. Roovers (*Graessley, Roovers, 1979; Roovers, 1985*). The characteristics of these materials are summarized in Table 2.2.

Table 2.2: Characteristics of the 4-arm star polymer chains.

Sample	M_w (kg/mol)	T_{ref} , °C
Polybutadiene		
F	45.2	27
E	84.3	27
D	121	27
Polystyrene		
S111A	154	170
S121A	93.5	170
S141AB	521	170
S221A	897	170

*Used notations are in accordance with the original publication.

** Experimental data of all the samples was kindly provided by J.Roovers.

2.4. Results and discussions.

In Figure 2.1 and Figure 2.2 we superimpose slip-spring predictions with experimental data of frequency dependent loss and storage moduli for 4-arm star polybutadienes published earlier by J.Roovers (*Roovers, 1985*) and 4-arm star polystyrenes (*Graessley, Roovers, 1979*). We constrain the selection of the samples for this validation from the longest accessible computational time of 5 days, which is equivalent to time required for simulation of star chain with ~ 75 beads/arm.

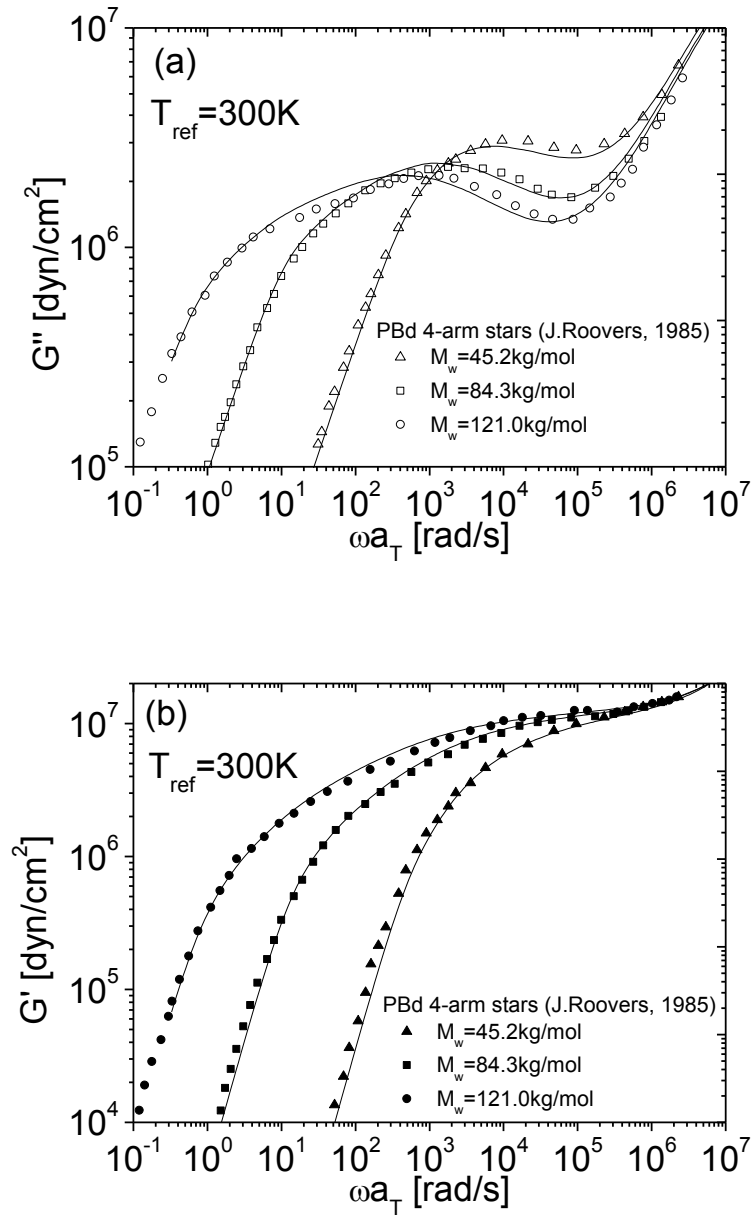


Figure 2.1: Simulation results of the slip-spring model (solid lines) superimposed with published in (Roovers, 1985) (a) experimental dynamical loss and (b) storage moduli of monodisperse 4-arm symmetric stars polybutadienes with different molecular weights measured at $T_{ref}=300K$ (markers). All slip-spring simulations are done with the same parameters: $M_0 \sim 0.37$ kg/mol, $G_0 = 8$ MPa and $\tau_0(T_{ref}=300K) = 3.855 \mu s$.

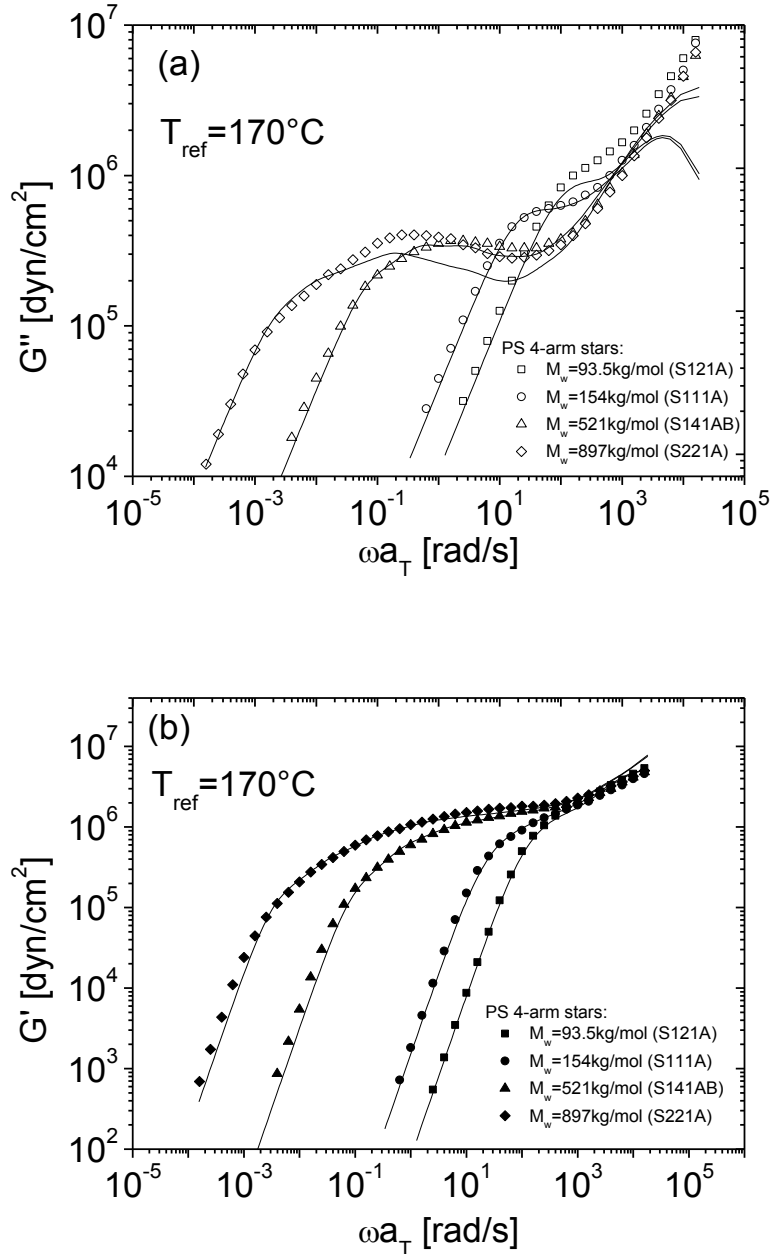


Figure 2.2: Simulation results of the slip-spring model (solid lines) superimposed with published in (Graessley, Roovers, 1979) (a) experimental dynamical loss and (b) storage moduli of monodisperse 4-arm symmetric stars polystyrenes with different molecular weights measured at $T_{ref}=170^\circ\text{C}$ (markers). All slip-spring simulations are done with the same parameters: $M_0 \sim 3.7$ kg/mol, $G_0 = 1$ MPa and $\tau_0(T_{ref}=170^\circ\text{C}) = 1 \times 10^{-3}$ s.

In Figure 2.1, a good match over whole relaxation time range can be observed for all the stars. All simulations are done with the same parameters which are in accord with values used in other studies with the same materials (Shivokhin *et al.*, 2014).

Comparison of the model predictions with the experimental data in Figure 2.2a show good match over entire measured frequency range. Despite good prediction of the terminal relaxation zone in the loss modulus (Figure 2.2b) there are some discrepancies in the intermediate and high frequency range for the samples with the longest ($M_w=897$ kg/mol) and shortest molecular weights ($M_w=93.5$ kg/mol). Indeed, number of entanglements per arm of S121A is slightly more than 1 (corresponding to only 6 beads/arm), therefore observed discrepancies of $G''(\omega)$ at high frequency are not surprising and related to the coarse-grained level of description incorporated in the model. With respect to the sample with the highest molecular weight (S221A) it should be noted that given the observed pronounced deviations in G'' , one would expect to see similar albeit smaller discrepancies for G' . However, this is not the case. Besides, an identical trend for discrepancies has also been observed for this specific sample in predictions using time-marching algorithm (TMA) and branch-on-branch algorithm (BoB) tube models in a recent study by (*Shchetnikava et al., 2014*). In order to further analyze the observed discrepancy, we will simulate stress relaxation of a monodisperse star with equivalent number of entanglements, in the next chapter.

2.5. Conclusions and perspectives

Despite the good quality of obtained predictions, the restricting assumptions used in this model (slip-links are not allowed to cross the branch point and binary nature of all entanglements) can result in erroneously high prediction of the terminal relaxation zone for stars with high molecular weight. However due to the large number of relaxation modes, these discrepancies can be smeared out in the viscoelastic stress relaxation data, but are well pronounced when comparing with respective dielectric relaxation data (*McLeish, 2003; Shanbhag et al., 2001*). To a large extent, the model can be used as an ideal experiment that allows simulating different physical observables simultaneously. Moreover, it allows deactivating and separating different stress relaxation contributions. This can be used for constructing a number of “toy” models and enables deeper validation of each relaxation contribution by confrontation with the center-of-mass diffusivity, rheo-dielectrics data or following the probe-rheology method proposed by C.-Y. Liu (*Liu et al., 2006*).

In the next chapter we will demonstrate the application of this methodology to the simplest binary mixtures including branched structures. Namely, in monodisperse star/monodisperse linear blends, we will first identify the effect of constraint release induced by short linear chains, we will then test existing theory of the constraint release and finally “manually” reconstruct complex combinations of all involved relaxation mechanisms and validate them by comparison with the simulation results. As a complete theory for monodisperse stars is still under development we rely on simulation results validated by the rheological experiments.

Chapter 3:

UNDERSTANDING CONSTRAINT RELEASE IN STAR/LINEAR POLYMER BLENDS.

Abstract.

In this chapter we exploit the stochastic slip-spring model to quantitatively predict the stress relaxation dynamics of star/linear blends with well-separated longest relaxation times and we analyze the results to assess the validity limits of the two main models describing the corresponding relaxation mechanisms within the framework of the tube picture (Doi's tube dilation and Viovy's constraint release by Rouse motions of the tube). Our main objective is to understand and model the stress relaxation function of the star component in the blend. To this end, we divide its relaxation function into three zones, each of them corresponding to a different dominating relaxation mechanism. After the initial fast Rouse motions, relaxation of the star is dominated at intermediate times by the "skinny" tube (made by all topological constraints) followed by exploration of the "fat" tube (made by long lived obstacles only). At longer times, the tube dilation picture provides the right shape for the relaxation of the stars. However, the effect of short linear chains results in time-shift factors that have never been described before. Based on the analysis of the different friction coefficients involved in the relaxation of the star chains we propose an equation predicting these time-shift factors. This allows us to develop an analytical equation combining all relaxation zones, which is verified by comparison with simulation results.

Materials used in this chapter were synthesized and characterised in the group of Prof. Nikos Hadjichristidis. All simulation results presented in this chapter were obtained in the frame of a collaboration with Prof. Alexei Likhtman and published in M.E.Shivokhin et al., *Macromolecules*, 2014, 47(7), 2451.

List of functions.

In order to help the reader we collect functions introduced throughout the text of this chapter in the table below.

Function	Description
$\mu(t)$	Simulated fraction of initial tube segments of the star component which are still oriented at time t .
$\mu_{sub}(t)$	Simulated fraction of initial tube segments of the star component from which modes slower than $\tau_{e,FT}$ have been subtracted.
$\Phi(t)$	Simulated end-to-end vector autocorrelation function of the star component
$G_{star}(t)$	Simulated total stress relaxation function of the star component in the star/linear blends.
$R(t, \tau_{d,lin}, \phi_{lin})$	Simulated stress relaxation function due to constraint release of the star component in the blends
$G_{star,zone1}(t)$	Stress relaxation function of the star component in zone 1, predicted as a product of $\mu_{sub}(t)$ and $R(t, \tau_{d,lin}, \phi_{lin})$
$G_{star,zone2}(t)$	Stress relaxation function of the star component in zone 2, described as the shifted relaxation in the fat tube.
$G_{star,zone2}^{sub}(t)$	Stress relaxation function of the star component in zone 2 from which fast Rouse relaxation modes have been subtracted
$G_{total}(t)$	Theoretical prediction of total relaxation function for the star component in the star/linear blends.

3.1. Introduction.

The tube theory, initially developed in 70-80s of last century (*de Gennes, 1971; Doi, Edwards, 1986*) and continuously refined since, plays a central role in our present understanding of the interrelation between the molecular structure of synthetic polymers and their viscoelastic properties as well as complex flow-behaviour. Mathematical models developed based on tube theory have now reached, in many cases, a quantitative level of prediction for the linear rheological characteristics of well-defined molecular structures with narrow distribution of molecular weights (*Likhtman, McLeish, 2002; Van Ruymbeke et al., 2005; Larson, 2001; Das et al., 2006*). However, understanding the viscoelastic properties of complex molecular architectures, such as those used in industrial applications, still raises many crucial questions arising from the coupling of molecular relaxation mechanisms, in particular, the effect on the relaxation dynamics of a given “probe” chain by relaxing surrounding chains. This effect is partly taken into account by the mechanism called Constraint Release (CR), which describes the motions of the tube surrounding the probe chain. These motions are due to the relaxation of the surrounding chains and lead to the loss and creation of new entanglements along the probe chain.

In order to gain deep understanding of this process, it is of prime importance to study the dynamics of well-defined model systems. In particular, bidisperse mixtures with well-separated molecular weights, such as binary blends of monodisperse linear chains (*Struglinski, Graessley, 1985; Wang et al., 2003; Watanabe et al., 2004; Park, Larson, 2004; Park, Larson, 2006*) and star/linear mixtures (*Struglinski, Graessley, 1988; Milner et al., 1998; Yoshida et al., 1991; Lee et al., 2005; Lee, Archer, 2002*), allow us to clearly point out the CR effect of a fast component on the motion of a slow relaxing component.

Understanding CR and its effect on the other relaxation mechanisms in such simplified systems should help us build a general understanding that could be later extended to more complex cases of polydisperse linear and branched polymer mixtures.

Competing theories based on two extreme approaches, i.e. tube dilation (*Doi et al., 1987; Lin, 1989; Ball, McLeish, 1989*) and tube rearrangement (*de Gennes, 1971; Graessley, 1982; Klein, 1978; Daoud, de Gennes, 1979; Viovy et al., 1991*), have been proposed for describing effects of CR on diffusion and stress relaxation of the slow relaxing chains in binary blends.

The first approach assumes that fast chains, as soon as they have reached their terminal time, act as a solvent for still unrelaxed chains, causing enlargement of the tube diameter. This allows the long (unrelaxed) chains to move in a dilated tube with a diffusion coefficient defined by chain friction only. This approach was applied to predict stress relaxation in polydisperse melts of linear chains (*Doi et al., 1987*), melts of stars (*Ball, McLeish, 1989*), and polymers with more complex branched topologies (*Van Ruymbeke, et al., 2006; Ahmadi et al., 2011; Snijkers et al., 2011*).

At the other extreme, the tube rearrangement approach assumes that a long chain is constrained by the so called skinny tube, which comprises entanglements with short *and* long chains, even *after* the relaxation of the short component. However, in addition to the chain motions in the skinny tube, the tube itself can move and explore the fat tube, which only includes entanglements with the other long chains and which constrains the skinny tube. Thus, the long chains are diffusing within the skinny tube while the skinny tube itself is exploring the fat tube by Rouse motion, or by tube reptation motion in the case long chains are mutually entangled. In this picture, the terminal time is determined by a competition between these relaxation mechanisms (*Viovy et al., 1991*). In the discussion below we will refer to these two CR pictures as Doi and Viovy theory, respectively.

In their original implementation, both of the above mentioned theories were tested for predicting the stress relaxation and longest relaxation time of binary linear blends. Numerous published experimental data on binary linear blends have shown dependence of the terminal time on the concentration of the long chains. This observation thus seems to favour the Doi picture. However, it must be mentioned that neither of these two theories accounts for CLF.

D. Read et al., in reference (*Read et al., 2012*), rather follow Viovy but include the influence of CLF. They argue that diffusive motion along skinny tube combined with

local CR motion provides enough freedom for CLF to take advantage of the fat tube. This improvement to the original Viovy theory is able to provide an explanation for the long chains concentration dependence of the terminal time.

In order to gain a fundamental insight in the complex interrelated relaxation mechanisms in bidisperse systems, it is useful to compare tube theory predictions with more detailed models. In this respect, the single chain stochastic model, referred to as the slip-spring model (*Likhtman, 2005*), is an interesting candidate since it combines a refined description of molecular dynamics with the ability to predict stress relaxation at long time-scales and allows an overlap with all tube relaxation processes. For maximal discrimination, we test the Doi and Viovy constraint release theories with the help of specially synthesized star/linear blends, characterized by a strong separation between terminal relaxation times of the pure components and a significant level of entanglements.

In order to understand CR in these blends and its contribution to stress relaxation, we first use the slip-spring model as benchmark to correctly predict the individual stress relaxation functions of the star and linear chains, first on their own, then, without any further parameter adjustment, for blends at all compositions. The agreement is found to be quantitative. Next, we reconstruct the stress relaxation function of star chains in the blends and study the relative contribution of each mechanism at different time scales. The slip-spring model allows us to objectively compare the effects of different CR assumptions on the relaxation of the star chains in the blends and assess their validity in different circumstances. Thus, in our study we simulate and analyse the relaxation of star chains, either in the monodisperse state or blended with linear chains, avoiding direct reliance on CR theories. This objective is in line with the works of Watanabe and co-workers (*Watanabe et al., 2000; Matsumiya, Watanabe, 2001; Watanabe et al., 2002; Watanabe, 2001*), who are using dielectric spectroscopy measurements of polymers with electrical dipoles aligned along the chain backbone in order to evaluate the time-dependence of the tube survival fraction, $\phi'(t)$, without relying on any model. By comparing the stress relaxation function, $\mu(t)$, obtained from viscoelastic measurements with $\phi'(t)$, the authors demonstrate that CR in monodisperse stars predicted by the tube dilation picture cannot be validated. In our chapter, the extra information is coming from slip-spring simulations, rather than from dielectric data.

In order to validate our approach, we prepare polymer mixtures of monodisperse star and linear chains, where both components are well entangled and their longest relaxation times are well separated, and measure their linear viscoelastic behaviour. This will allow us to validate the slip-spring simulation results as well as to further discuss the role of CR.

This chapter is arranged as follows: in the experimental section we describe details of the synthesis and molecular structure of the polybutadiene polymers used in this study. Details of the experimental measurements and data processing are also provided. In the theoretical section we describe a stochastic slip-spring model and its main parameters. In the results and discussion section, the model is validated by comparison with the experimental data and detailed analysis of the corresponding main relaxation zones (as defined in tube theory) is provided. In the conclusions section we summarize the key results of this study and propose possible steps towards generalizing the proposed approach to more complex cases.

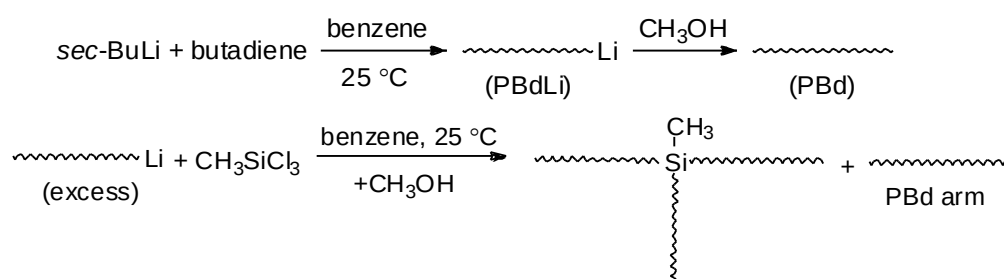
3.2. Experimental section.

3.2.1. Materials.

The synthesis of the linear ($M_w=7.5$ kg/mol) and 3-arm star ($M_w=76.0$ kg/mol) polybutadienes (PBds) was achieved by anionic polymerization high vacuum techniques. All manipulations were performed, under high vacuum, in home-made glass reactors provided with break-seals for the addition of reagents and constrictions for removal of products. The reactors were previously washed with a benzene solution of n-butyllithium (Aldrich) followed by rinsing with benzene, the polymerization solvent. The purification of the monomer butadiene (99%, Aldrich), the solvent benzene (99.8%, Aldrich), the terminating agent methanol (99.9%, Aldrich) and the linking agent $(\text{CH}_3)_3\text{SiCl}_3$ (99%, Aldrich) to the standards required for anionic polymerization, was performed according to well-established high-vacuum procedures⁴³. Sec-Butyllithium (sec-BuLi), the initiator, was prepared in *vacuo* from sec-butylchloride (99.9%; Aldrich) and a lithium dispersion (99%, high sodium, Aldrich).

SEC experiments were carried out at 25 °C using a Waters Model 510 pump and Waters Model 401 differential refractometer. A four μ -Styragel columns set with a continuous porosity range from 10^5 to 10^1 nanometre was used. Chloroform was the carrier solvent at a flow rate of 1 mL/min. Polybutadiene standards were used to calibrate the instrument. The microstructure of the dienic precursors was analyzed by ^1H -NMR (Bruker AC200) spectroscopy in CDCl_3 at 30 °C.

The general reactions for the synthesis of the linear and 3-arm star PBds are given in Scheme 3.1.



Scheme 3.1: General reactions for the synthesis of linear and 3-arm star PBds

The linear PBd was prepared by polymerization of butadiene with sec-Buli as initiator, in benzene at room temperature for 24 h, followed by neutralization with methanol. The SEC trace of the linear PBd is given in Figure 3.1.

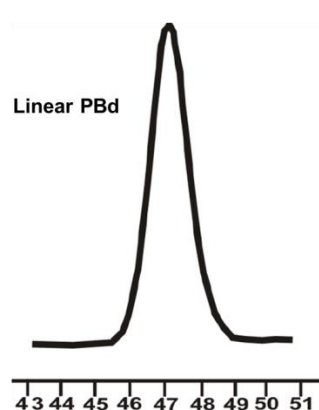


Figure 3.1: SEC trace of linear PBd

The 3-arm star PBd was prepared by reaction of excess (25%) living PBd with trichlorosilane under the same conditions for 5 days. Prior to the addition of the

coupling agent, a sample of the linear arm was removed and terminated with methanol for characterization. The SEC traces of the arm precursor and the fractionated 3-arm PBd are given in Figure 3.2

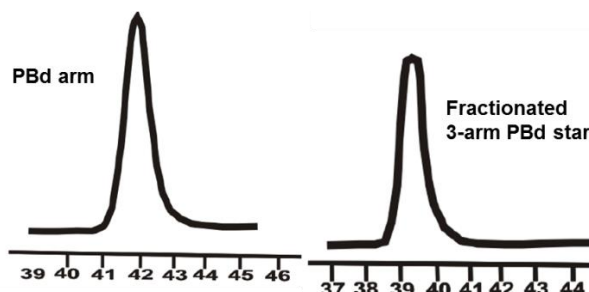


Figure 3.2: SEC traces of the arm and fractionated 3-arm star PBd

The star-branched polymer was separated from the unreacted excess of PBd by two consecutive fractional precipitations from a benzene-methanol mixture containing 4-methyl-2,6-di- tert-butylphenol as antioxidant (0.02%). The final samples were dried to constant weight and stored under vacuum in the dark.

The molecular weight characteristics of the samples, given in Table 3.1, show that the synthesized samples are well-defined with very low polydispersity index (PDI). The microstructure of all samples determined by $^1\text{H-NMR}$ in CDCl_3 was 10% 1,2 and 90% 1,4.

Table 3.1: Molecular characteristics of the linear and 3-arm star PBd

Sample	Linear PBd or Arm of the 3-Arm Star		3-Arm Star PBd	
	M_w (kg/mol)	PDI (M_w/M_n)	M_w (kg/mol)	PDI (M_w/M_n)
Linear PBd	7.5	1.02	-	-
Star PBd	24.5	1.02	76.0	1.04

* M_w and PDI were determined by SEC in THF at 30°C , calibrated with PBd standards

** Synthesis and SEC were carried out in the group of Prof. Nikos Hadjichristidis.

All blends analyzed in this chapter are fully miscible. They are prepared by mixing in an excess of toluene. After complete dissolution of the polymer by continuous stirring during 1-2 days the solvent is evaporated in a vacuum oven for at least 7-10 days until the sample has less than 0.1% of solvent left (as measured by weighing).

3.2.2. Measurements.

For all studied star/linear blends and monodisperse components rheological measurements have been conducted at small deformation to ensure linear response to applied excitation. An ARES (TA Instruments) rheometer was used in oscillatory shear mode with an 8 mm plate-plate fixture. For determining storage, G' , and loss modulus, G'' , throughout the whole relevant frequency range, time-temperature superposition was used (TTS). The values of storage and loss moduli in the angular frequency range from 0.01 to 100 rad/sec were measured at temperatures between 25°C and -75°C (in nitrogen environment) and shifted horizontally towards a reference temperature $T_{ref}=25^\circ\text{C}$ according to shift factors obtained using WLF equation with parameters $C_1=4.66$, $C_2=154.33\text{K}$. We account for influence of different T_g on WLF parameters by introducing iso-free-volume correction to the shift factors $\log_{10}a_T = -C_1(T - T_{ref} + C_{Tg}/M_w)/(T + C_2 + C_{Tg}/M_w)$, where $C_{Tg}/M_w = (T_g^{inf} - T_g)$ and $C_{Tg}=13$ is an empirical Flory-Fox parameter that is related to the free volume for a given polymer chemistry (Fox, Flory, 1950). For taking into account the change of density with temperature, the vertical shift factor,

$$b_T = \frac{\rho(T)T}{\rho(T_{ref})T_{ref}} = \frac{(\rho_0 - T.C_3.10^{-3})(T + 273.15)}{(\rho_0 - T_{ref}.C_3.10^{-3})(T_{ref} + 273.15)}$$

was introduced, with relevant values of the parameters for PBd $C_3=0.69$, and $\rho_0=\rho(T=0^\circ\text{C})=0.95\text{g/cm}^3$ (Ferry, 1988). The results are presented in Figure 3.4.

3.3. Theoretical section.

3.3.1 The slip-spring model parameters.

The slip-spring model is a single chain bead-spring model describing dynamics of entangled polymers developed by Likhtman (*Likhtman, 2005*). The main distinctive feature of the slip-spring model resides in the way interactions with surrounding chains are implemented. Effects from entanglements are modelled via slip-links along the chain. Each slip-link is connected with its anchored end via a virtual spring with parabolic potential (see Figure 3.3). All implementation details of this model for the case of binary blends are equivalent to the monodisperse case and can be found in the introduction chapter.

Before simulating stress relaxation of the blends, we first calibrate the material parameters used in the model by fitting predicted stress relaxation curves to the experimental data for the same monodisperse star and linear polymers as used in the blends. Next, we use the same values of the material parameters for simulating the viscoelastic properties of the blends at all concentrations. The number of chains for respective blend components are chosen according to the blend composition: $\phi_{star} = N_{c,star} \cdot N_{star} / (N_{c,star} \cdot N_{star} + N_{c,linear} \cdot N_{linear})$, where N_c and N are total number of (star or linear) chains and number of beads per (star or linear) chain, respectively. The minimum number of chains per one component is 10 and minimum number of simulations per one sample is 5.

For mapping the length-scale of the model to the experimental data, we fit the molecular weight represented by one bead as $M_0 = 0.38$ kg/mol for the star chains and $M_0 = 0.42$ kg/mol for the linear chains. The discrepancy is about 10% which is in the range of typical experimental error of SEC. For mapping the simulated time-scale and stress to the experiment, we multiply the dimensionless values by $\tau_0(T_{ref} = 25^\circ\text{C}) = 5.13 \cdot 10 \mu\text{s}$ and $G_0 = 7.5$ MPa, respectively.

A small discrepancy in G_0 and M_0 is observed with respect to PBd data presented in chapter 2. This can be explained by small differences between the microstructure of samples originating from different laboratories. However deeper analysis including verification of molecular weights would be required to confirm this.

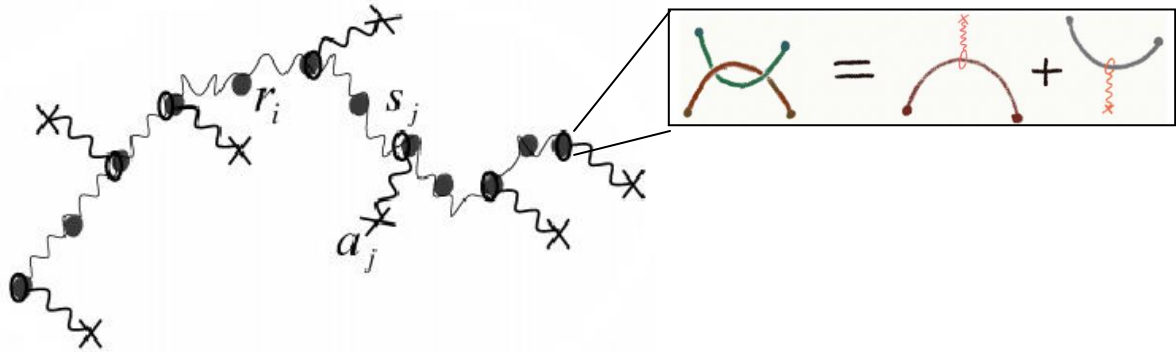


Figure 3.3: Schematic representation of a slip-spring model (adapted from references Likhtman, 2005; Likhtman, 2012).

3.4. Results and discussion.

3.4.1. Predicted viscoelastic data based on the slip-spring model.

In Figure 3.4, the storage and loss moduli predicted by the slip-spring model are compared to the experimental data for the different mixtures of symmetric star and linear chains. A very good agreement is obtained, whatever the proportion of star chains in the blend. In particular, the level of the second plateau, which appears at low frequency in the storage modulus, is well predicted despite the fact that, in the model, entanglements are always considered as binary events. This corresponds, in the tube picture, to a dynamic dilution exponent, d , equal to 1 (*Kelley, Bueche, 1961*). Furthermore, one can also observe a good match between experimental and predicted curves in the transition zone localized between the relaxation of the linear and star chains. Understanding the mechanisms dominating this zone is particularly interesting since most tube-based approaches fail to correctly capture the viscoelastic curves in this region, as they show too abrupt decrease of the storage modulus.

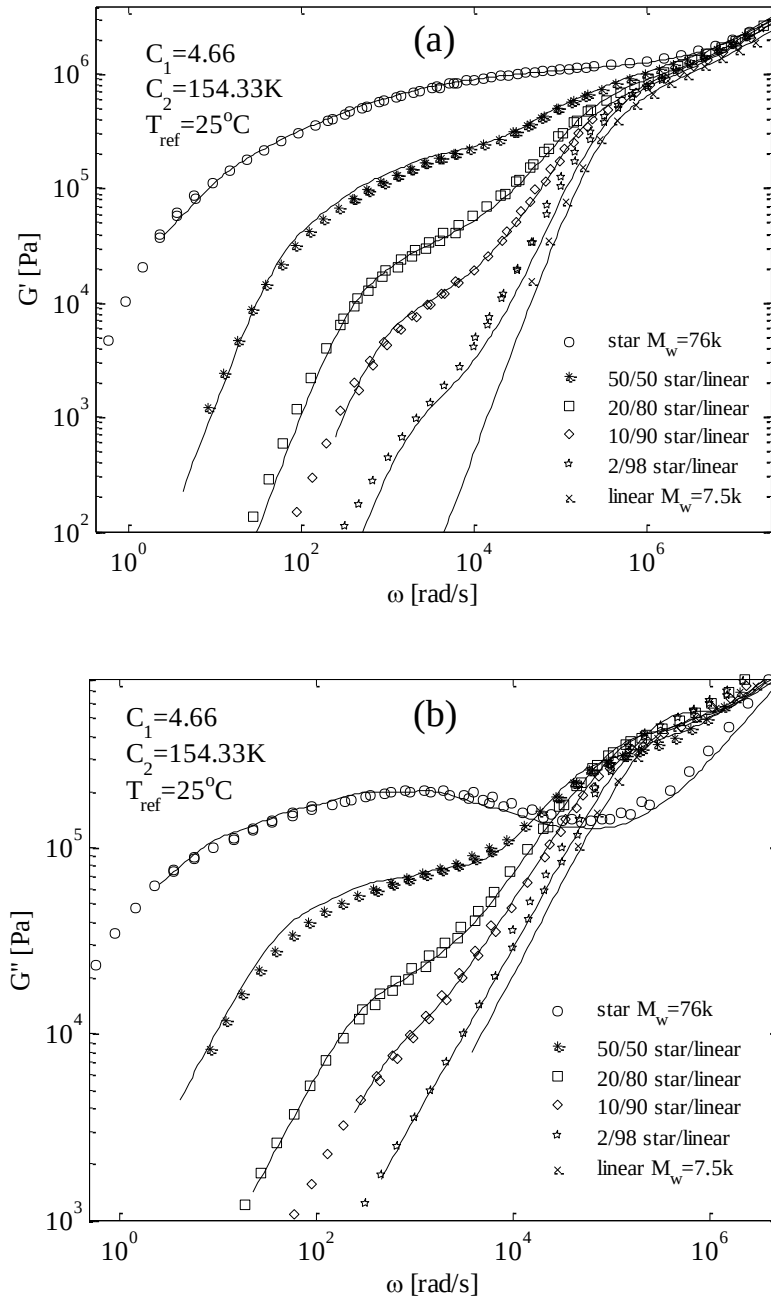


Figure 3.4: Simulation results of the slip-spring model superimposed with (a) the experimental dynamical storage and (b) loss moduli of binary polymer mixtures of symmetric star $M_w = 76\text{ kg/mol}$ and linear chains $M_w = 7.5\text{ kg/mol}$. Concentration of components varies from 100% of stars (upper curve) to 100% of linear chains (lower curve). Simulations results and experimental data are indicated with solid lines and markers, respectively.

To our knowledge, this is first time that predictions of the stress relaxation by the slip-spring model are presented for pure stars. Despite the fact that the focus of this chapter is not on pure stars, this is of great significance to validate the slip-spring model by

confronting its predictions with published data for ‘nearly monodisperse’ stars with different molecular weights (see also Chapter 2).

The slip-spring model can hence be used as a benchmark for predicting the viscoelastic behavior of star-linear blends. It is interesting to further analyze these results and map them to the relaxation mechanisms identified in tube theory (such as arm retraction and constraint release). Indeed, as discussed in the introduction, many questions are still open today in tube theory, such as, for example, how to account for the influence of the fast relaxing component (which are the linear chains in our case) on the relaxation of the slow component (the star chains in our case). Do these slow components relax in a skinny tube or a fat tube? Decomposing the slip-spring data into these different contributions should help us addressing these questions.

To do so, since the relaxation of the linear chains is relatively well understood, we focus only on the relaxation function of the star chains, $G_{star}(t)$. We propose to divide the stress relaxation function predicted by the slip-spring model into three main relaxation zones and to analyze the different relaxation mechanisms, which are active in each of them. As illustrated in figure 3.5 for the 20/80 star/linear blend, the three zones correspond to (i) the relaxation of the star molecules before reptation of the fast linear chains (zone 0), (ii) the relaxation of the star chains just after the reptation of these linear chains, when the star molecules are expected to relax by constraint release (zone 1), and (iii) the terminal relaxation of the slow relaxing star chains (zone 2).

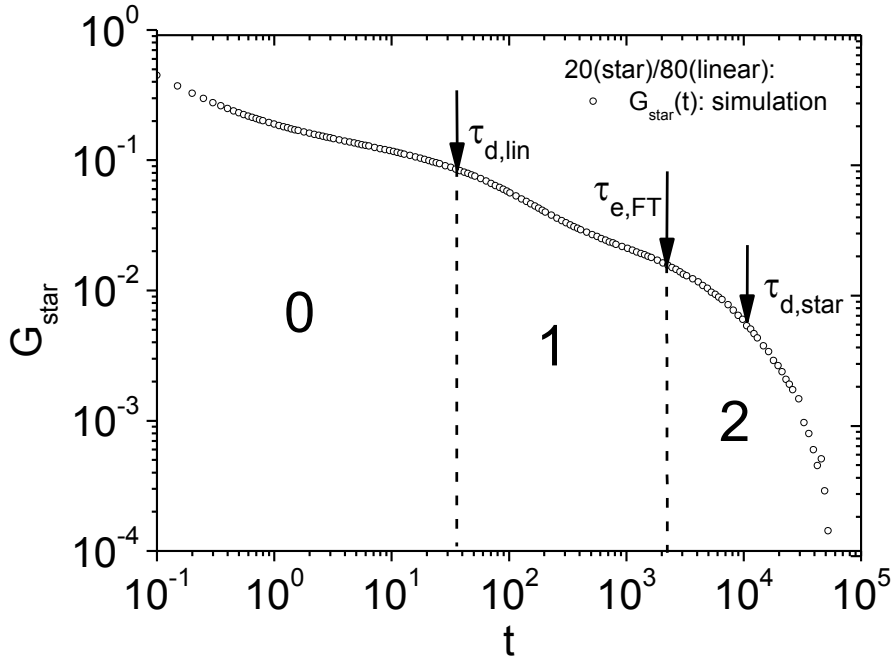


Figure 3.5: Slip-spring prediction of stress relaxation function of star components in the 20/80 star/linear blend. Arrows show reptation time of the linear components, $\tau_{d,lin}$, constraint release Rouse equilibration time along span of two star arms, $\tau_{e,FT}$, and terminal time of the star components, $\tau_{d,star}$. The arrows represent virtual separation on characteristic relaxation zones according to dominant relaxation mechanisms: 0. Fast Rouse relaxation modes at $t < \tau_{d,lin}$; 1. Rouse constraint release zone at $\tau_{d,lin} < t < \tau_{e,FT}$; 2. Fat tube zone at $t > \tau_{e,FT}$.

The relaxation mechanism in zone 0 is well defined: in this region, the chains mainly relax by fast Rouse and arm retraction relaxation modes. Since the times considered are shorter than the relaxation time of the fast relaxing linear chains, we can consider that all initial entanglements are still present and therefore the chains are still confined in their original skinny tube, which corresponds to the equilibrium molecular weight between entanglements, $M_{e,0}$.

Contrary to zone 0, the main relaxation mechanisms in zones 1 and 2 need to be further investigated. To do so, we propose to analyse these two zones separately with the help of slip-spring simulations for different binary star/linear blends presented in this work. In particular, by comparing simulation results obtained for actual star/linear blends to the predictions obtained by considering the same star chains, in same proportion, but relaxing either in a fixed network (which corresponds to a “skinny tube” approach) or in

a virtual solvent (which corresponds to a “fat tube” approach), we should be able to analyse the influence of the fast relaxing linear chains on the motion of the star molecules. In order to combine these two relaxation zones, we will then propose a mixing rule (see Section 3.4.4). In such a way, an analytical expression for the stress relaxation will be obtained, which can be used to describe the relaxation of the star component in star/linear blends of different concentrations at any time-scale.

3.4.2. Relaxation of the star chains in zone 1.

As mentioned in Section 3.4.1, zone 1 starts just after the reptation of the fast relaxing linear chains. We therefore expect to observe in this area the consequence of the relaxation of these linear chains on the motion of the star molecules. Indeed, the star/linear entanglements can now disappear and appear again somewhere else along the star arms, at the rhythm of the linear chains motions. This blinking feature of the star/linear entanglements allows the star chains to move, even if at this time scale, the star/star entanglements can still be considered as permanent.

The corresponding motions of the star chains are usually described by the constraint release Rouse process (CRR), which considers Rouse-like motions of the skinny tube (including both star/linear and star/star entanglements) in the fat tube, which only accounts for star/star entanglements. In order to determine this fat tube, all the star/star entanglements should be considered as permanent.

Thus, the longest time for equilibration of the skinny tube, with diameter a and number of tube segments n , can be determined from the Rouse reorientation time:

$$\tau_{CRR} = \frac{\zeta n^2 a^2}{3\pi^2 k_B T} \quad (3.1)$$

with ζ the effective friction coefficient per single bead. The effective friction coefficient can be calculated in the one dimensional case as:

$$\zeta = \frac{k_B T}{D} = \frac{2\tau_{CR} k_B T}{(A_{CR} \cdot b)^2}, \quad (3.2)$$

where k_B is the Boltzmann constant, τ_{CR} is the time for a single CR hop, b is the size of the

Kuhn segment, A_{CR} is an unknown prefactor and $(A_{CR}b)^2$ is a hop amplitude. We expect $A_{CR}b$ to be of order of the tube diameter. In section 3.4.5 we will determine the value of this prefactor.

We can now calculate the necessary time to fully equilibrate n skinny tube segments per single fat tube segment. If the fat tube does not exist due to a very low concentration of the star chains then $n=2Z_{arm}$, where Z_{arm} is a number of entanglements per star arm. On the contrary, for higher concentrations of stars, we have $n=Z_{arm}/(Z_{arm}\cdot\phi_{star})=1/\phi_{star}$. Now we can determine the time required for the full equilibration of a single fat tube segment including n skinny tube segments as (Read et al., 2012; Auhl et al., 2009; Klein, 1978; Daoud, de Gennes, 1979):

$$\tau_{e,FT} = \frac{2}{3\pi^2} \tau_{CR} n^2 \quad (3.3)$$

We assume that all entanglements between stars and linear chains are released at same frequency $1/\tau_{CR}$, where τ_{CR} is the longest relaxation time of the linear chains in the star/linear blends. This is realized in the simulation by removing each slip-spring at every step with a probability dt/τ_{CR} , where dt is the timestep of the simulation. In our theoretical calculations we use $\tau_{CR}=\tau_{d,lin}=60$ (in the model dimensionless time units) for every blend composition. This value is an average (with precision of $\pm 15\%$, depending on the fraction of the star chains in the blends) for the longest relaxation times obtained from simulated end-to-end autocorrelation functions of the linear chains.

In this expression we do not account for the difference between effective CR hop distance, $A_{CR}b$, and tube diameter, a .

The expression (equation 3.3) is valid only in the range $\tau_{d,lin} < \tau_{e,FT} < \tau_{d,star}$. It should also be noted that an increase of linear chains molecular weight will result in the overlap between star and linear chain relaxation spectra. Thus, our assumption of the molecular fractions participating in the CR motion being equivalent to the star and linear weight fractions may not be valid.

It must be noted that $\tau_{e,FT}$, which represents the longest CRR relaxation mode of a single fat tube segment and thus does not depend on the arm length, also defines the transition between zone 1 and zone 2 (see Figure 3.5).

On the other hand, although in zone 1, the relaxation of the star chains is dominated by CRR, their arms can also partially relax via a retraction mechanism. Since in this zone, equilibration of the chains in their fat tube is not complete, we assume that this retraction process is constrained by all entanglements, with other star chains as well as with linear molecules. This assumption, which will be validated below, is equivalent to considering the star chain motion within a skinny tube. On this basis, we can determine $\mu(t)$, the average fraction of initial tube segments which are still oriented at time t , as equal to the predicted stress relaxation function of the star chain in a permanent network. This is shown in Figure 3.6 by blue diamonds.

However, the CR process can also speed up the relaxation of the chain inside the skinny tube. To check this we compute the end-to-end vector autocorrelation function of the star chains, $\Phi(t)$, for every blend composition, and compare it with $\mu(t)$ computed from pure star simulations (see equation 3.4b and plotted by red diamonds in Figure 3.6).

Retraction and CRR processes must next be combined for determining the stress relaxation function of the star chains, $G_{star,zone1}(t)$, in a star/linear blend. To do so, we follow the idea of Graessley (Graessley, 1982), assuming independence between the chain motions inside the skinny tube and the Rouse-like dynamics of this skinny tube itself inside the fat tube:

$$G_{star,zone1}(t) = \mu(t)R(t, \tau_{d,lin}, \phi_{lin}).G_N^0 \quad (3.4a)$$

$$G_{star,zone1}(t) = \Phi(t)R(t, \tau_{d,lin}, \phi_{lin}).G_N^0, \quad (3.4b)$$

where $R(t, \tau_{d,lin}, \phi_{lin})$ is the skinny tube relaxation function of the star chains in the blends due to CR. This function is obtained by running a slip-spring simulation with all star/linear entanglements “blinking” with the same frequency, $1/\tau_{d,lin}$, and star/star entanglements having infinite relaxation time, τ_{inf} . Besides that, escape of chain ends from slip-links representing entanglements with other chains is prohibited. This condition is equivalent to neglecting contribution to relaxation by escape of the chain from the tube by arm retraction or reptation. The so obtained function R includes combined relaxation contributions from CR motion of the skinny tube and Rouse stress equilibration of the chain. Moreover we prohibit slip of entanglements along the backbone, thus we do not account in $R(t, \tau_{d,lin}, \phi_{lin})$ for the longitudinal Rouse relaxation modes, which are not active.

For calculation of $R(t, \tau_{d,lin}, \phi_{lin})$, all Rouse relaxation modes faster than entanglement equilibration time, τ_e , have been subtracted in order to avoid double counting of these modes with those accounted for in $\mu(t)$ or $\Phi(t)$ in zone 0. Details of the mode subtraction procedure will be discussed in section 3.4.4. For simplicity, in the following discussion we will refer to this newly introduced function, $R(t, \tau_{d,lin}, \phi_{lin})$, as the tube relaxation function. The function $R(t, \tau_{d,lin}, \phi_{lin})$ is normalized such that $R(0)=1$.

In equations 3.4a and 3.4b, we introduce a prefactor G_N^0 , which ensures that in the absence of relaxation $\mu=1$, $R=1$ and no longitudinal relaxation the resulting stress level is equal to the plateau modulus.

In the Appendix A we compare the time dependence of the newly proposed function $R(t, \tau_{d,lin}, \phi_{lin})$ with another function traditionally used for modeling tube relaxation in bidisperse blends. This function is obtained by simulating the Rouse dynamics of an unentangled star chain containing “slow” and “fast” beads (*Rubinstein et al., 1987*).

Once all necessary parameters have been defined, the relaxation function $G_{star,zone1}(t)$ of the star component in the different star/linear blends can now be determined, based on equations 3.4a or 3.4b. Comparison between these curves and the relaxation function predicted by direct simulation of the blend relaxation (as presented in Figure 3.2) is shown in Figure 3.6:

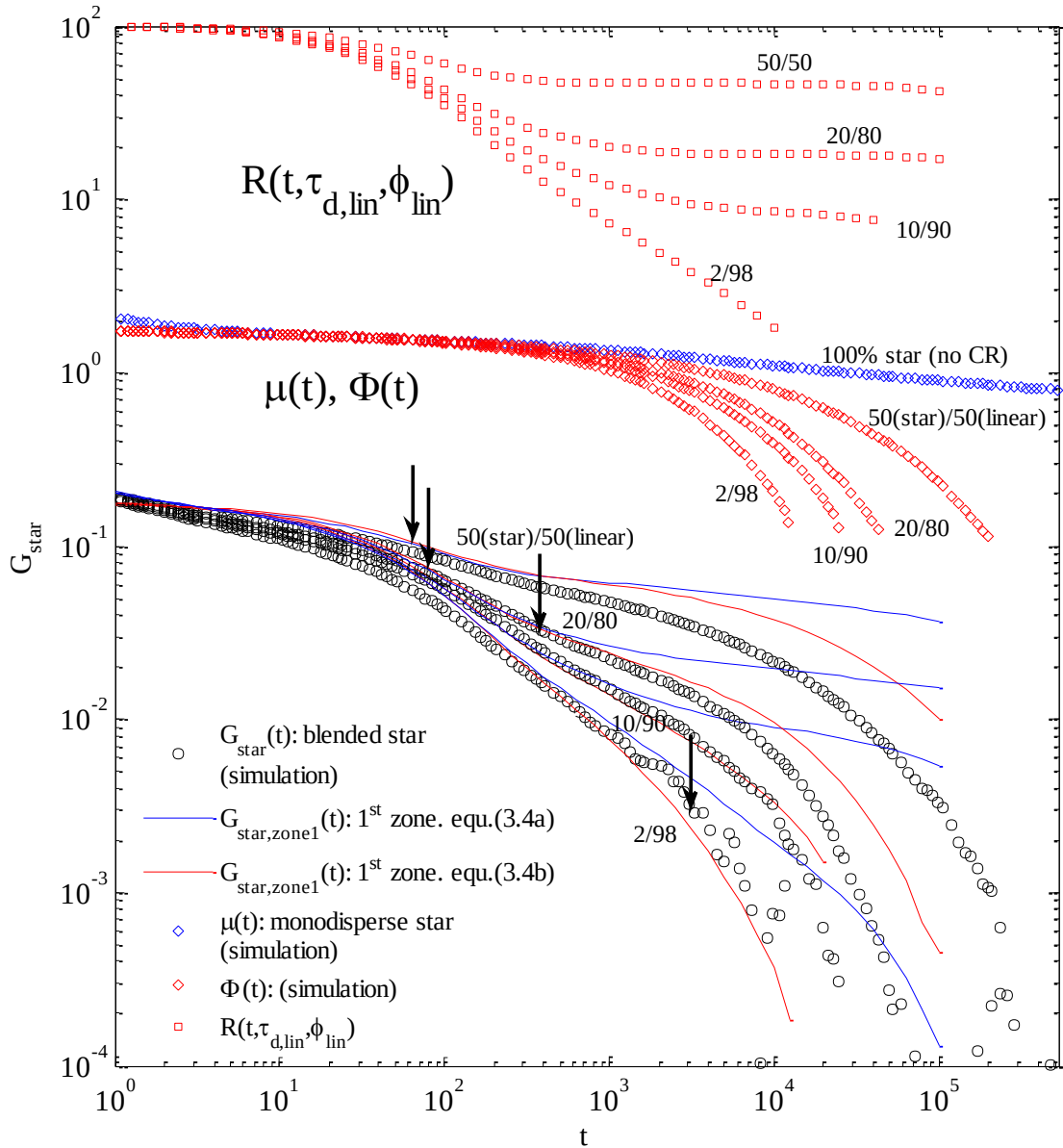


Figure 3.6: Simulation results: In the lower part of the plot we show comparison between the star stress relaxation function obtained by simulating the motion of the full blends (circles), and the stress relaxation function obtained based on equations 3.4(a) - blue solid curves and 3.4(b) – red solid curves. The relaxation function of the star component in the skinny tube, $\mu(t)$, obtained by running slip-spring simulations of the monodisperse star with deactivated CR is shown (blue diamonds) in the central part of the plot. The end-to-end vector autocorrelation functions of the star component at every blend composition, $\Phi(t)$, are shown by red diamonds. Red squares in the upper part of the plot show tube relaxation function, $R(t, \tau_{d, \text{lin}}, \phi_{\text{lin}})$, dominated by balance between CR skinny tube motion and stress equilibration of the chain by Rouse process. Different ratios of star/linear components from 50/50 to 2/98 have been considered. Solid arrows represent transition between zone 1 and zone 2 (equation 3.3). $\Phi(t)$, $\mu(t)$ and $R(t, \tau_{d, \text{lin}}, \phi_{\text{lin}})$ curves were freely vertically shifted for better visual representation.

All predictions by equations 3.4a and 3.4b, shown by solid red and blue curves in the lower part of Figure 3.6 demonstrate systematic deviations at $t = \tau_{d, \text{lin}}$ (shown with a solid

arrow for a 50(star)/50(linear) blend). This can be attributed to the simplified relaxation spectrum of the linear chains used in the calculations. In our calculations we only account for their longest relaxation time, whereas moderately entangled linear chains have much broader distribution of possible relaxation times, including chain fluctuations and reptation modes. However, we allow this simplification as the major part of the chain is still relaxing by reptation.

We find that in zone 1, limited by solid arrows, the agreement between both methods and full simulation is very good for the blends containing at least 10 wt% of star chains. That means that in this region and for $\phi_{star}=10\text{wt.}\%$ the star relaxation is not influenced by CR from the linear chains.

By contrast, for the blend with the lowest star concentration (2wt.%), the CR contribution from linear chains does contribute significantly to the star relaxation. This is validated by the fact that theoretical predictions shown by solid red and blue curves deviate from each other in the time-scale limited by the arrows. Thus for best fitting of the total stress relaxation function, $G_{star}(t)$ for the lowest star concentration we have to use equation 4b, with concentration dependent star relaxation function, $\Phi(t)$. At this blend composition, the concentration of star chains is very low: $N_{arm}\phi_{star}/N_e < 1$. Therefore, the fat tube does not exist and the star chain relaxation is terminated by CRR motion in zone 1. This blend is the exception from the general rule which we can draw for the other blend compositions. Namely, before the full equilibration of the star chains by CRR ($t < \tau_{e,FT}$), the retraction mechanism of the star chains takes place in the skinny tube, which, itself, is moving in a fat tube, similarly to a Rouse chain containing beads with different lifetimes. Further, these two relaxation processes are independent.

We should also note that the solid arrows showing the CR equilibration time of the skinny tube inside the fat tube segment ($\tau_{e,FT}$, end of zone 1) often do not coincide with the onset of deviations between $G_{star,zone1}(t)$ (solid lines in Figure 3.6 corresponding to equation 4) and $G_{star}(t)$ (slip-spring predictions shown by black circles). That could be

ascribed to the existence of some transition zone which is still strongly affected by the linear chains even after the fat tube has already been explored.

At longer times, the predictions of equations 3.4(a,b), strongly deviate from the results obtained by the simulation of the star/linear blends at all compositions except for the blend with 2wt% of star chains. As discussed in the next section, this is most probably due to the fact that arm retraction does not happen in the skinny tube at that time-scale.

3.4.3. Relaxation of the star chains in zone 2.

In this section, we discuss relaxation of the star chains at times larger than fat tube CR-equilibration time. In this time zone, the star chains are assumed to move in the fat tube created by the star/star entanglements. As already mentioned, two main ideas can be followed: the first one (*Doi et al., 1987*) considers that the linear chains act as a solvent. The star/linear entanglements can then simply be ignored and the effective molecular weight between two entanglements is considered as equal to $M_{e,0}/\phi_{star}^d$, where $d=1$ (*Kelley, Bueche, 1961*). On the other hand, according to the second idea (*Viomy et al., 1991*), the star chains stay constrained by the skinny tube even after its complete CR-equilibration in the fat tube.

As shown in Figure 3.6 (solid lines), if we consider that the arm retraction of star chains happens in the skinny tube, the predicted star relaxation function is far too slow compared to the reference results of the slip-spring simulations. Since we consider that in this time zone, arm retraction is the only possible relaxation process (CR-equilibration has reached the limit of the fat tube), this picture cannot be validated here.

Next, we test the idea proposed by Doi, according to which the arm retraction in zone 2 takes place in the fat tube. To do so, the results obtained by simulating the motions of the star/linear blends are compared to the results obtained by simulating the relaxation of truly diluted monodisperse star chains containing the same average number of star/star entanglements as the star chains in the star/linear blend, i.e.

$M_{e, \text{diluted star}} = M_{e,0}/\phi_{star}$. According to Doi's picture, these two curves should be identical in time zone 2.

In Figure 3.7, we plot the pure contribution from star/star entanglements to the total stress relaxation function, $G_{star,zone2}^{sub}(t)$, after having subtracted the fast Rouse modes of the “diluted” star as in zone 1. Further details about subtracting the fast Rouse modes will be discussed in section 3.4.4. While the *shape* of the relaxation function of the diluted monodisperse star chains correctly fits the star relaxation function, a quantitative overlap between these curves, which is shown in Figure 3.7, is only obtained after a horizontal shift of this diluted star data towards longer times. These shift factors, which are discussed below, are due to the fact that in the star/linear blends the motions of the star chains are directly depending on the ‘blinking’ motions of the linear chains and thus on their reptation time. Therefore, the probe chain cannot move freely inside the fat tube in the same way as it moves in a true solvent. Instead, the chain sometimes has to wait for the fast entanglements to disappear. In other words, the effective friction inside the fat tube will depend on the reptation time of short linear chains. Understanding the value of these shift factors is thus of prime importance, in order to get a quantitative picture of the relaxation mechanisms.

These shift factors, $X(\phi_{star})$, have been determined from the condition that the shifted relaxation functions of the “diluted” monodisperse star chains, $G_{star,zone2}(t)$, match well with the simulation results of the star/linear blends:

$$G_{star,zone2}(t) = G_{star} \left(t \cdot X(\phi_{star}), \frac{M_e}{\phi_{star}} \right). \quad (3.6)$$

They will be analyzed in details in Section 3.4.5.

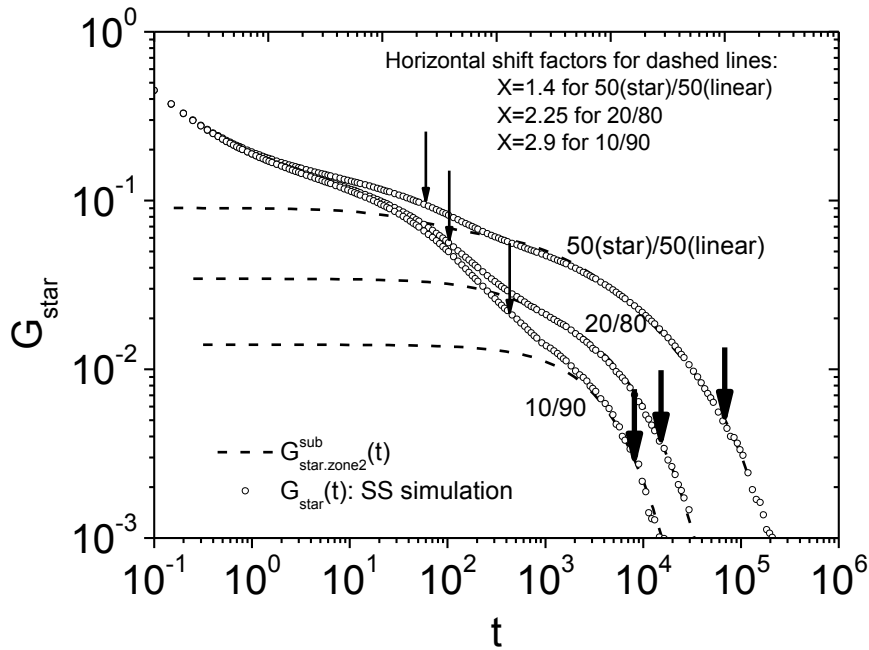


Figure 3.7: Comparison between the simulated star relaxation function in the star/linear blends and horizontally shifted relaxation function of “diluted” monodisperse star containing the same average number of star/star entanglements and having subtracted fast Rouse relaxation modes, $G_{star,zone2}^{sub}(t)$. The results are shown for all studied star/linear compositions, having fat tube zone (from 50(star)/50(linear) to 10/90). Thin arrows highlight the transition between zone 1 and zone 2 (see Figure 3.5). The thick arrows highlight the longest relaxation time of the star component.

Based on Figure 3.7, we observe that a good agreement between the simulation results for the star/linear blends and for the “diluted” monodisperse star chains does not start at the same time for different blends, and seems to depend on their composition.

It must also be noted that according to Doi, zone 2 must be completely dominated by the relaxation of the star component in the dilated tube. Therefore, in order to validate this picture, the gap between thin and thick arrows in Figure 3.7, corresponding to the time scale of zone 2, should completely overlap with the dashed lines representing the star component contribution, which is not the case. Besides, Doi’s original picture does not allow for a horizontal shift of the relaxation curves and hence clearly overestimates the dilation effect on the longest relaxation time of the star, especially at low star concentration.

On the other hand, we can observe that, at high star concentrations, a good overlap is obtained over a wide time window because the actual star relaxation function, $G_{star}(t)$, is completely dominated by the slow modes correctly described by the tube dilation approximation, $G_{star,zone2}(t)$, when allowing for a suitable time-shift.

By contrast, at lower values of ϕ_{star} , complete match can be observed only at much longer times near the terminal zone.

By comparing Figure 3.6 and Figure 3.7 we can conclude that the effect of the linear chains is dominating star relaxation well beyond zone 1, whereas the tube dilation picture can be validated for blends with star chains concentration of at least 10wt.%, if one accounts for the shift factors.

3.4.4. Mixing rule for first and second relaxation zones.

In this section, we propose a mixing rule, in order to merge the relaxation behaviour observed in zone 1 (Section 3.4.2) and zone 2 (Section 3.4.3) into a single equation, assuming that we know the shift factors $X(\phi_{star})$, which will be discussed in Section 3.4.5.

As concluded in section 3.4.3, the relaxation in zone 2 of a star probe chain in a star/linear blend can be modelled by the shifted relaxation function of the equivalent diluted monodisperse star component, $G_{star,zone2}(t)$. In order to be able to also use this relaxation function in zone 1, it is necessary to remove the contribution of the fast Rouse relaxation modes.

First, we fit $G_{star,zone2}(t)$ using a Prony series for the shear relaxation modulus

$$G_{star,zone2}(t) = \sum_{i=1}^N G_i \exp(-t / \tau_i) \text{ where } G_i \text{ and } \tau_i \text{ are moduli and relaxation times of the}$$

Maxwell modes. All those modes which are faster than entanglement Rouse equilibration time, defined as $\tau_e = \tau_{e,0} / \phi_{star}^2$ where $\tau_{e,0}$ is the entanglement equilibration time in undiluted case, are next subtracted. Obtained in this way, $G_{star,zone2}^{sub}(t)$ for every blend composition is constant at time scale of $t < \tau_e$, as shown in Figure 3.7.

As discussed in sections 3.4.2 and 3.4.3, relaxation zones 1 and 2 can be modelled by considering only the corresponding dominant relaxation mechanism. It does not imply that relaxations by other involved mechanisms are frozen, however their effect is hidden by the dominant relaxation. Here, we would like to consider an expression for the total stress relaxation function, $G_{total}(t)$, which accounts for all these relaxation mechanisms, even if they are negligible in certain time zones. This will ensure the validity of $G_{total}(t)$ at every time. To this end, since in the case considered here the relaxation of the linear chains and of the star chains are well-separated, we use a multiplicative mixing rule, which is based on the assumption of independence between relaxation mechanisms dominating zones 1 and 2 (Rubinstein *et al.*, 1987; Graessley, 1982):

$$G_{total}(t, \phi_{star}) = G_N^0 \cdot R(t, \tau_{d,lin}, \phi_{lin}) \mu_{sub}(t) \cdot \frac{G_{star,zone2}^{sub}(t)}{G_{star,zone2}^{sub}(0)} \quad (3.8)$$

In this expression, $R(t, \tau_{d,lin}, \phi_{lin})$ is the skinny tube relaxation function defined in Section 3.4.2, including the subtraction of fast Rouse modes. The term $\mu_{sub}(t)$ represents the orientation survival function of the probe chain obtained by slip-spring simulations and plotted as blue diamonds in Figure 3.6, from which modes slower than $\tau_{e,FT}$ have been subtracted. The product $R(t, \tau_{d,lin}, \phi_{lin}) \cdot \mu_{sub}(t)$ hence represents the dominating relaxation in zone 1. $G_{star,zone2}^{sub}(t)$ is the stress relaxation function of a diluted monodisperse star after subtraction of the fast Rouse modes and accounting for time-shift factor, $X(\phi_{star})$ described in Section 3.4.5. It thus represents the dominating relaxation in zone 2. The prefactor $1/G_{star,zone2}^{sub}(0) \sim 1/\phi_{star}^2$ is introduced for normalizing contributions from both relaxation mechanisms. Indeed, in zone 1, $R(t, \tau_{d,lin}, \phi_{lin})$ is dominating G_{total} , and $G_{star,zone2}^{sub}(t) \sim \phi_{star}^2$ is constant whereas, in zone 2, $G_{star,zone2}^{sub}(t)$ is dominating the total relaxation function and $R(t, \tau_{d,lin}, \phi_{lin}) \mu_{sub}(t)$ is constant $\sim \phi_{star}^2$.

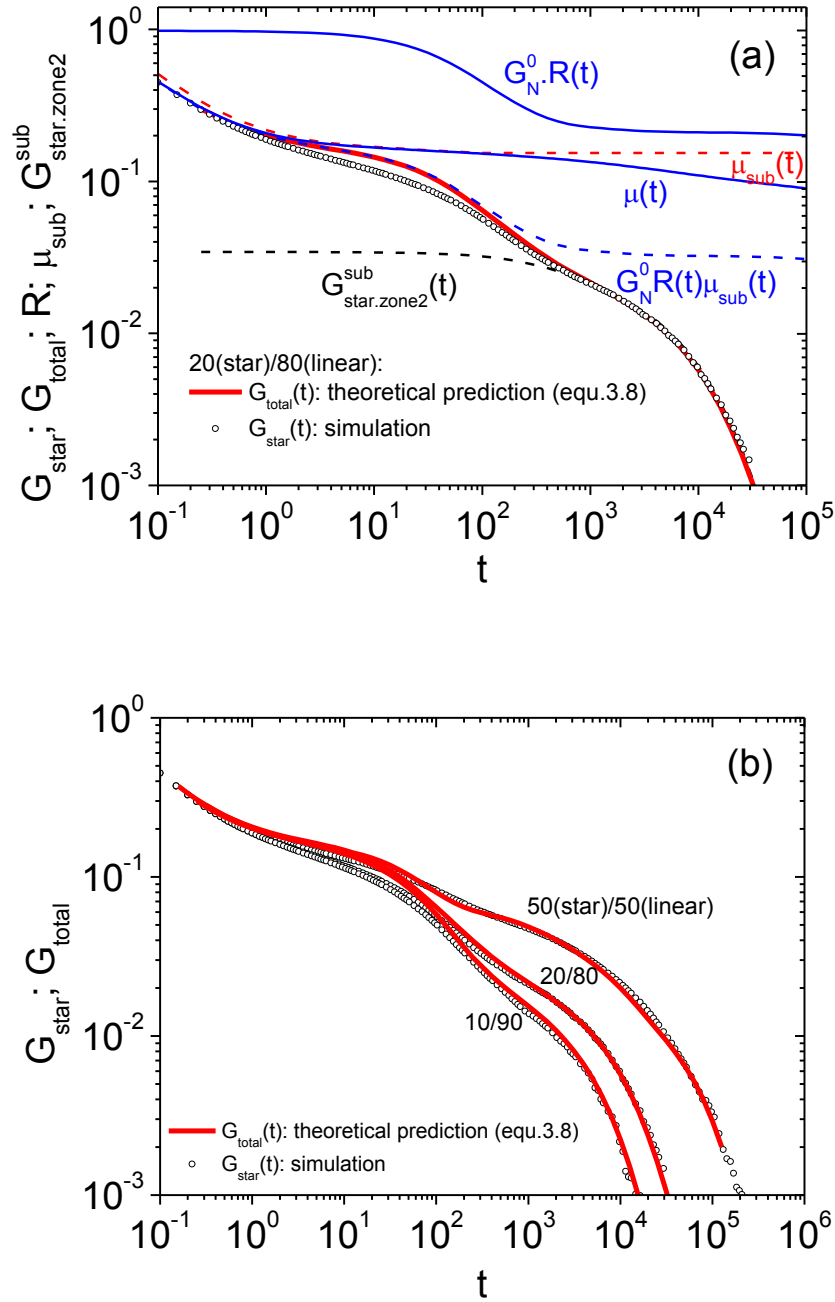


Figure 3.8: (a): Simulation results of the star relaxation in single blend composition with 20wt% of the star chains; all components of equation 3.8 including total star relaxation function $G_{\text{total}}(t)$ (red solid line) superimposed with the corresponding simulation data (black circles). (b): Simulation results superimposed with the theoretical predictions. Total relaxation function of star component in the star/linear blend determined by merging two characteristic relaxation zones using equation 3.8 (red solid lines), superimposed with prediction by slip-spring model (black circles). Different ratios of star/linear components from 50/50 to 10/98 are presented from up to down.

As shown in Figure 3.8, a good agreement is obtained between the simulation results for the star/linear blends and the predictions based on the mixing rule (equation 3.8). The stress relaxation function of the star component in blend 2/98 is not shown Figure 3.8, because it is completely predicted by equation (3.4b), describing stress relaxation in zone 1 (see Figure 3.6). However, some discrepancies can be observed in the proximity of the plateau at early times. This can be attributed to the neglected distribution of disentanglement times of the linear chains. For simplicity we assume that all linear chains in the blend disentangle at their reptation time.

We therefore have all necessary ingredients to predict the star relaxation in star/linear blends from separate simulations apart from the time shift factors $X(\phi_{star})$, which we compute in the next section.

3.4.5. Effective friction in the fat tube.

From comparison of the terminal zone relaxation with the simulation of pure diluted stars (Figure 3.7) we have seen that the distribution of relaxation modes (shape of the relaxation) agrees very well, but the full simulation results are shifted towards longer times by a significant factor. This can be explained by noticing that the effective friction of the chain inside the fat tube is larger than the bare friction of the free chain. The reason is quite obvious: the chain can not move freely in the fat tube because it is still constrained by the skinny tube, or by the entanglements with the short linear chains. Ignoring these fast entanglements, as was done in our diluted simulations, will clearly lead to faster relaxation. This is the effect which was overlooked in the tube dilution theory of Ball-McLeish (*Ball, McLeish, 1989*) and Milner-McLeish (*Milner, McLeish, 1997*), who assumed that the friction in the fat tube is the same as the friction of the bare chain.

The quantitative theory to predict effective friction in the fat tube was recently developed by D.J.Read et. al. (*Read et al., 2012*). It considers two main modes of motion of the chain inside the fat tube. The first is straightforward reptation in the skinny tube, which obviously results in the chain escaping from the fat tube as well. The second mode is reptation in the fat tube due to CR of the short chains.

The friction associated with the first mode ζ_{eff} is independent of CR rate, and the friction associated with the second one is directly proportional to CR rate. One can assume that these two contributions are independent, and therefore the total friction in the fat tube is given by

$$\frac{1}{\zeta_{tot}} = \frac{1}{\zeta_{CR}^{tot}} + \frac{1}{\zeta_{eff}} \quad (3.9)$$

For clarity, for all mechanisms, we shall compute the total friction of the whole chain, i.e. the centre of mass friction. Since all relaxation mechanisms discussed here are local, the centre of mass friction is $N\zeta^{mon}$, where ζ^{mon} is the corresponding friction per monomer.

According to the pure reptation theory of Doi and Edwards, the reptation time is given by

$$\tau_d = \frac{L^2 \zeta_0^{cm}}{\pi^2 k_B T} ,$$

where ζ_0^{cm} is the friction coefficient of the whole chain in the skinny tube. If the only relaxation mode in a fat tube is reptation in the skinny tube, the reptation times in both tubes must be the same. This has to be the case because at the moment the chain escapes from the skinny tube, it escapes from the fat tube as well. By equating these two reptation times, we get

$$\tau_d^{fat} = \tau_d^{skinny} \rightarrow L_{fat}^2 \zeta_{eff} = L_{skinny}^2 \zeta_0^{cm} .$$

We know that the fat tube is shorter than the skinny tube, therefore the friction in the fat tube must be larger to produce the same reptation time. More precisely, since the tube length is equal to

$$L = \frac{Nb^2}{a} = \frac{Nb}{\sqrt{N_e}} ,$$

and N_e changes with concentration as $N_e = N_e^{melt}/\phi_{star}$, the ratio of the skinny and fat tube lengths squared must be

$$\left(\frac{L_{fat}}{L_{thin}} \right)^2 = \phi_{star} ,$$

which means that

$$\zeta_{eff} = \frac{\zeta_0^{cm}}{\phi_{star}} \quad (3.10)$$

This is a central result of ref. (Auhl *et al.*, 2009), which is also manifested by the fact that the corresponding Rouse time in the fat tube is larger than the bare Rouse time by a factor of $1/\phi_{star}$.

We plot the predictions of equation 3.10 in Figure 3.10 (dashed line) and compare them with the shift factors we determined empirically (circles and squares). According to equation 3.9, our simple equation 3.10 is an upper estimate for the friction.

Indeed, the empirical shift factors lie below this simple prediction, because CR reduces the total friction. To estimate this friction ζ_{CR} independently, we run separate simulations of the star Rouse chain with slip-springs which do not slip along the chain (and thus never escape from the tube), but appear and disappear with constant rate given by $1/\tau_{CR}$ (this simulation model is described in section 3.4.2). Therefore the chain dynamics at long timescales is solely determined by slip-springs and their creation/destruction rate. We next use two methods to extract an effective friction of the chain centre of mass due to CR. The first is to measure the centre of mass mean square displacement of the chain at long times. We get

$$\zeta_{CR}^{MSD} = \frac{k_B T}{\lim_{t \rightarrow \infty} g_3(t) / (6t)}, \quad (3.11)$$

where $g_3(t) = \langle (R_{cm}(\tau+t) - R_{cm}(\tau))^2 \rangle$ is the centre of mass mean square displacement.

Another method is to assume that at long length scales the CR dynamics obeys the Rouse theory, and therefore CR friction can be extracted from the terminal time of the end-to-end relaxation τ_ϕ using Rouse expression for a star polymer

$$\tau_\phi = \frac{(2N_{arm})^2 \zeta_{mon} b^2}{3\pi^2 k_B T},$$

where $\zeta_{mon} = \zeta_{CR}^\phi / (N_{arm} \cdot M)$ is the friction per monomer, M is the number of star arms and N_{arm} is the star arm length.

This gives

$$\zeta_{CR}^{\Phi} = \tau_{\Phi} \frac{3\pi^2 k_B T}{4N_{arm} b^2} M \quad (3.12)$$

We perform simulations of this model for the 3-arm star polymer with $N=75$ for a wide range of constraint release times τ_{CR} , and extract CR friction from equations 3.11, 3.12. The results are plotted in Figure 3.9.

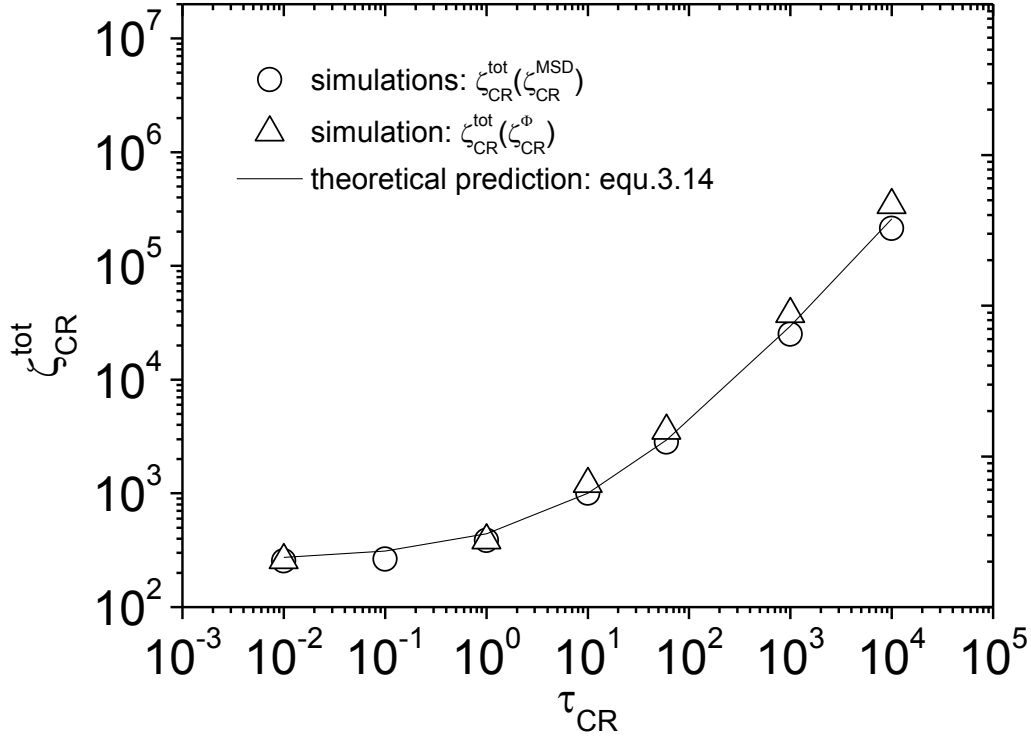


Figure 3.9: Total CR friction coefficient of star chain, ζ_{CR}^{tot} , obtained by simulating rouse chain with slip-springs not allowed to slip along the chain but appearing and disappearing with constant frequency $1/\tau_{CR}$. *Triangles:* ζ_{CR}^{tot} obtained from measuring mean square displacement of the center of mass of the star chain at long time scales. *Circles:* ζ_{CR}^{tot} extracted from the terminal times of the end-to-end vector relaxation. Solid line: theoretical prediction by equation 3.14 with free parameter $A_{CR}=4.3$.

Two limiting cases are apparent. In the limit of $\tau_{CR} \rightarrow 0$, the friction obviously reduces to the bare friction of the chain, $\zeta_{CR}^{tot} \rightarrow \zeta_0^{cm}$. In the opposite limit $\tau_{CR} \rightarrow \infty$, it is clear that the effective friction must become directly proportional to τ_{CR} . A simple model of a particle hopping a constant distance d at every time interval τ_{hop} leads to the following effective friction

$$\zeta_{hop} = \frac{2\tau_{hop}k_B T}{d^2} \quad (3.13)$$

By analogy, we expect

$$\frac{\zeta_{CR}}{N_{arm}M} = \frac{2\tau_{CR}k_B T}{(A_{CR}b)^2} \text{ as } \tau_{CR} \rightarrow \infty$$

where A_{CR} is an unknown prefactor with a clear physical meaning: $A_{CR}b$ is an effective monomer hopping distance during a single CR event. We expect $A_{CR}b$ to be of order of tube diameter. Ref. (*Read et al., 2012*) assumes that for intermediate values of τ_{CR} , the effective friction is given by the sum of two limiting terms. We find that our results can not be fitted with this assumption, but an expression

$$\zeta_{CR}^{tot} = \left(\sqrt{\zeta_0^{cm}} + \sqrt{\frac{2\tau_{CR}k_B T N_{arm} M}{(A_{CR}b)^2}} \right)^2 \quad (3.14)$$

fits the simulation results very well (solid lines in Figure 3.9) with $A_{CR}=4.3$. We also see that the two methods of extracting effective friction give almost identical results within the error bars, which validates our assumption that CR dynamics at very long timescales, of order of $\tau_{CR}Z^2$, is similar to Rouse dynamics. Note however that simulations presented in the Appendix A, show that Rouse predictions can not fit the whole stress relaxation curve, because the dynamics at small timescales of order of CR time τ_{CR} deviates from Rouse predictions. If one overlaps small timescales, the functions diverge at the terminal time.

Finally, we need to combine equations (3.14) and (3.10) in the case when only a fraction $1-\phi_{star}$ of entanglements is blinking with characteristic time τ_{CR} , and the other entanglements are permanent. Ref. (*Read et al., 2012*) suggests that in the limit of small τ_{CR} the total chain friction must always remain ζ_0^{cm} independent on $1/\phi_{star}$, whereas, in contrast to equation (3.14), ζ_{CR}^{tot} becomes dependent on mobile fraction of entanglements through additional chain friction. The following equation satisfies all these requirements:

$$\frac{1}{\left(\sqrt{\zeta_{CR}} + \sqrt{\zeta_+}\right)^2} + \frac{1}{\zeta_{eff}} = \frac{1}{\zeta_0^{cm}},$$

where $\zeta_{CR}^{tot} = \left(\sqrt{\zeta_+} + \sqrt{\zeta_{CR}} \right)^2$ with ζ_{CR} being infinitesimally small (at $\tau_{CR} \rightarrow 0$) and ζ_+ is the additional friction contribution from the chain in the case when only fraction $1 - \phi_{star}$ of entanglements is involved into CR tube motion.

We can thus compute this additional friction contribution as

$$\zeta_+ = \frac{\zeta_0^{cm}}{1 - \phi_{star}} \quad (3.15)$$

The time-shift factor, $X(\phi_{star})$, between the stress relaxation function of the truly diluted monodisperse star, $G_{star,zone2}(t)$ (equation 3.6), and that of the star-linear blend, $G_{star}(t)$, can now be obtained by calculating the ratio of corresponding total friction coefficients using components derived in equations 3.9, 3.10 and 3.15:

$$X = \frac{(\zeta_{tot})}{(\zeta_0^{cm})} = \left(\phi_{star} + \frac{1}{\frac{\zeta_{CR}}{\zeta_0^{cm}} + \frac{1}{1 - \phi_{star}}} \right)^{-1}, \quad (3.16)$$

where ζ_{tot} is the total effective friction coefficient in the fat tube and ζ_0^{cm} is a total friction coefficient of the chain in the skinny tube.

We now plot the predictions of equations (3.16) in Figure 3.10 (solid line) and compare them with the empirical shift factors obtained earlier (squares in Figure 3.10). We find that our estimation of the ζ_{CR} predicts higher friction when measured directly by the shift factors. The empirical results however can be fitted very well by eq.3.16 if A_{CR} is adjusted to $A_{CR}=11$. There can be at least two reasons for this deviation. First, the friction coefficients ζ_{CR}^{MSD} and ζ_{CR}^ϕ were measured for three-dimensional motion in free space, with all constraints blinking. In the diluted star simulation, only a fraction of slip-links were blinking, and the friction we are interested in is the friction associated with one-dimensional motion along the fat tube. These might easily be different, as for example shown in ref. (Likhtman et al., 2013).

The second reason is that the fat tube theory (Read et al., 2012) presented here is slightly different from the slip-spring model. In particular, one might imagine that the

fat tube would be better modelled with softer slip-springs, i.e. one can change the strength of virtual slip-springs with concentration $N_s = N_s^{melt}/\phi_{star}$. We have performed such simulations, which can also be shifted towards our binary blends simulations. The resulting shift factors are shown in Figure 3.10 by circles. We see that in this case the fat tube theory underestimates the resulting friction. We find however that such simulations are not consistent with binary blends of linear chains, and therefore we use constant N_s simulations throughout this chapter.

In summary, we find that the friction in the fat tube can be adequately predicted by the theory of Read et al. (*Read et al., 2012*) with two modifications: the non-linear mixing rule (eq.3.14) and the need to adjust a model-dependent prefactor A_{CR} .

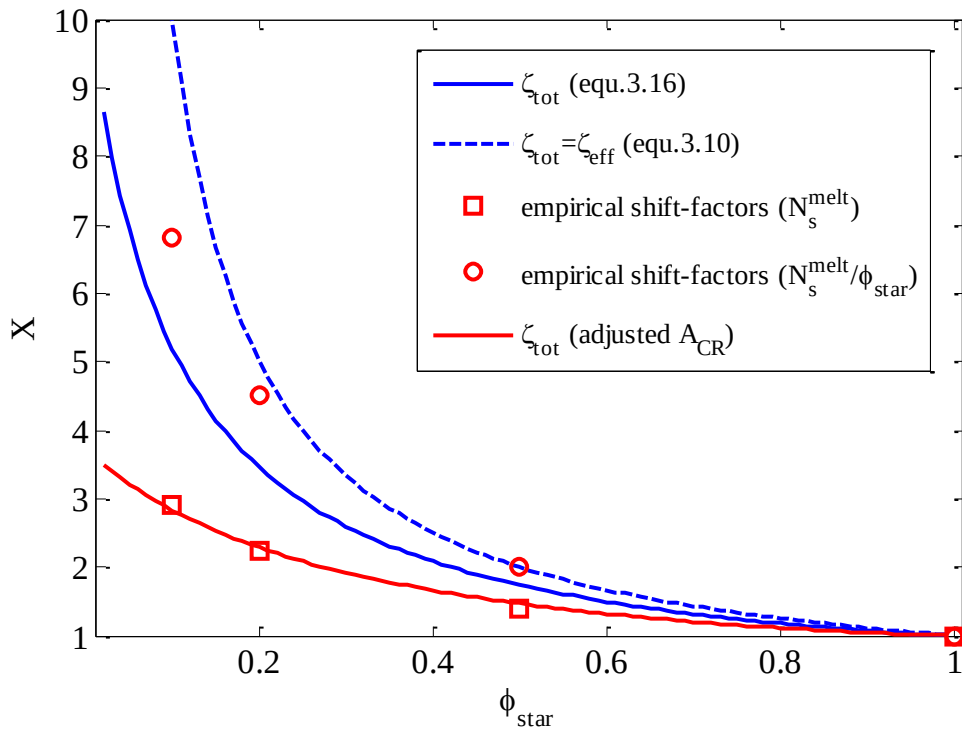


Figure 3.10: The time shift factors calculated by equation 3.16 superimposed with the empirically obtained shift factors. *Dashed blue line:* calculated total FT friction coefficient ζ_{tot} as a bare friction coefficient of the chain (equation 3.10). *Solid blue line:* calculated total FT friction coefficient takes into account total CR friction, ζ_{CR}^{tot} (equation 3.14). *Circles and squares* correspond to empirical shift factors obtained for concentration dependent softer slip-links $N_s = N_s^{melt}/\phi_{star}$ and with constant N_s^{melt} , respectively.

3.5. Conclusions

In this study we have analyzed the relaxation dynamics of star chains in well controlled star/linear blends by comparing quantitative predictions from the slip-spring model to the predictions obtained from various options in tube theory. We separate the relaxation function of the stars in three characteristic time zones. At short times, zone 0 is dominated by Rouse relaxation modes and contour length fluctuations in the skinny tube. At intermediate times, the “skinny” tube (made by all topological constraints) around the star chains explores the “fat” tube (made by long lived obstacles only). This zone is limited by the time required for exploration of a single fat tube segment by CR Rouse motion of the skinny tube. CR contribution of the star chains themselves in this time zone is found to be small and hence neglected. For most of the blends investigated here, we observe that arm retraction is only slightly affected by CR from linear chains. However this effect is getting more pronounced at low star concentrations (e.g. 2wt.%). Zone 2 corresponds to the stress relaxation of the star chains in the fat tube, and is accompanied by the tube dilation due to CR from other stars. We propose a simple multiplicative mixing law for combining the description of relaxation in the three regions.

It was demonstrated that the effective friction of the star chains in the fat tube is larger than the bare friction of the free chain due to the blinking nature of the star-linear topological obstacles in zone 2. Therefore, the slow relaxation modes of the stars present in the blends are shifted towards longer times compared to the slow relaxation modes of stars diluted in true solvent. Applying this time-shift factor, both star relaxation functions were found to superimpose very well in the terminal regime. The shift factors can at least be semi-quantitatively predicted.

In summary, the use of a stochastic model capable of quantitatively predicting chain dynamics at long time scales and validated by comparison with the experimental data is found to be a promising method to investigate fundamental questions and further improve the prediction of the relaxation processes in the framework of tube theory. Results obtained in this chapter can be used for improving predictions of the stress relaxation function by tube models. Namely, a more accurate account of constraint

release effects on chain diffusion coefficient has been introduced. This is generally a point of confusion in existing CR theories that has resulted in erroneous prediction of terminal relaxation zone. In the next chapter we implement obtained here results for improving predictions of the tube survival fraction of probe chain in any monodisperse and binary environments of topological constraints.

APPENDIX A: Constraint release relaxation functions.

In this appendix we discuss our method for obtaining the constraint release relaxation function $R(t)$ and compare it with other models and analytical expressions. In the slip-spring model, the constraints, modelled by individual slip-springs, are appearing and disappearing at the ends of each chain due to reptation and CLF, but also everywhere along the chain due to CR. To isolate the relaxation due to CR from other mechanisms, we run the slip-spring model without slip, where slip-links are permanently attached to their monomers. This kills reptation, CLF and longitudinal modes inside the tube, leaving only fast Rouse modes and the CR. CR is then modelled by deleting and inserting a fraction ϕ_{fast} of slip-springs (shown in the top insert of Figure 3.11 with green circles) with the constant rate $1/\tau_{CR}$, i.e. the probability of slip-spring being deleted at each step is dt/τ_{CR} , where dt is the simulation timestep. The remainder of slip-springs, shown in Figure 3.11 with crosses (fraction $\phi_{slow}=1-\phi_{fast}$), is permanent and does not blink.

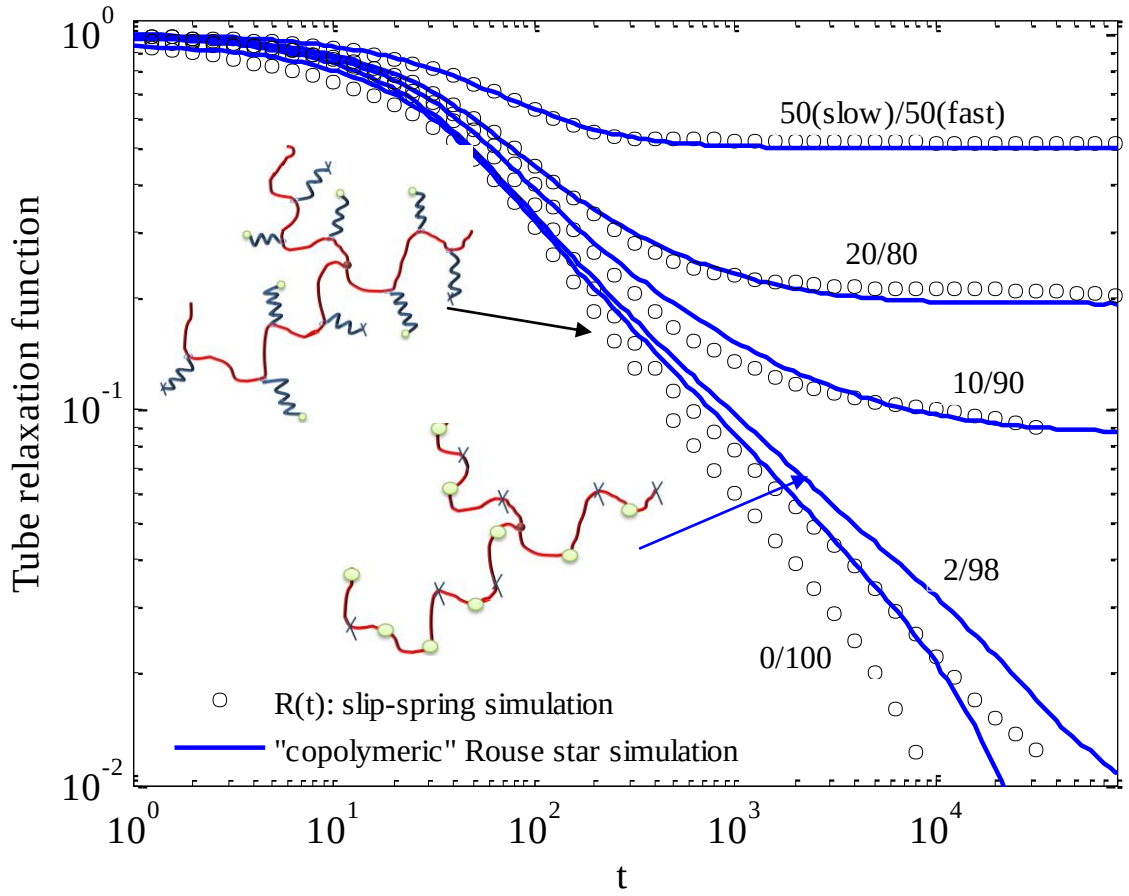


Figure 3.11: Comparison between slip-spring simulation of the tube relaxation function, $R(t)$, shown by *black circles* and relaxation function predicted by simulation of a “dual bead” Rouse model (*thick blue lines*) for a star-shaped chain, with number of entanglements in the first model equivalent to the total number of beads in the second model. Variable fraction of randomly distributed “slow” beads in the “dual bead” Rouse model is equivalent to number of entanglements with infinite life time in the slip-spring simulations. All mobile beads in the Rouse model have the same friction, ζ_{fast} , corresponding to life time of “fast” entanglements, τ_{CR} , in the slip-spring model.

We compute the stress relaxation of such a model (also reported in ref. (*Read et al.*, 2008) for the case $\phi_{slow}=0$) and then subtract the fast Rouse modes by fitting the results with a set of Maxwell modes and then subtracting the contribution of all modes with characteristic times smaller than τ_e , and normalize $R(t)$ in such a way that $R(0)=1$. The results are shown by circles in Figure 3.11 for $\tau_{CR}=60$, which is the reptation time of our linear chains, and for the range of concentrations. By definition, all curves start from 1 and go to a long time plateau equal to the fraction of slip-springs which do not blink, ϕ_{slow} . These are the results which were used in the main part to fit the full simulations.

It is desirable to obtain simpler ways of computing these curves without having to do the simulations for every concentration and CR time. In this Appendix we briefly show a comparison with other simpler methods, none of which is fully adequate in all cases. We leave the derivation of correct analytical solution of this problem to future publications.

First, we simplify the model by removing the virtual springs, and replacing them by beads with different friction coefficients. To this end, we simulate stars made of random copolymer chains with $Z=N/4$ beads per arm. The friction of each bead is selected at random at the beginning of simulation, and it is equal to ζ_{fast} with probability ϕ_{fast} (shown in the lower insert of Figure 3.11 by green circles) and to infinity (i.e. bead fixed in space, shown in Figure 3.11 by crosses) with probability $1-\phi_{fast}$. The simulation results using 1000 chains are shown in Figure 3.11 by lines. The 0/100 case corresponds to all beads having the same friction, therefore obeying perfect Rouse dynamics. The friction $\zeta_{fast}=700$ was chosen here to make results overlap at early times. As apparent from simulations with low concentration of slow beads, the long time dynamics of our copolymer model is slower than that of the full slip-springs CR model. Alternatively, one can overlap late times, in which case the copolymer model would predict faster relaxation at early times.

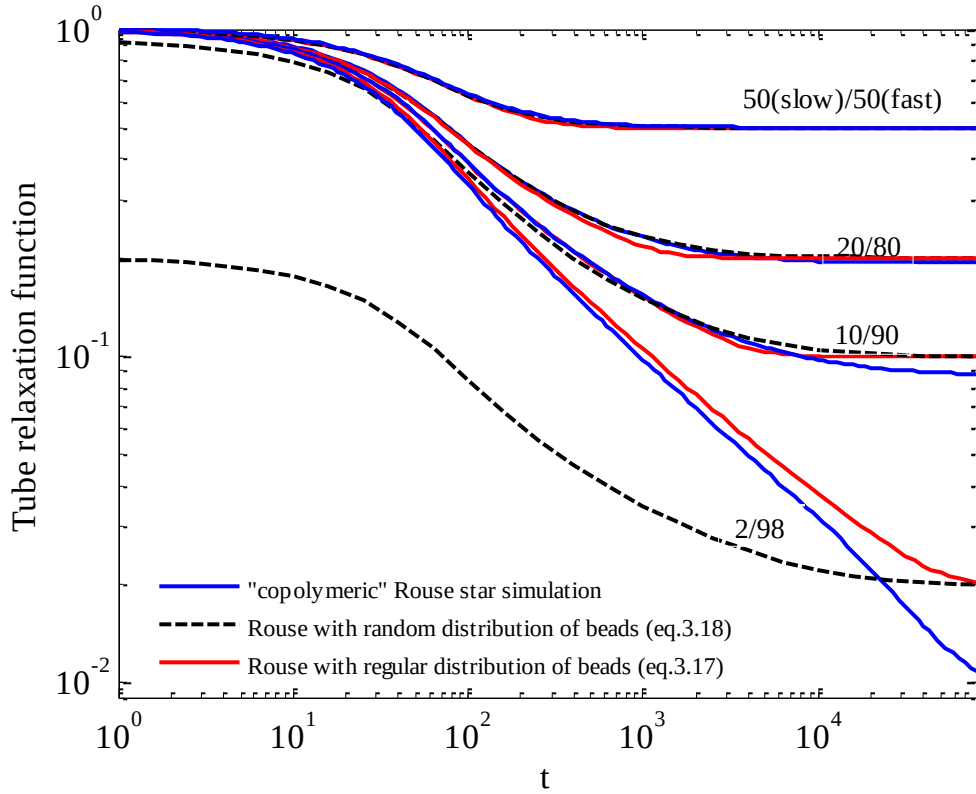


Figure 3.12: Comparison of stress relaxation function obtained by simulations of unentangled “copolymeric” star chain with those predicted by Rouse theory. Total number of beads per arm is equal to $Z=19$ for all cases. Ratio of slow beads with infinite friction and fast beads with friction $\zeta_{fast}=700$ are varying from 50/50 to 2/98. **Thick blue line:** Simulations results of the star chain with different fractions of randomly distributed fast and slow beads. **Dashed black line:** Stress relaxation function predicted by equation 3.18. Fast beads and slow beads are randomly distributed. **Red line:** Stress relaxation function for the chain with evenly distributed fast and slow beads (see equation 3.17).

Next, we compare copolymer simulation results with the prediction of Rouse theory for a regular copolymer, where the slow beads are distributed evenly along the chain. In this case the stress relaxation function is given by

$$R(t) = \phi_{slow} + \phi_{fast} \phi_{slow} \sum_{q=1}^{1/\phi_{slow}} \exp \left(- \frac{24t}{\zeta_{fast} b^2} \sin^2 \left(\frac{\pi q}{2 \left(\frac{1}{\phi_{slow}} + 1 \right)} \right) \right) \quad (3.17)$$

which is shown in Figure 3.12 by *red lines* and compared with random copolymer simulations (*thick blue line*). We see that the agreement is reasonable apart from the 2% concentration, which contains only about 1 slow bead per star molecule. Finally, ref ¹⁵ provides an analytical expression for the random copolymer case:

$$R(t) \approx \phi_{slow} + \phi_{slow}^2 \sum_{n=1}^{2Z} \phi_{fast}^n \sum_{q=1}^n \exp\left(-\frac{24t}{\zeta_{fast} b^2} \sin^2\left(\frac{\pi q}{2(n+1)}\right)\right) \quad (3.18)$$

which is valid in the limit of very long chains with many slow beads in each chain. We plot this prediction in Figure 3.12 by dashed black lines. It works pretty well for large ϕ_{slow} , and fails for $\phi_{slow}=0.1$ and 0.02 . In particular, it does not obey the obvious requirement $R(0)=1$, but satisfies $R(infinity)=\phi_{slow}$. Since the main aim of this chapter is to understand the interplay between different physical processes at different timescales, we use $R(t)$ directly simulated from the sip-spring model rather than analytical approximations presented here. This allows us to separate physical assumptions from the mathematical approximation

Chapter 4:

UNDERSTANDING THE EFFECT OF CONSTRAINT RELEASE ENVIRONMENT ON THE END-TO-END VECTOR RELAXATION TIME OF LINEAR CHAINS.

Abstract

In this chapter we exploit simplified slip-spring “toy” models for simulating fluctuations of the end-to-end vector of a probe chain in a binary blend. Our main objective is to understand and predict the effect of composition and lifetime of the entanglements on the longest relaxation time of the probe’s end-to-end vector. In combination with the results obtained in previous chapter this completes the analysis of the effect of topological constraints on different stress relaxation components. For this purpose we first validate the standard slip-spring model by simultaneous prediction of published dielectric and viscoelastic relaxation of type-A polymers. Next, we generate and analyze a set of experimental rheological data of binary mixtures of short and long linear chains. Further, we prepare and analyze a set of ternary mixtures in order to isolate only the effect of constraint release from the short chains. We build our analysis of the experimental data on a picture, where the longest relaxation time of the probe chain end-to-end vector is determined by a competition between the longest relaxation times of the effective CR motions of the fat and skinny tubes as well as the motion of the chain itself in the skinny tube. In order to test this picture we define *three model systems* which are specifically selected in order to separate and estimate every single contribution involved in the relaxation of the probe’s end-to-end vector in the binary blend system. Finally, we derive simple analytical equations for predicting the longest relaxation time of the probe end-to-end vector in any monodisperse and binary environment of topological constraints and we verify it by comparison with the simulation data.

Some of the materials used in this chapter were synthesized in the group of Prof. Nikos Hadjichristidis. We thank Prof. H.Watanabe for kindly providing experimental data. Results of this study are currently being prepared for the publication.

List of variables and functions

In order to help the reader we summarize and describe all numerous variables and functions used in this chapter in the table below.

Variable or function	Description
Relaxation times	
$\tau_{CR,TT}$	Lifetime of all slip-links in case when all of them are blinking with same frequency. In case when there are at least two blinking frequencies this denotes lifetime of fastest ones.
$\tau_{CR,FT}$	Lifetime of slip-links blinking with lower frequency in the case when there are at least two distinct blinking frequencies.
$\tau_{CRR,TT}$	Relaxation time due to the CR Rouse motion of the skinny tube
τ_{TT}	Relaxation time of the probe chain due to the effective CR motion of the skinny tube
τ_{FT}	Relaxation time of the probe chain due to the CR motion of the fat tube
τ_p	Longest relaxation time of the probe chain having all slip-links blinking with the same frequency
$\tau_{p,ternary}$	Longest relaxation time of the probe chain having some slip-links blinking with single frequency while others are permanent
$\tau_{p,binary}$	Longest relaxation time of the probe chain having slip-links blinking with two precise frequencies.

Friction coefficients	
$\zeta_{CR,TT}$	Friction due to CR hopping of the skinny tube
$\zeta_{CR,FT}$	Friction due to CR hopping of the fat tube
ζ_{TT}	Total friction of the skinny tube
$\zeta_{TT,eff}$	Total friction of the skinny tube in its projected motion along the skinny tube contour.
ζ'_{TT}	Total friction of the skinny tube constrained by a fraction ϕ of permanent slip-links
ζ_{FT}	Total friction of the fat tube
$\zeta_{FT,eff}$	Total effective friction of the fat tube in its projected motion along the fat tube contour.
ζ_{cm}^0	Bulk chain friction
ζ_{eff}	Effective friction of the chain in its projected motion along the fat tube contour
ζ_+	Additional friction contribution due to the blinking nature of the topological constraints in the case when there are at least two distinct CR times.
$\zeta_{p,ternary}$	Total friction coefficient of the probe chain having some slip-links blinking with single frequency while others are permanent.
$\zeta_{p,binary}$	Total friction coefficient of the probe chain having slip-links blinking with two constant frequencies.
ζ_{TT}^{MSD}	Obtained from simulated MSD of chain's center of mass total friction coefficient of the probe chain constrained by slip-links blinking with the same frequency.
ζ_{FT}^{MSD}	Obtained from simulated MSD of chain's center of mass total friction coefficient of the probe chain constrained by slip-links with two finite lifetimes.

4.1 Introduction.

The basic tube model initially proposed by Doi, Edwards and de Gennes (*Doi, Edwards, 1978; de Gennes, 1975*) describes the dynamics of a probe chain in a fixed environment of topological constraints. It is a “single body” description, with the meaning that such expression carries in physics and mechanics. On the other hand, the real situation is clearly a simultaneous multibody relaxation, with complex feedback effects. Not surprisingly, a correct description of the effect of multi-chain environment on the probe chain relaxation still remains a challenging issue.

The first models for implementing the effect from constraint release (CR) has considered the tube as a Rouse chain with segments having the size of the of the tube diameter (*Klein, 1978; Daoud, de Gennes, 1979*). Mobilities of the segments were considered inversely proportional to the lifetimes of the entanglements. We will refer to these models as tube rearrangement models. An alternative picture for modeling effect of CR on stress relaxation was introduced by Marrucci in (*Marrucci, 1985*). Marrucci suggested to consider the already relaxed fraction of the melt as an effective solvent for still oriented chain segments. This so-called dynamic tube dilation (DTD) or dynamic dilution theory considers an effective tube diameter continuously widening in the course of stress relaxation and thereby facilitating chain motion. Doi in (*Doi et al., 1987*) proposed to combine both CR pictures and defined the effective tube diameter as a crossover between mean squared displacement of the free chain and motion of the tube described by Rouse dynamics. Finally, Viovy et al. (*Viovy et al., 1991*) further extended the original tube rearrangement picture for the case of binary linear melts. Namely, they proposed to consider CR motion of the tube effectively separated in two regimes: (i) CR Rouse motion, which is only relevant in the diffusion scale limited by the fat tube diameter and (ii) further relaxation of the tube governed by CR reptation along the fat tube contour.

Regardless of the CR picture used most authors have adapted assumption of independent contributions from the tube and chain motions. Thus for computing the

overall stress relaxation function the two contributions are then combined by a multiplicative mixing law.

The ability to experimentally separate the relaxation of a probe chain in its tube from the relaxation of the environment is an important issue since it can help discriminate between CR models. Whereas linear rheology measurements conflate all relaxation mechanisms (reptation, fluctuations and constraint release) in a single response, other techniques can distinguish between different effects. Among those, dielectric spectroscopy, which measures the relaxation of dielectric permittivity $\epsilon(t)$ usually from the frequency response through Fourier analysis. This technique is attractive as complement to rheological measurements and is widely used to study relaxation dynamics of polymers. Its limitation comes from the requirement that non canceling electrical dipoles have to be present along the chain. For the so-called “type-A” polymers having dipoles parallel to the chain backbone (*Stockmayer, 1967*) relaxation of an induced polarization of the chain is equivalent to the fluctuation of its end-to-end vector. As an alternative to this method C.-Y. Liu in (*Liu et al., 2006*) proposed an experimental probe rheology method for studying relaxation contributions due to the tube motion. In binary melts he suppressed the relaxation contribution from the environment by diluting short probe chain in an excess of much longer matrix chains. By assuming that relaxation spectra of the probe and matrix are uncoupled, he subtracted the relaxation function of the probe and considered it as being unaffected by CR. Despite its obvious theoretical value, application of this method is limited in terms of probe concentration. Namely, concentration of the probe should be very low in order to avoid CR effect from entanglements with chains of the same molecular weight. Moreover, the matrix should not be affected by dynamics of the probe. This can be tested by comparing terminal relaxation time of the matrix with and without probe. On other hand the low concentration of the probe is automatically reflected in the low intensity of the subtracted signal.

H. Watanabe and co-workers in various publications have extensively used a combination of linear rheology and dielectric spectroscopy on polyisoprene (PI) (typical type-A polymer) for understanding effect of environment on viscoelastic relaxation of the polymer. As opposed to viscoelastic relaxation, no dielectric relaxation of the chain is activated by the motion of its environment, except for a contribution from chain fluctuations at the edge of the dilated tube (*Watanabe, 2001*). Hence, the tube survival fraction, $\phi'(t)$, can be directly extracted from the dielectric relaxation function $\Phi(t)$. The authors find viscoelastic relaxation is linked to dielectric relaxation in a straightforward way for linear polyisoprene: $\mu(t) = G(t)/G_N^0 = \phi'(t)^{1+d}$, where G_N^0 - plateau modulus and d ($\approx 1.1..1.3$) is the dilation exponent. This confirms a direct relationship between two relaxation functions.

The effect of environment represented by constraint release (CR) on the relaxation of the end-to-end vector in monodisperse star and linear polymers and binary blends of linear chains has been addressed by many authors but a clear picture has yet to emerge. The most recent publications include:

In (*Pilyugina, et al., 2012*) authors applied a discrete slip-link model (DSM) in order to predict experimental data of the viscoelastic and dielectric relaxation functions in monodisperse melts of linear and star polymers and binary mixtures of short and long linear chains. In agreement with ref. (*Glomann et al., 2011*) they concluded that the end-to-end vector autocorrelation function of monodisperse *linear* chains is not affected by their CR dynamics. In contrast, relaxation of the end-to-end vector of monodisperse *star* polymers is drastically influenced by constraint dynamics.

Finally, in (*Matsumiya et al., 2012*) authors have recently investigated the effect of CR on dielectric relaxation of entangled linear chains by comparing experimental signal of short chains in monodisperse and bidisperse systems. They conclude that the end-to-end relaxation time of short chains of different M_w diluted in an excess of longer chains is

significantly delayed by comparison with that observed in the monodisperse systems regardless of their molecular weight.

The main objective of this study is to understand the effect of constraint release on the relaxation of the end-to-end vector of *long* linear probe chains in binary mixtures with short linear chains. For this purpose we progressively complexify the constraint release environment of the probe chain with the help of *three model systems* which are specifically chosen in order to highlight the various CR contributions to relaxations of the end-to-end vector. We first validate the slip-spring model (*Likhtman, 2005*) by simultaneous comparison with experimental rheo-dielectric relaxation data from literature and linear rheology data for specially prepared binary and ternary mixtures of linear chains with well separated molecular weights. Next, from simulations of the slip-spring model, we extract longest relaxation times of the end-to-end vector of the probe chain in different constraint release environments and analyze the results in the frame of the tube model.

As this study is fundamentally an illustration of a methodology that can be extended to the systems with variable complexity of CR spectra, we allow some simplifications that do not influence the final objective but significantly facilitate derivation of the final equations. In our analytical equations we do not account for the distribution of CR times in every component of the mixture. This could be represented by multiple fat tubes constraining the motion of the single skinny tube and the probe chain. Instead, for every component of the blend, we only consider the largest possible constraint release time represented by its reptation time. Neither do we account for the effect of CLF on the longest relaxation time of the chain in the fixed environment.

This study is arranged as follows: in the methodology section we introduce the three main model systems characterized by dominant constraint release contributions. In the experimental section we describe details of the synthesis and molecular structure of the materials. We also provide details of the small angle oscillatory shear measurements and data processing. The theoretical section describes the necessary details of the slip-

spring model. In the results and discussion section, we validate the slip-spring model by comparison with the dielectric and linear rheology data. Next, individually for every model system we propose straightforward analytical equations predicting the corresponding longest relaxation times and validate them by stochastic simulations of the accordingly modified slip-spring models. In the conclusion, we summarize the key results of this study and highlight possible perspectives.

4.2 Methodology

For analyzing the effect of the CR environment, we adopt the picture of the skinny and fat tubes constraining lateral motion of the chain. The skinny tube is formed by entanglements of a given probe chain with all chains (long, i.e. other probe chains, and additional short ones), whereas the fat tube includes only entanglements with other probe chains.

We propose a picture where the longest relaxation time of the probe chain end-to-end vector is determined by a competition between the longest relaxation times of the effective CR motions of the fat and skinny tubes as well as the motion of the chain itself in the skinny tube (see Figure 4.1). In order to test this picture we define *three model systems* which are specifically selected in order to separate and estimate every single contribution involved in the relaxation of the probe's end-to-end vector in the binary blend system (see Figure 4.2).

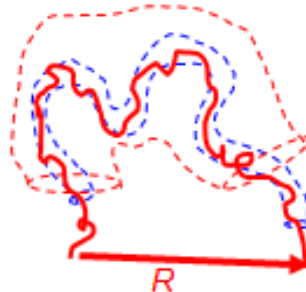


Figure 4.1: Schematic representation of the probe chain in the binary CR environment (system #3). Topological constraints due to the entanglements with short and probe chains and other probe chains only are illustrated by skinny blue tube and fat red tube, respectively. Solid red arrow shows end-to-end vector of the probe chain, R .

End-to-end vector of probe chain:

In the 1st system we dilute probe chains in the sea of very long chains, which are not relaxing at the time scale of the analysis (below referred to as “gel”). In this system probe chains are not entangled with other probe chains, but only with the “gel”. Hence, CR is essentially turned off for the probe chains. The only possible relaxation mechanism is by reptation motion of the chain in the skinny tube. This mechanism is of course also present in both 2nd and 3rd systems.

End-to-end vector of the skinny tube:

In the 2nd system, we substitute some fraction of the gel chains by short chains. By doing this, and assuming that long chains of the gel are effectively immobile at the timescale of relaxation of the probe chains, we get a controlled amount of CR from entanglements with the short chains (which we call “short” entanglements). This mobile fraction of entanglements leads to CR motion of the skinny tube, itself partially constrained by the fat tube (entanglements with gel chains).

End-to-end vector of the fat tube:

The 3rd system is a binary blend of short and probe chains. A fraction ϕ_p of the probe chains entanglements is with other probe chains. The complementary fraction ϕ_s with short chains is the same for the 2nd and 3rd systems.

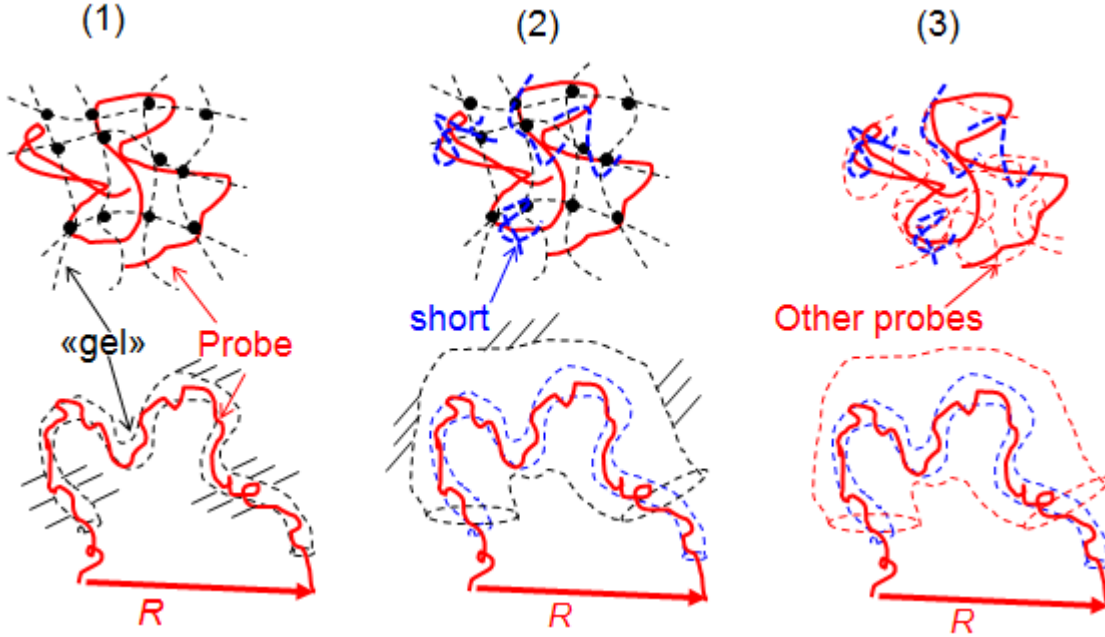


Figure 4.2: Schematic representation of three systems highlighting every component of end-to-end vector in the binary CR environment. At the upper part of all pictures probe chain is shown by red solid line; «gel» is shown by network of black thin lines; other probe chains are shown by thin red lines. At the lower part of all pictures skinny tube is shown by dashed thin black (1) and blue lines (2,3); fat tube is shown by dashed thin red line. (1) Probe chain in a «gel»; (2) Probe chain entangled with short and «gel» chains; (3) probe chain entangled with short and other probe chains. Solid red arrow shows end-to-end vector of the probe chain, R .

In this study, we utilize the single-chain slip-spring model for simulations of equilibrium polymer dynamics (*Likhtman, 2005*). This model allows estimating stress relaxation and end-to-end vector autocorrelation function of every blend component individually without relying on any subtraction procedure.

First, we validate the model by simultaneous comparison with published data of the stress relaxation and dielectric relaxation in binary mixtures of linear polymers. Next, we use our own rheology data in order to by means of the slip-spring model estimate end-to-end vector autocorrelation function of the probe chain in different model systems. Since simulations of the end-to-end vector autocorrelation function can be conducted for any type of polymer we are not restricted to type-A polymers traditionally used in the dielectric spectroscopy experiments.

In order to obtain the longest relaxation time of the end-to-end vector in every system we fit the respective $\Phi(t)$ to a set of Maxwell modes using REPTATE software and

extract the relaxation time of the longest mode (Ramirez, Likhtman. <http://reptate.com>, 2009).

4.3 Experimental section:

4.3.1 Materials

The synthesis details for the linear Polybutadiene (PBd) samples with $M_w \sim 7.5\text{kg/mol}$ (PDI=1.02) and $M_w \sim 51\text{kg/mol}$ (PDI=1.04) with 90% of 1,4 addition have been reported in ref. (Shivokhin *et al.*, 2014). These samples have been kindly provided along with the SEC-data by Nikos Hadjichristidis.

Narrow distribution linear PBd with $M_w \sim 300\text{k}$ (PDI=1.08) (1,4 addition > 90%) has been purchased from Polymer Source, Inc.

Throughout the chapter, samples with molecular weights 7.5k, 51k and 300k will be referred to as short, probe and gel chains, with molecular weights $M_{w,s}$, $M_{w,p}$ and $M_{w,G}$, and longest relaxation times $\tau_{d,short}$, $\tau_{d,probe}$, $\tau_{d,G}$, respectively.

The procedure of the blend preparation is similar to the one discussed in section 3.1.1.

4.3.2 Measurements:

In this section we present results of experimental SAOS measurements for all model systems introduced in the methodology section. All measurements are done using an ARES (TA Instruments) rheometer equipped with a plate-plate fixture of 8 mm diameter.

After conducting frequency-sweep measurements at 25, 0, -25, -50 and -70°C under nitrogen atmosphere, we apply time-temperature superposition principle (TTS) for constructing master curves covering a much broader range of frequencies as compared to the individual master curve segments measured at constant temperature. The shifting procedure is conducted in accordance with shift-factors predicted by the WLF equation, using parameters $C_1=3.63$, $C_2=142.11\text{ K}$ at $T_{ref}=25^\circ\text{C}$. By introducing iso-free-volume

correction to the horizontal shift-factors we account for differences in components T_g : $\log_{10}a_T = -C_1(T - T_{ref} + C_{Tg}/M_w)/(T + C_2 + C_{Tg}/M_w)$, where $C_{Tg}/M_w = (T_g^{inf} - T_g)$, where $C_{Tg} = 13$ is an empirical Flory-Fox parameter related to the free volume for a given polymer chemistry.

Material density correction due to the temperature change is taken into account by introducing vertical shift factors $b_T = \rho(T)T/\rho(T_{ref})T_{ref}$.

Obtained results represented by frequency sweep data of storage and loss moduli are compared with predictions of the slip-spring model in Figures 4.6 - 4.8.

4.4 Theoretical section.

The slip-spring model.

All numerical simulations in this study are conducted using Likhtman's stochastic single chain slip-spring model (*Likhtman, 2005*). This model is based on Rouse chain comprising N beads connected by $N-1$ springs. The effect of entanglements is implemented by slip-links randomly distributed along the chain. Every slip-link is connected by a virtual spring with parabolic potential to an anchoring point.

Successful applications of this model for predicting stress relaxation in low polydispersity linear and binary mixtures of star and linear entangled polymer melts have been reported in ref (*Likhtman, 2005; Shivokhin et al., 2014*). Besides, in ref (*Likhtman, 2005*) the model has demonstrated quantitative prediction capability of polymer dynamics when confronted with experimental data by three different techniques: neutron spin-echo (NSE), linear rheology and molecular diffusion.

All implementation details and description of the model parameters can be found in reference (*Likhtman, 2005*) and in the introduction chapter of this thesis. In this chapter we also utilize a number of simplified “toy models” based on standard slip-spring

implementation in order to separate relaxation contributions. In particular, we can deactivate reptation and CLF mechanisms by prohibiting slip-links from sliding over the chain ends. We can also assign exact (as opposed to originally distributed) engagement/disengagement frequencies for slip-links. Thus, by assigning infinite lifetime to the slip-links we can completely shut down relaxation contribution due to CR. In this way, we are able to separate and control relaxation contributions due to sliding and CR dynamics of the chain.

For simulations of the stress relaxation we first fit unit mass parameter M_0 for all monodisperse components. Next, all binary and ternary mixtures are predicted without additional parameter fitting. The algorithm for simulating CR of binary and ternary mixtures is identical to the standard CR algorithm described in the introduction chapter of this thesis. The number of chains corresponding to every blend component in simulations is computed in accordance with its respective weight fraction.

As a result of these simulations we extract the overall and individual stress relaxation functions and end-to-end vector autocorrelation functions for every component. For mapping the time and stress of the model to those of the experimental data, we multiply them by τ_0 and G_0 , respectively (see Table 4.1).

Table 4.1: Fitted values of the slip-spring model parameters

	M_0 , kg/mol	τ_0 , μ s	G_0 , MPa
PI ($T_{ref}=40^\circ\text{C}$)	1	6.83	2.36
PBd ($T_{ref}=25^\circ\text{C}$)	~ 0.4	0.45	7.0

It should be noted that the stress of the model is calculated in units of $G_0 = \rho RT/M_0$ with ρ , R and T being the polymer density, universal gas constant and absolute temperature, respectively. By using $\rho(\text{PBd})=900\text{kg/m}^3$, $\rho(\text{PI})=681\text{kg/m}^3$, $T(\text{PI})=313\text{K}$, $T(\text{PBd})=298\text{K}$, $R=8.31\text{ m}^3\cdot\text{Pa}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and by substituting the fitted values of M_0 we can compute $G_0(\text{PBd})=6.0\text{MPa}$ and $G_0(\text{PI})=1.8\text{ MPa}$. These values are different from the fitted G_0 of PBd and PI by 16 and 30%, respectively. This model stress G_0 should not be confused with the plateau modulus G_N^0 .

Besides, there is some discrepancy between the PBd data presented in Table 4.1 and to those used in chapters 2 and 3. The fitted values for M_0 of the probe (51k), gel (~300k) and short (7.5k) chains are equal to 0.38, 0.37 kg/mol and 0.42kg/mol, respectively, whereas in the previous chapters we used $M_0 \sim 0.37 \dots 0.38$. The largest discrepancy with respect to the central value of $M_0 \sim 0.38$ kg/mol is for the short chains (~13%). This is very close to the typical experimental error of SEC measurements. We use $M_0 = 0.4 \pm 0.02$ kg/mol for all samples in this chapter.

Small discrepancies between values of τ_0 reported in different chapters can be attributed to small uncertainties on the WLF parameters.

Finally, there is small discrepancy, consistent with the range of typical experimental error (~7%) between fitted values of G_0 reported in chapter 3 and this chapter.

4.5 Results and Discussions:

4.5.1 Validation of the slip-spring model by comparison with published rheo-dielectric data of monodisperse and binary linear mixtures.

Dielectric relaxation of type-A polymers reveals the end-to-end vector autocorrelation function. According to our knowledge, the simulation results of the slip-spring model have never been confronted in published literature with experimental dielectric relaxation data. In this section we validate the slip-spring model by comparison with published data of Watanabe et al. in references (*Watanabe et al., 2004 (1, 2)*) on dielectric and viscoelastic relaxation of the same set of polyisoprene data at the same reference temperature.

The model parameters M_0 , τ_0 and G_0 are calibrated by fitting small angle oscillatory shear (SAOS) data of monodisperse linear chains of $M_w = 21$ kg/mol, 94 kg/mol and 308 kg/mol. The stress relaxation and end-to-end vector autocorrelation function are estimated from the same simulations and therefore after we have fitted material parameters on SAOS data of both monodisperse components all stress and end-to-end

vectors in all blend compositions are predicted without additional adjustment of the parameters.

In Figure 4.3 we demonstrate comparison between experimental rheological and dielectric data and the slip-spring model predictions with the same set of parameters.

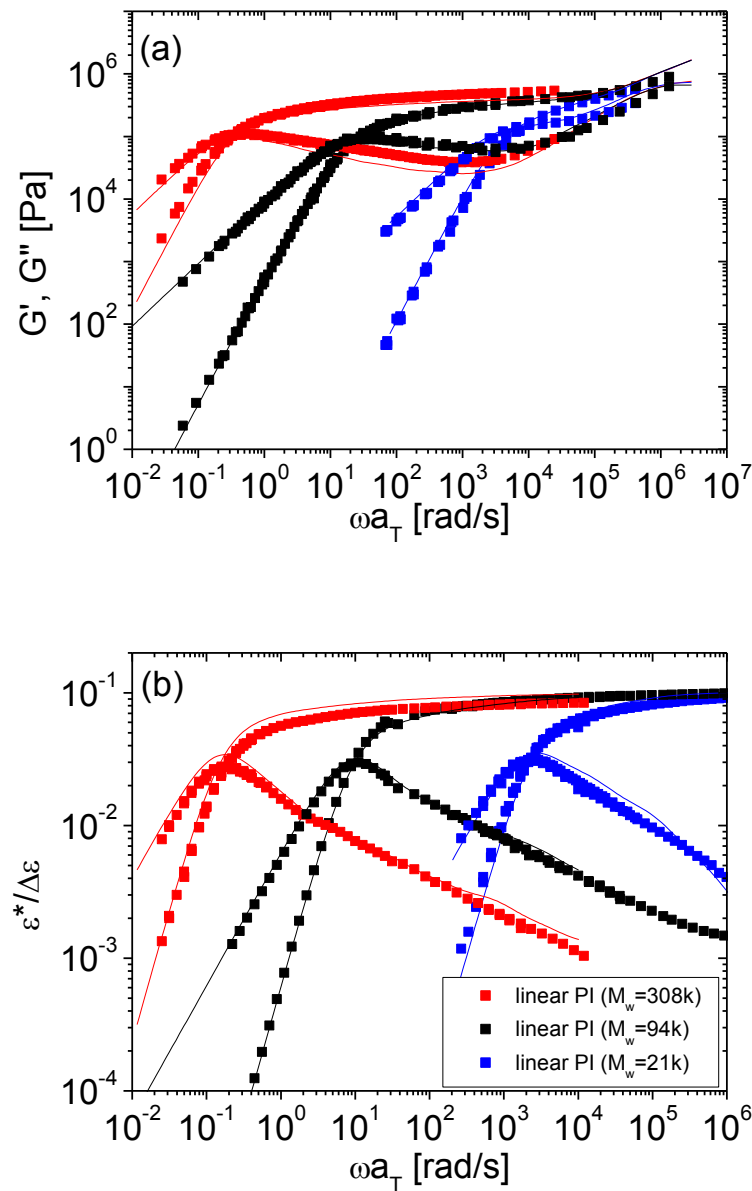


Figure 4.3: Comparison of simulation results with experimental dynamic rheological (a) $G^*(\omega)$ and (b) dielectric $\epsilon^*(\omega)$ data of monodisperse linear polyisoprene with $M_w = 21$ kg/mol, 94 kg/mol and 308 kg/mol. Symbols represent experimental data and lines indicate the slip-spring predictions. All simulations are made with material parameters $M_0 = 1$ kg/mol, $G_0 = 2.36$ MPa; $\tau_0 = 6.83$ μ s. The experimental data is measured at $T_{ref} = 40^\circ\text{C}$. Color code in (a) is the same as in (b).

Besides some discrepancy observed between experiments and simulations for the longest chains ($M_w=308k$) in Figure 4.3 all other simulation results demonstrate quantitative prediction of both rheological and dielectric data using the same values of the parameters.

Next, in Figure 4.4 and Figure 4.5 we analyze the slip-spring prediction for binary mixtures of linear PI. For this purpose we superimpose predictions of the slip-spring model with the experimental data of complex dielectric permittivity and complex viscoelastic relaxation modulus of different ratios 0/100, 5/95, 10/90, 20/80, 50/50 and 100/0 of 308k/21k.

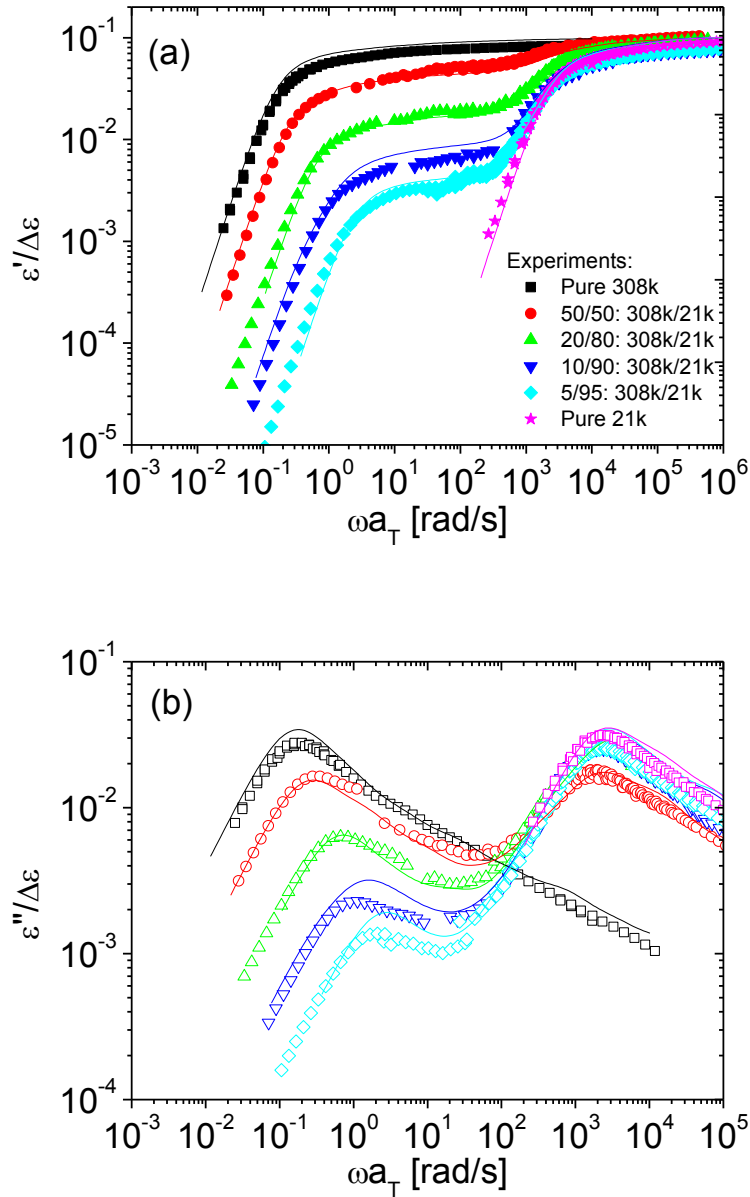


Figure 4.4: Comparison of simulation results with experimental dynamic (a) storage, $\varepsilon'(\omega)$, and (b) loss, $\varepsilon''(\omega)$, dielectric permittivity data of monodisperse and binary mixtures of linear polyisoprene with $M_w=21$ kg/mol and 308 kg/mol. Symbols are the data and lines indicate the slip-spring predictions. All simulations are made with material parameters $M_0=1$ kg/mol, $\varepsilon_0=0.1$; $\tau_0=6.83$ μ s. The experimental data is measured at $T_{ref}=40^\circ\text{C}$. Color code in (b) is the same as in (a).

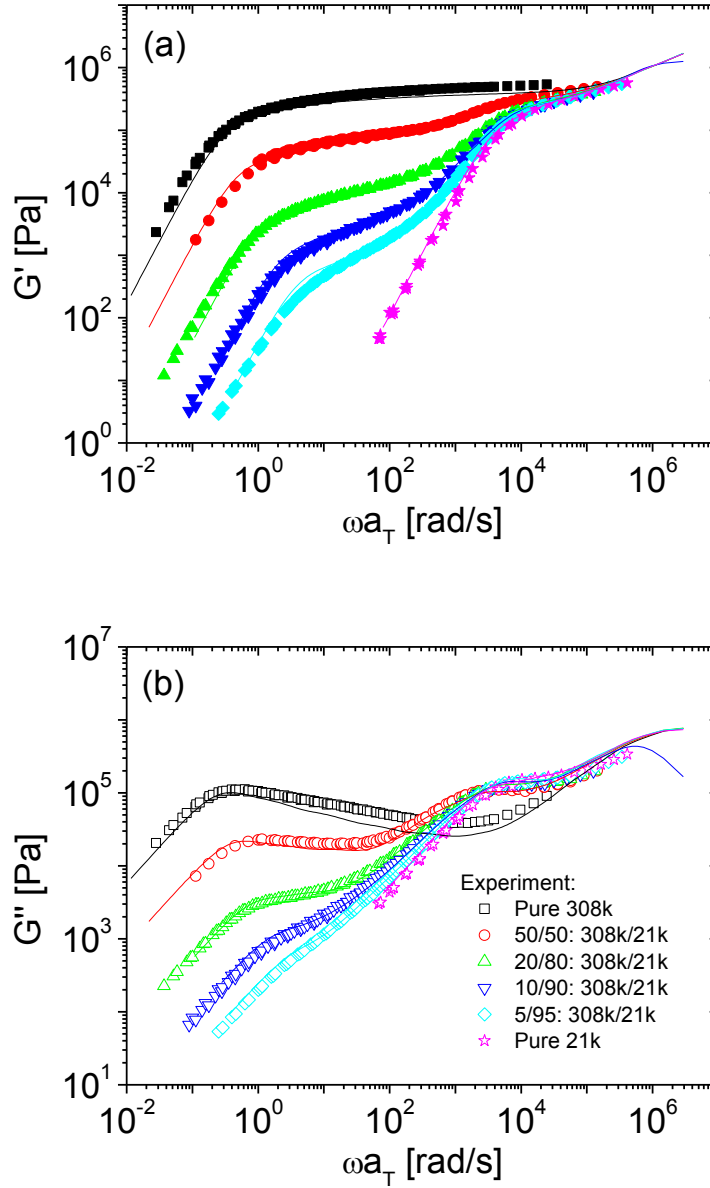


Figure 4.5: Comparison of simulation results with experimental (a) dynamic storage, $G'(\omega)$, and (b) loss, $G''(\omega)$, moduli of monodisperse and binary mixtures of linear polyisoprenes with $M_w=21$ kg/mol and 308 kg/mol. Symbols are the data and lines indicate the slip-spring predictions. All simulations are made with material parameters $M_0=1$ kg/mol, $\tau_0=6.83$ μ s, $G_0=2.36$ MPa. The experimental data is measured at $T_{ref}=40^\circ\text{C}$. Color code in (a) is the same as in (b)

Results of comparing dielectric and viscoelastic relaxation data presented in Figure 4.4 and Figure 4.5, respectively, reveal a qualitatively good match over the whole frequency range for all blend compositions. However, a few discrepancies can be observed. Relatively high polydispersity of the long component (PDI=1.08) not taken into account in the simulations is resulting in broader experimental low frequency peak of G'' as

compared to the simulation data. It must be noted that discrepancy between the slip-spring prediction and rheological experimental data of pure 308k in Figures 4.3-4.5 is in the order of 30-40% in the vertical direction. The comparison with experimental data for other monodisperse linear chains ($M_w=21k$ and $94k$) does not reveal such significant discrepancy. Therefore we assume that this could partially be attributed to sample loading differences or transducer calibration. In order to verify this assumption comparison with other experimental data of well entangled monodisperse PI samples would be required.

Despite some discrepancy in vertical direction, the model correctly predicts localization of the low frequency peak in the dielectric spectra for all blend compositions. This fact is of main importance for this study since we are analyzing only longest relaxation times of the end-to-end vector which can approximately be attributed to the frequency corresponding to this peak.

Simultaneous comparison by two different techniques is certainly a very strong test for the model. Therefore, overall quality of the slip-spring model prediction of the viscoelastic and dielectric data can certainly be considered satisfactory.

4.5.2 Predicted viscoelastic relaxation of the monodisperse, binary and ternary mixtures of linear chains using the slip-spring model.

In this section, simulation results of the standard slip-spring model are compared with small angle oscillatory shear experimental data. As discussed in the methodology section, we analyze CR of linear probe chains in a blend with the help of three simplified systems allowing us to separate and analyze the main relaxation contributions.

First, we analyze the relatively simple system consisting of a very small fraction of short and/or probe chains diluted in a sea of unrelaxing chains, called “gel chains” (represented by linear PBd chains with $M_w=300k$). Gel chains are effectively immobile in the relaxation timeframe of short and probe chains.

In Figure 4.6 we compare experimental viscoelastic relaxation data of pure gel chains and their binary mixtures with 20% of short chains ($M_w=7.5k$) or 3% of probe chains ($M_w=51k$). The concentrations are selected in a way that the short or probe chains are only entangled with gel chains. Simulations of all mixtures containing gel chains (N804) were made to run for 21 days but the terminal zone for most of the cases was still not reached. However, the covered frequency range was broad enough to include both peaks in loss modulus corresponding to relaxation of the short and probe chains.

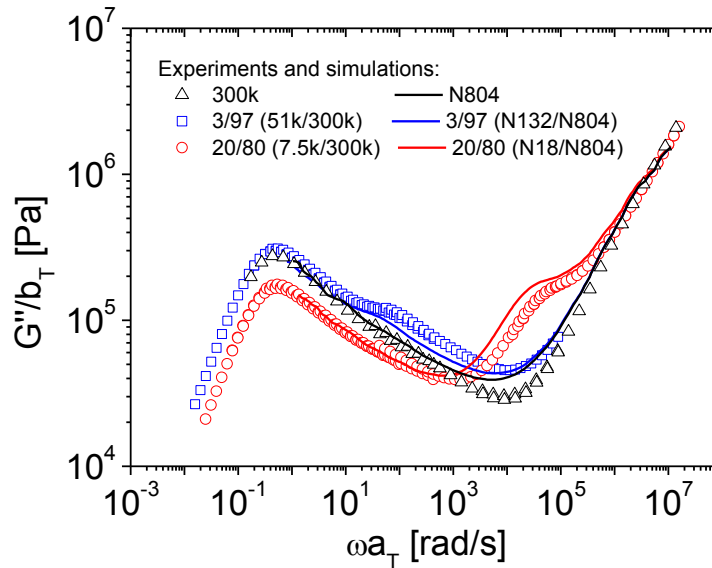


Figure 4.6: Linear shear loss modulus of low polydispersity and binary mixtures of PBd linear chains with $M_w=7.5k$, $51k$ and $300k$. Comparison of simulation predictions (solid lines) and experimental SAOS data (markers). All simulation data obtained using parameters: $M_0 \sim 0.4$ kg/mol, $G_0=7.0$ MPa and $\tau_0=0.45$ μ s. All measurements are conducted at $T_{ref}=25^\circ\text{C}$.

Next, in the system with a small fraction of probe chains diluted in an excess of gel chains, we introduce various fractions of short chains. We expect that short chains will impose CR dynamics on the probe chains and thus we can analyze their effect on relaxation of the end-to-end vector of the probe.

In Figure 4.7 we present experimental loss modulus data for two ternary mixtures containing 3% probe chains diluted in 20/77 and 80/17 short/gel chains mixtures, respectively.

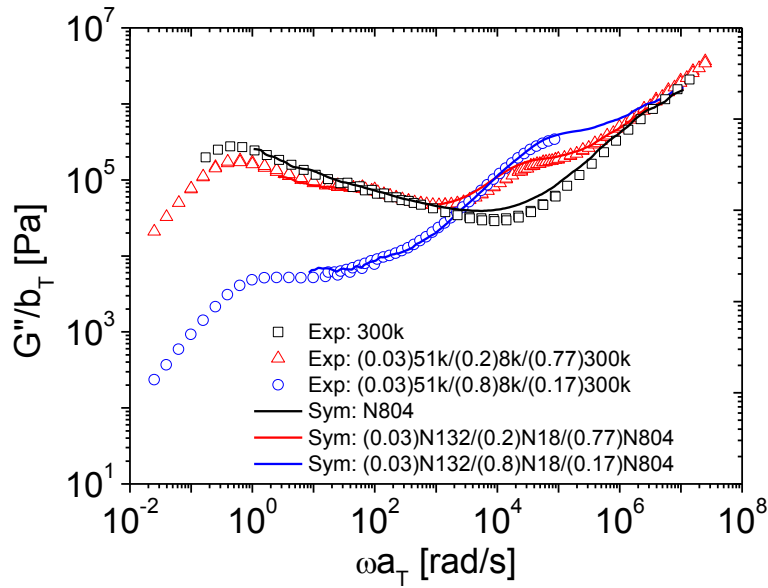


Figure 4.7: Linear shear loss modulus of ternary mixtures of PBd linear chains with 20 and 80wt.% of $M_w=7.5k$, 3wt.% of 51k, and 77 and 17wt.% of 300k. Comparison of simulation predictions (solid lines) and experimental SAOS data (markers). All simulation data obtained using parameters: $M_0 \sim 0.4$ kg/mol; $G_0=7.0$ MPa and $\tau_0=0.45$ μ s. All measurements are conducted at $T_{ref}=25^\circ\text{C}$.

Finally we completely substitute gel chains by other probe chains but keeping the same fraction of short chains as in previous systems. By comparison with the previous system, we anticipate to see effect of other probe chains on the end-to-end vector longest relaxation time.

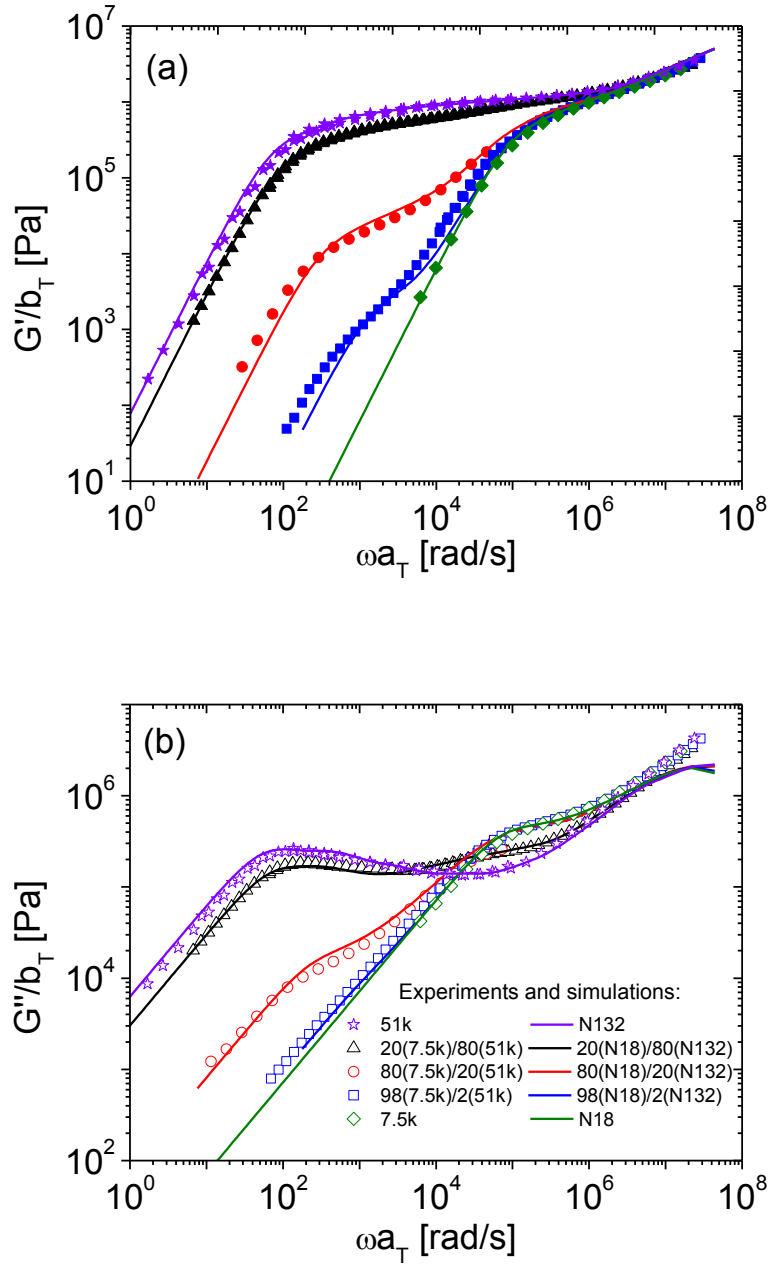


Figure 4.8: Linear shear (a) storage and (b) loss moduli of monodisperse and binary mixtures of PBd linear chains with $M_w=7.5k$ and $51k$. Comparison of simulations and experimental SAOS data. All simulation data obtained using parameters: $M_0 \sim 0.4$ kg/mol; $G_0=7.0$ MPa and $\tau_0=0.45$ μ s. Color code in (a) is the same as in (b)

Comparison between linear shear rheology data and simulation results of the slip-spring model presented in Figure 4.6 - Figure 4.8 reveals satisfactory overlap through whole covered frequency range for all studied mixtures. However, small discrepancies can be observed. Namely, some mismatch in the high-frequency scale for mixtures containing

“gel chains” of $M_w=300k$ can probably be attributed to small differences in their microstructure with respect to that of the short and probe chains which were made in the same lab. This mismatch could be reduced by slightly adjusting the value of τ_0 ($=0.34 \mu s$). However, for consistency we have chosen to keep all parameters constant for all binary and ternary mixtures.

Considering the satisfactory simultaneous predictions of viscoelastic and dielectric relaxation data for a set of polyisoprene binary blends (section 4.5.1) and the quantitative prediction of PBd viscoelastic data shown in the present section, we can consider that the slip-spring model is adequate for analysis of the end-to-end vector relaxation of probe chain affected by CR.

In the next sections, we use the slip-spring model for simulating dynamics in simplified systems consisting of probe chains constrained by slip-links which are ‘blinking’ at a single or two precise frequencies spanning a broad range of values. These systems represent very simplified cases of monodisperse and binary systems and will be used for the purpose of theoretical understanding the CR effect on the end-to-end vector relaxation of probe chains.

In the following sections of this chapter we will derive equations for predicting longest and-to-end vector relaxation times and confronting them with the simulation data validated in section 4.5.2.

4.5.3 Relaxation of the probe chain in a single tube.

In this section we analyze dynamics of probe chains diluted in a sea of very long “gel” chains (system#1 in Figure 4.2). Probe chains in this system are not entangled with other probe chains, but only with the “gel”, whereby CR is essentially turned off during relaxation of the probe chains. The only possible relaxation mechanism is by reptation motion in the skinny tube comprising entanglements with all other chains.

Chain dynamics in this system activates all relaxation mechanisms present in more complicated CR environments comprising entanglements with various lifetimes (2^{nd} and

3rd systems in Figure 4.2). Therefore this system serves as a reference for analyzing the effect of CR on dynamics of entangled probe chains.

For the theoretical analysis, we utilize a methodology allowing us to calculate the effective friction in the fat tube, recently proposed by D.Read in ref (*D.Read et al., 2012*) and the mixing rule proposed in ref (*Shivokhin et al., 2014*). The central idea of this theory is to separate two independent modes of chain motion. The first mode is related to longitudinal (i.e. sliding) dynamics of the chain constrained by all types of entanglements. This motion is not affected by the environment, therefore the corresponding friction is just the total chain friction, $\zeta_0^{cm} = N\zeta_0$, where N -total is the number of chain beads (Kuhn segments) and $\zeta_0=1$ is the friction of a single bead.

The second mode is activated by the blinking nature of entanglements and allows the chain to explore new conformations by tube hopping motions in the transverse direction. This second mode is directly proportional to the blinking frequency of entanglements and is further affected by the motion of the chain entrapped inside the tube. We have found in chapter 3 of this thesis that the total friction coefficient due to the second mode can be adequately albeit empirically represented as follows:

$$\zeta_{TT} = \left(\sqrt{\zeta_{CR,TT}} + \sqrt{\zeta_0^{cm}} \right)^2, \quad (4.1)$$

where the CR friction coefficient $\zeta_{CR,TT}$ for Z blinking segments is derived from a simple model of particle hopping over a constant distance in 1D-space:

$$\zeta_{CR,TT} = \frac{2\tau_{CR}k_B T}{(A_{CR}b)^2} Z \quad (4.2)$$

In equation (4.2), $b=1$ is the size of the Kuhn segment, $A_{CR}b$ is a hop amplitude with A_{CR} a yet unknown prefactor, the thermal energy $k_B T=1$, τ_{CR} is the time per single hop. Below, we show how to determine the value of A_{CR} by fitting simulation data in Figure 4.9a.

By combining expressions for both independent modes of chain motion we can derive an equation for the total friction coefficient of the system having entanglements blinking with a single frequency.

However, first we have to link global motions of these two modes by projecting them on the same diffusion contour $L=Za$, where $Z= N/N_e$ is the total number of entanglements per chain, and $a=N_e^{1/2}b$ is a skinny tube diameter. If we assume that the chain relaxes only due to CR motion of the skinny tube, then the time spent on this motion projected on L with friction coefficient $\zeta_{TT,eff}$ must be the same as the time required for the same motion on the chain's end-to-end distance $R=aZ^{1/2}$ with friction coefficient ζ_{TT} .

The equality of the two relaxation times can be expressed as follows.:

$$L^2 \zeta_{TT,eff} = R^2 \zeta_{TT}$$

Hence, we can compute the effective friction of the skinny tube as

$$\zeta_{TT,eff} = \frac{\zeta_{TT}}{Z} \quad (4.3)$$

Now, the total friction coefficient for the motion of the chain having entanglements all blinking at the same frequency can be represented as

$$\frac{1}{\zeta_{tot}} = \frac{1}{\zeta_{TT,eff}} + \frac{1}{\zeta_0^{cm}} \quad (4.4)$$

As chain motion due to reptation along the skinny tube and motion due to CR tube dynamics are now projected on the same contour L , the respective longest relaxation time of this system can be computed as

$$\tau_p = \frac{L^2}{\pi^2 k_B T} \zeta_{tot} \quad (4.5)$$

Another important characteristic relaxation time which has to be mentioned here is the relaxation time of the probe chain due to effective CR motion of the skinny tube.

$$\tau_{TT} = \frac{L^2}{\pi^2 k_B T} \zeta_{TT,eff}$$

For validating the derived analytical equations, we run simulations of probe chain dynamics with slip-links blinking at frequency $1/\tau_{CR}$, where τ_{CR} varies over a broad

range of values ($\tau_{d,probe} > \tau_{CR,TT} > \tau_e$). This is a simplified model for the probe chains diluted in an excess of ideal monodisperse melt.

For validating the total friction coefficient corresponding to the relaxation of the chain due to constraint release only, we effectively fix chain ends. This is done by prohibiting the slip-links in the model from sliding over the chain ends. Thus, reptation and CLF mechanisms are deactivated, but sliding motion of the slip-links along the chain allows longitudinal stress equilibration. Apart from that the only possible relaxation mechanism is the effective tube motion. In future discussion we will refer to the systems where slip-links are not allowed to pass through the chain ends as “fixed chain ends”, whereas the standard system will be referred to as “free chain ends”.

From these simulations we extract the mean square displacement of the center of mass (MSD), R_c . As at $t \rightarrow \infty$, tube relaxation is dominated by CR motion, we can thus compute the total skinny tube friction coefficient as follows:

$$\zeta_{TT}^{MSD} = \frac{k_B T}{\lim_{t \rightarrow \infty} \langle R_c^2(t) \rangle / (6t)} \quad (4.6)$$

Results of these simulations are plotted by markers in Figure 4.8a.

In Figure 4.9b we plot the longest relaxation times of the end-to-end vector autocorrelation function for the systems with fixed (dashed line) and free chain ends (thin solid line): $\Phi(t) = \langle R(t)R(0) \rangle / \langle R_0^2 \rangle$, where R is the end-to-end vector of the chain.

The two inclined thick solid lines show theoretical values of Rouse and reptation time of the chain $\tau_R = Nb^2 \zeta_0^{cm} / (3\pi^2 k_B T)$ and $\tau_{rept} = L^2 \zeta_0^{cm} / (\pi^2 k_B T)$ normalized by $\tau_{CR,TT}$. The horizontal dashed line represents the longest relaxation time dominated by the CR Rouse tube motion $\tau_{CRR,TT} = \lim_{\tau_{CR,TT} \rightarrow \infty} \tau_{TT} = 2\tau_{CR} Z^2 / 3\pi^2$ (Read et al., 2012; Auhl et al., 2009; Shivokhin et al., 2014).

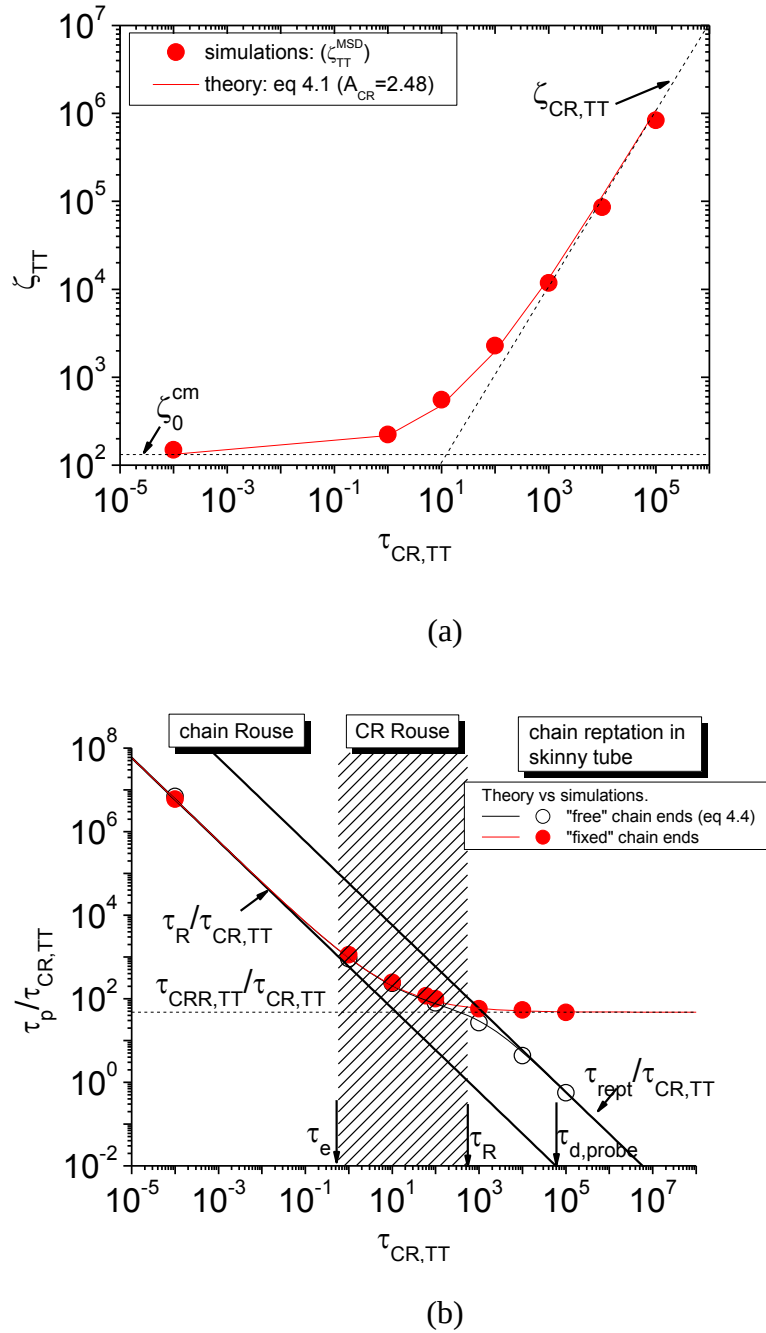


Figure 4.9: Comparison between theoretical predictions (dashed and solid lines) and simulation results (filled and empty circles). All entanglements of the probe chain have the same lifetime, τ_{CR} . (a) Effective friction coefficient of the skinny tube with probe chain having fixed ends. Dashed lines represent ζ_0^{cm} and $\zeta_{CR,TT}$, corresponding to two extreme cases at $\tau_{CR,TT} \rightarrow 0$ and $\tau_{CR,TT} \rightarrow \infty$, respectively. (b) Longest relaxation time of the end-to-end vector of the probe chain in the same systems. Filled red circles and red line represent simulation data and theoretical prediction of the chain with fixed chain ends, τ_{TT} . Black empty circles and thin solid line represent simulation data and theoretical prediction of the chain with free chain ends. Black solid lines demonstrate terminal relaxation zones dominated by Rouse motion of the chain, reptation of the chain in the skinny tube and CR Rouse of the tube. Arrows show characteristic times of the chain relaxation τ_R , $\tau_e = \tau_R/Z^2$ and longest relaxation time of the probe chain, $\tau_{d,probe} \sim 57544$.

From Figure 4.8a we have extracted the best fit value for parameter $A_{CR}=2.48$ which defines the jump amplitude of the chain upon disappearance of a single slip-link.

It must be noted that the theoretical prediction of the longest relaxation time for the system with effectively fixed chain ends is obtained by substituting eq. (4.3) in eq. (4.4).

Based on Figure 4.9b, three dominant scenarios for terminal relaxation can be highlighted depending on the lifetime of the entanglements with respect to relaxation time of the probe chain:

1. Lifetime of entanglements, τ_{CR} , is comparable to the Rouse stress equilibration time of a single entanglement strand of the probe chain, τ_e . In this case the probe chain is effectively not feeling the presence of the tube and thus relaxes by *Rouse*.
2. Lifetime of entanglements is longer than τ_R . In this case, the terminal relaxation is completely dominated by *CR Rouse tube motion*. This regime can only be clearly observed in a very narrow window of τ_{CR} . In Figure 4.8b this regime is shown by a horizontal dashed line.
3. Lifetime of the entanglements is longer than reptation time of the chain, hence the tube is effectively fixed at this time-scale and the terminal relaxation is due to chain reptation in the skinny tube.

Between these three regimes, we have two transition scenarios:

4. Lifetime of entanglements is longer than τ_e but shorter than τ_R . In this case terminal relaxation is due to CR Rouse tube motion combined with Rouse motion of the chain and the terminal relaxation time is getting proportional to τ_{CR} but not yet matching the horizontal dashed line in Figure 4.9b

In the following sections we will refer to tube relaxation due to combined contribution from the chain and CR tube motions as *effective CR tube motion*.

5. In the case when CR time $\tau_R < \tau_{CR} < \tau_{rept}$ the end-to-end vector relaxation terminates by combination of effective CR tube motion and chain reptation in the skinny tube.

4.5.4 Two-tube system with a fraction of never relaxing entanglements.

In order to further increase complexity with respect to the systems discussed in the previous section, we now consider the probe chain partially constrained by slip-links with infinite lifetime, whereas other slip-links are blinking at the same constant frequency as in the previous section. This is equivalent to the probe chain being entangled with a mixture of gel and short chains, at different compositions. In terms of the tube model, this can be interpreted as a probe chain constrained by both the skinny and fat tubes, formed by entanglements with all chains and only by entanglements with never relaxing chains, respectively. This type of systems is shown in Figure 4.2 (system #2).

In the case when only a fraction $(1-\phi)$ is blinking with frequency $1/\tau_{CR,TT}$ whereas other entanglements are permanent, previous works (*Read et. al, 2012; Shivokhin et al., 2014*) suggest that in the limit of small $\tau_{CR,TT}$ ($\zeta_{CR,TT} \rightarrow 0$) the total chain friction must always remain ζ_0^{cm} independent on ϕ , whereas, ζ_{TT} becomes dependent on the mobile fraction of entanglements through additional contribution from chain friction, ζ_+ . The following equation satisfies all these requirements:

$$\frac{1}{\left(\sqrt{\zeta_{CR,TT}} + \sqrt{\zeta_+}\right)^2} + \frac{1}{\zeta_{eff}} = \frac{1}{\zeta_0^{cm}} \quad (4.7)$$

In this equation ζ_{eff} is the effective friction coefficient due to the sliding motion of the chain projected on the fat tube contour, $L_{FT} = \phi^{1/2}L$. The theoretical expression for this projected motion can be derived by recognizing that, in the system where reptation is

the only relaxation mechanism, the escape times of the chain from the skinny tube and the fat tube are the same. Therefore:

$$\zeta_{eff} L_{FT}^2 = \zeta_0^{cm} L^2.$$

Thus effective friction for the chain's sliding motion projected on the fat tube contour can be computed as:

$$\zeta_{eff} = \frac{\zeta_0^{cm}}{\phi} \quad (4.8)$$

Next, by substituting eq. (4.8) in eq. (4.7) we can derive an expression for the additional friction contribution activated due to the blinking nature of the entanglements

$$\zeta_+ = \frac{\zeta_0^{cm}}{1-\phi} \quad (4.9)$$

The total friction of the skinny tube constrained by a fraction ϕ of permanent entanglements is defined as

$$\zeta_{TT}' = \left(\sqrt{\zeta_{CR,TT}} + \sqrt{\zeta_+} \right)^2 \quad (4.10)$$

Next, by assuming independence between CR motion of the skinny tube and sliding motion of the chain we can now derive an equation for the total friction coefficient of the chain constrained by blinking and permanent entanglements:

$$\frac{1}{\zeta_{p,ternary}} = \frac{1}{\zeta_{TT}'} + \frac{1}{\zeta_{eff}} \quad (4.11)$$

By analogy with eq (4.5) we convert eq (4.11) to the time scale and compute the longest relaxation time of the chain in the semi-fixed topological environment diffusing along the fat tube contour with friction coefficient $\zeta_{p,ternary}$:

$$\tau_{p,ternary} = \frac{L_{FT}^2}{\pi^2 k_B T} \zeta_{p,ternary} \quad (4.12)$$

For validating these theoretical conclusions, we run simulations of the chain dynamics with a fraction $1-\phi$ of entanglements blinking with characteristic time $\tau_{CR,TT}$ varying over a broad range of values, while others are permanent but can slip along the

backbone and thus can only disappear if the probe chain releases its end from the corresponding slip-link by sliding motion.

In Figure 4.10 for a broad range of $\tau_{CR,TT}$ values, we plot simulation results of the longest relaxation time of the end-to-end vector of the probe chains.

Theoretical predictions plotted as dashed colour lines are computed using eq (4.12).

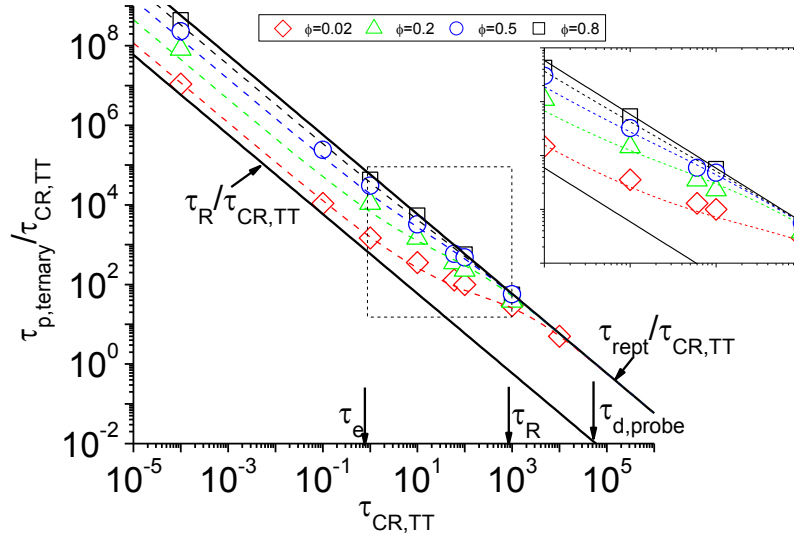


Figure 4.10: Comparison between theoretical predictions (solid colour lines) and simulation results (markers) of the end-to-end vector of a probe linear chain with $N=132$ constrained by blinking and permanent entanglements. Fraction $(1-\phi)$ of blinking entanglements have the same lifetime, $\tau_{CR,TT}$. Black solid lines indicate terminal relaxation zones dominated by Rouse motion of the chain and reptation of the chain in the skinny tube. The leftmost inclined black solid line represents terminal relaxation dominated by Rouse motion of the chain; the rightmost – reptation of the probe chain. Arrows show characteristic times of the chain relaxation τ_R , $\tau_e = \tau_R/Z^2$ and longest relaxation time of the probe chain, $\tau_{d,probe} \sim 57544$. The inlet shows zoomed in data points in the rectangular area.

By analogy with the system discussed in the previous section, all longest relaxation times corresponding to different compositions of the permanent and “blinking” entanglements are localized between τ_R and τ_{rept} . In Figure 4.10 the two inclined black solid lines show theoretical values of Rouse and reptation time of the chain normalized by $\tau_{CR,TT}$. At intermediate values of τ_{CR} , we observe a shoulder (with two inflexion points) reflecting the dominant contribution of CR tube motion to the terminal

relaxation time. After the second inflexion point, all curves representing different compositions of blinking and permanent entanglements are overlapping with the rightmost inclined black solid line representing terminal relaxation dominated by chain reptation in the skinny tube.

In order to demonstrate effect of fat tube motion on results presented in Figure 4.10 we substitute in our model fraction of slip-links having infinite lifetime by those representing entanglements with other probe chains. The lifetime of these slip-links is originally distributed and controlled by standard CR algorithm of the slip-spring model in contrast with the previous graphs, where CR times were fixed at constant values. In Figure 4.11 we superimpose predictions of this modified model with theoretical predictions plotted in Figure 4.10.

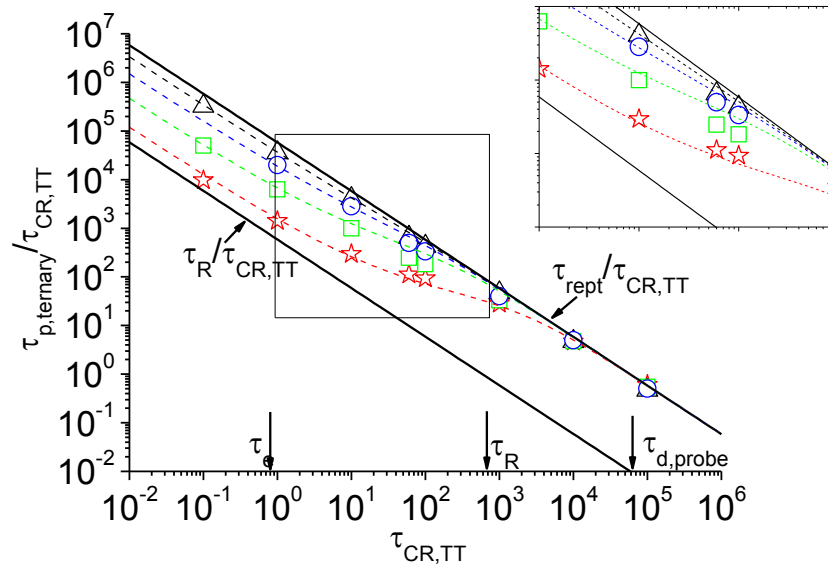


Figure 4.11: Comparison between theoretical predictions (solid colour lines) and simulation results (markers) of the longest relaxation time of the of probe chains entrapped inside moving skinny and fat tubes. All entanglements of the probe chain with the skinny tube have the same lifetime, $\tau_{CR,TT}$. Entanglements with other probe chains (represented by fat tube) have the original distribution of CR times $\tau_e < \tau_{CR,FT} < \tau_{rept}$ with major part relaxing at $\tau_{CR,FT} \sim \tau_{rept}$. The leftmost inclined black solid line represents terminal relaxation dominated by Rouse motion of the chain; the rightmost – reptation of the probe chain. Arrows show characteristic times of the chain relaxation τ_R , $\tau_e = \tau_R/Z^2$ and longest relaxation time of the probe chain, $\tau_{d,probe} \sim 57544$. The inlet shows zoomed in data points in the rectangular area. Color code is the same as in Figure 4.10.

Discrepancies between theory and simulations observed in Figure 4.11 can be explained by the influence of CR motion of the fat tube on the distribution of disentanglement times among the probe chains. The major part of the disentanglement times is still equal to τ_{rept} , however, a fraction of the probe chains now relaxes faster when $\tau_{CR,FT} < \tau_{rept}$ and this accelerates its terminal relaxation. Indeed, with respect to the theoretical predictions, simulation results show a slight deviation towards shorter relaxation times in the shoulder region (see inset in Figure 4.11), where relaxation is dominated by the skinny tube motion and therefore is proportional to $\tau_{CR,TT}$.

By analyzing the results shown in Figure 4.10, we can summarize the results of this section. There are three distinct scenarios for terminal relaxation of this system:

1. At $\tau_e > \tau_{CR,TT}$, chain relaxation terminates by chain reptation in the fat tube;
2. At $\tau_e < \tau_{CR,TT}$ terminal relaxation is due to effective CR motion of the skinny tube constrained by a permanent fat tube.
3. At $\tau_{rept} < \tau_{CR,TT}$ terminal relaxation is due to chain reptation in the skinny tube.

In the next section we will further analyze the systems plotted in Figure 4.11 and thus converge to the case of probe chains relaxing in a binary mixture.

4.5.5 Systems with two moving tubes.

In this section we discuss the relaxation of probe chains constrained by entanglements with two finite lifetimes. As a representative case of these systems, we analyze probe chains dispersed in a binary blend with shorter chains having fixed CR time and with long chains of broadly varying CR times (see system#3 on Figure 4.2).

In section 4.5.4 we concluded that the total friction of the skinny tube constrained by the permanent fat tube ζ_{TT}' is determined by a combined contribution from $\zeta_{CR,TT}$ and ζ_+ . However due to the infinite lifetime of permanent entanglements forming the fat tube, their contribution to the total friction was neglected in our calculations.

In order to determine all contributions to the total fat tube friction coefficient ζ_{FT} , we first imagine that lifetimes of the fat tube entanglements are the same as those of the skinny tube. Following the same reasoning as in the system with a single moving tube, where $\zeta_{CR,TT}$ is affected by ζ_0^{cm} and thus total friction of the moving tube is determined by combined contributions from both components: $(\zeta_{FT})^{0.5} = (\zeta_{CR,FT} + \zeta_{CR,TT})^{0.5} + (\zeta_0^{cm})^{0.5}$, where both components $\zeta_{CR,FT}$ and $\zeta_{CR,TT}$ are considered independent and equivalently affected by ζ_0^{cm} , since both types of entanglements are blinking. We can now assume that the slow blinking fraction of entanglements has lifetime, $\tau_{CR,FT} > \tau_{CR,TT}$, and therefore the probe chain is entrapped by the skinny as well as the fat moving tube. In this case, all faster blinking entanglements will influence $\zeta_{CR,FT}$. We can now compute total friction of the fat tube where contributions of all components are not independent and combined by an empirical law:

$$\zeta_{FT} = \left(\sqrt{\zeta_{CR,FT}(\phi; \tau_{CR,FT})} + \sqrt{\zeta_{CR,TT}(1-\phi; \tau_{CR,TT})} + \sqrt{\zeta_0^{cm}} \right)^2, \quad (4.13)$$

where the friction coefficient due to CR motion of the skinny tube, $\zeta_{CR,TT}$, is computed for $Z(1-\phi)$ tube segments using eq (4.2). For computing $\zeta_{CR,FT}$ we first assume that enlargement of the hopping amplitude follows the dilation of the fat tube: $a_{FT}^2 = a^2/\phi$. Following this assumption, total friction due to CR motion of the fat tube comprising $Z\phi$ segments can be computed as

$$\zeta_{CR,FT} = \frac{2\tau_{CR,FT}k_B T}{(A_{CR}b)^2} Z\phi^2 \quad (4.14)$$

In this equation the parameter A_{CR} is the same as in the case of the skinny tube CR motion (see Figure 4.9a).

For validation of the derived analytical equations, we run simulations for the probe chains entangled with slip-links having two distinct lifetimes $\tau_{CR,TT}(=60) \gg \tau_e$, and a wide range of $\tau_{CR,FT} \geq \tau_{CR,TT}$. In order to highlight terminal relaxation dominated purely by CR fat tube motion, we do not allow slip-links to diffuse out of the chain ends thereby prohibiting relaxation by chain reptation or CLF. Thus, in the case of well separated lifetimes of the fast and slow slip-links we expect transition from terminal relaxation by effective CR motion of the skinny tube to that due to the fat tube. The

simulations are conducted with good statistics (1000 chains) and long computation time (21 day).

Theoretical predictions of eq (4.13) are compared in Figure 4.12 with friction coefficients obtained from simulating MSD of chain's center of mass at the limit of $t \rightarrow \text{infinity}$ (see eq (4.6)).

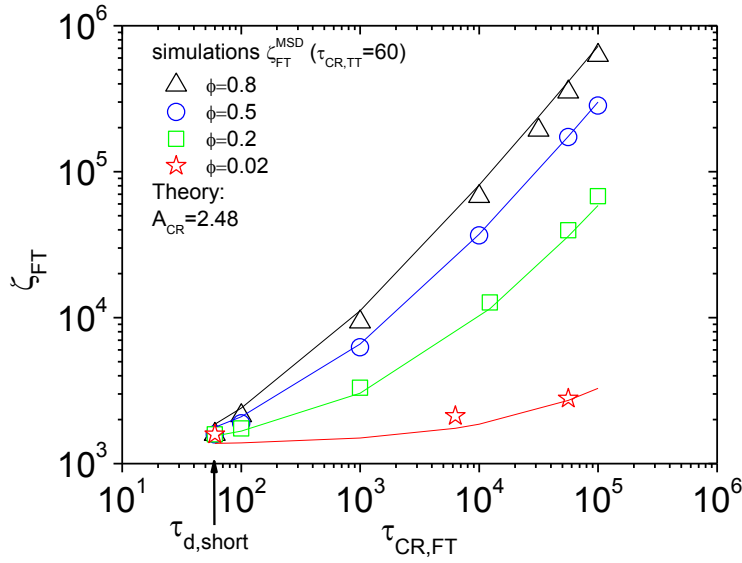


Figure 4.12 Total friction coefficient of the fat tube in the binary CR environment. Comparison of the theoretical predictions (solid lines) and the simulation results (markers). In the simulations, lifetime of slip-links representing entanglements with the short chains $\tau_{CR,TT}$ equals 60 for all the mixtures. Lifetimes of other slip-links representing entanglements with long chains vary over a broad range of values, $\tau_{CR,FT} > \tau_{CR,TT}$. Arrow shows longest relaxation time of the short chain $\tau_{d,short}=60$.

Comparison between theoretical predictions and simulations reveals slight systematic discrepancies at large $\tau_{CR,FT}$, where terminal relaxation is dominated by CR motion of the fat tube. This can be attributed to the increasing value of the prefactor $a^2/(A_{CR} \cdot b)^2$ defining jump amplitude of the chain with respect to the skinny tube diameter. This parameter has been considered constant in the case of single tube in eq (4.2).

Theoretical predictions of the terminal relaxation for chains with free ends and entangled with two types of finite lifetime obstacles can be computed by assuming

independence of effective motion of the fat tube, skinny tube and chain reptation in the skinny tube:

$$\tau_{p,binary} = \frac{L_{FT}^2}{\pi^2 k_B T} \zeta_{p,binary}, \quad (4.15)$$

where

$$\zeta_{p,binary} = \zeta_{FT,eff} + \zeta_{TT} + \zeta_{eff} \quad (4.16)$$

In the latter equation $\zeta_{FT,eff}$ is determined by projecting the chain motion of the fat tube due to the CR on L_{FT} . It can be computed by analogy with the previous sections:

$$\zeta_{FT,eff} = \frac{\zeta_{FT}}{Z\phi} \quad (4.17)$$

We can now compute the longest relaxation time due to CR motion of the fat tube by substituting eq. (4.17) in eq. (4.15):

$$\tau_{FT} = \frac{L_{FT}^2}{\pi^2 k_B T} \zeta_{FT,eff} \quad (4.18)$$

In order to validate eq (4.18), we run simulations of the probe chains constrained by different ratios of slip-links with two distinct lifetimes $\tau_{CR,TT}$ and $\tau_{CR,FT}$. As in simulations presented in Figure 4.9, the slip-links are not allowed to slip through the chain ends and thus chain relaxation is only due to CR motion of the skinny and fat tube. In Figure 4.13 we compare the simulation results and theoretical predictions of eq (4.18). Here termination by effective skinny tube motion combined with Rouse chain motions at $\tau_{CR,FT} \sim \tau_{CR,TT}$ is taken over by the effective fat tube motion with a broad transition zone in between. The inclined black solid line corresponds to termination by effective skinny tube motion, τ_{TT} . The horizontal dashed coloured lines indicate termination dominated by CR Rouse dynamics of the fat tube entanglements. The corresponding longest relaxation time is estimated as $\lim_{\tau_{CR,FT} \rightarrow \inf} \tau_{FT} \approx \frac{2}{3\pi^2} \tau_{CR,FT} (Z\phi)^2$.

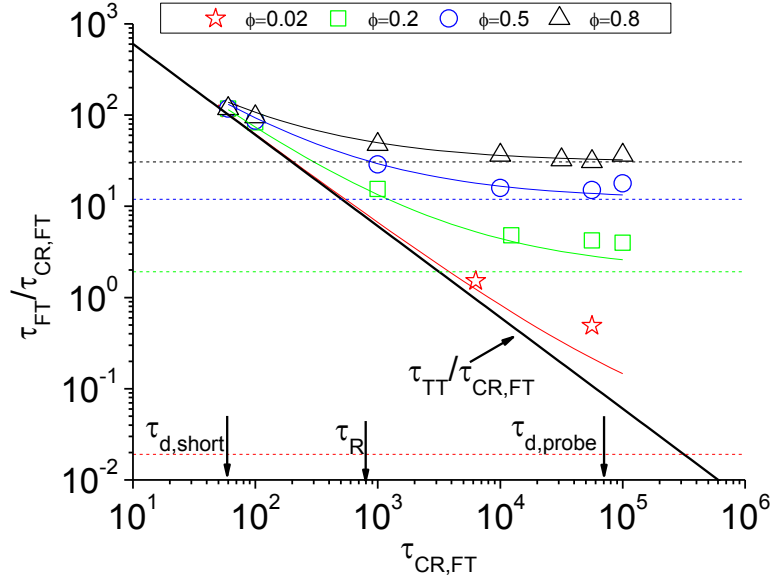


Figure 4.13: Normalized by $\tau_{CR,FT}$ longest end-to-end vector relaxation time of the chain due to CR motion of the fat tube. Markers and solid lines represent simulation data and theoretical prediction of the chain with fixed chain ends in different compositions of the “fast” and “slow” entanglements. Dashed coloured lines show longest CR Rouse time of the fat tube in corresponding compositions (see equation in the text). Inclined black solid line corresponds to extreme case when all entanglements have the same lifetime $\tau_{d,short} \sim \tau_{CR,TT} = 60$ and relax by effective skinny tube motion. Arrows show characteristic times of the chain relaxation τ_R , and longest relaxation time of the short and probe chains: $\tau_{d,short} = 60$ and $\tau_{d,probe} = 57544$.

Observed in Figure 4.13, systematic underprediction of the longest relaxation time in the range of large $\tau_{CR,FT}$ is in agreement with the corresponding observation for friction coefficients in Figure 4.12.

In order to validate eq (4.15) we run simulations of the probe chains constrained by different ratios of slip-links with two distinct lifetimes $\tau_{CR,TT}$ and $\tau_{CR,FT}$. Now the slip-links can freely diffuse out of the chain ends and thus permitting chain relaxation by reptation and CLF. In Figure 4.14 we compare simulation results of this model with the theoretical predictions of eq (4.15).

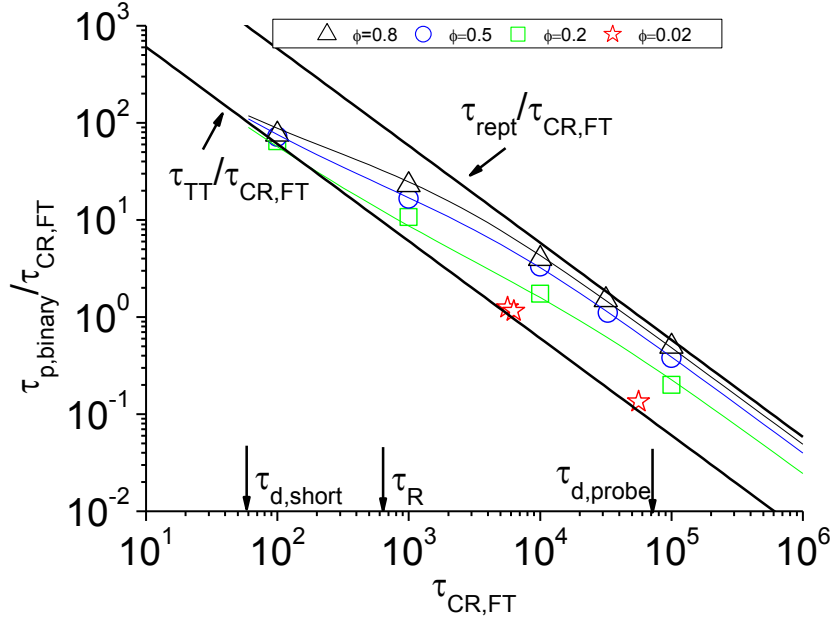


Figure 4.14: Normalized by $\tau_{CR,FT}$ longest relaxation time of the end-to-end vector of the probe chain with free chain ends in binary CR environment of different compositions. The theoretical predictions shown by dashed colored lines superimposed with the simulation data (markers). In all mixtures lifetime of entanglements with short chains $\tau_{CR,TT}=60$, whereas all entanglements with long chains have lifetime, $\tau_{CR,FT} \geq \tau_{CR,TT}$. The leftmost inclined black solid line corresponds to extreme case when all entanglements have the same lifetime and relax by the effective skinny tube motion, τ_{TT} ; the rightmost – reptation of the probe chain. Arrows show characteristic times of the chain relaxation τ_R , and longest relaxation time of the short and probe chains: $\tau_{d,short}=60$ and $\tau_{d,probe}=57544$.

Obtained results demonstrate the quantitatively good prediction of eq (4.15) as compared to the simulations. .

In Figure 4.14, all possible longest relaxation times depending on characteristic times and fractions of the fast and slow entanglements are localized between two inclined black solid lines designating terminal relaxations due to effective CR motion of the skinny tube, and chain reptation in the skinny tube, respectively.

The composition with the smallest fraction of long chains, shown by red stars in Figure 4.14, aligns with the left “border” thus indicating that concentration of long chains is not sufficient to form a fat tube ($N_{probe} \cdot \phi / N_e \leq 1$) and hence chains relax by competition

between chain reptation in the skinny tube and effective CR Rouse motion of the skinny tube (as discussed in section 4.5.3).

Data corresponding to larger fractions of long chains deviate from the left ‘border’ and pass through a shoulder at intermediate $\tau_{CR,FT}$. Unlike systems discussed in sections 4.5.4 and 4.5.3 the data points demonstrate a very broad shoulder spanning the range $\tau_{CR,TT} < \tau_{CR,FT} < \tau_{d,probe}$. This can be explained by a more complex correlation between all involved relaxation mechanisms, that significantly blurs separation of single dominant relaxation mechanisms for the analysed combinations of $\tau_{CR,TT}$ and $\tau_{CR,FT}$. As a result, discrepancies observed in figure 4.12 and discussed above in this section are screened by other relaxation modes.

None of compositions plotted in Figure 4.14 demonstrate terminal relaxation dominated purely by chain reptation in the skinny tube, as this would be illustrated by data aligned with the rightmost black inclined line. Instead, with further increase of $\tau_{CR,FT} > \tau_{rept}$, termination happens by effective CR motion of the skinny tube combined with a contribution from the chain reptation.

At largest $\tau_{CR,FT}$ we observe the same termination dominated by effective CR motion of the skinny tube as in Figure 4.10 at $\tau_{CR,TT} > \tau_e$. In order to observe termination dominated by τ_{rept} in the skinny tube, we would have to increase both $\tau_{CR,TT}$ and $\tau_{CR,FT}$ above τ_{rept} , otherwise effective CR motion of the skinny tube will always terminate relaxation.

To summarize, in this system with probe chains constrained by two types of entanglements, appearing and disappearing at constant frequencies $1/\tau_{CR,TT} = 1/60$ and $1/\tau_{CR,TT} > 1/\tau_{CR,FT}$, the terminal relaxation can be determined by one of the following scenarios:

- (1) If $\tau_{CR,FT} \sim \tau_{CR,TT}$ the relaxation terminates by effective CR motion of the single skinny tube;
- (2) If $Z\phi \gg 1$ and $\tau_{CR,TT} < \tau_{CR,FT} < \tau_{d,probe}$ the relaxation terminates by competition between effective CR motion of the fat and skinny tube;
- (3) If $\tau_{d,probe} < \tau_{CR,FT}$ the relaxation terminates by competition between chain reptation in the skinny tube and effective CR motion of the skinny tube constrained by the fat tube.

4.6 Effect of CR polydispersity (in monodisperse melts and binary blends).

Throughout this chapter, by analysing the effect of constant single and double CR rates on the relaxation of a probe chain, we have found that the longest relaxation time of the end-to-end vector of a probe chain is in fact affected by the dynamics of all topological constraints with a lifetime shorter than its own reptation time in the skinny tube.

For interpreting end-to-end vector relaxation times of the realistic systems presented in the experimental section 4.5.2 (the rheological data is presented in Figure 4.6-Figure 4.8) we have to take into account that the distribution of CR rates in these mixtures depends not only on the number of components in the mixtures but also on the relaxation times spectrum of every single component. Besides, the effect from other chains on those entangled with the probe should also be taken into account in the same way as was analysed in the previous sections. In this section we compare theoretically predicted $\tau_{p,ternary}$ and $\tau_{p,binary}$ with end-to-end vector relaxation times of a probe chain in the ternary and binary mixtures tested in section 4.5.2..

In the ternary blends (short+probe+gel), the fraction of the short chains varies from 0 to 80%, whereas the fraction of the probe chains is approx. 3%, which corresponds to the mutual entanglement limit $\phi = M_e/M_{w,p}$. Thus, the major part of probe chains entanglements is with effectively immobile gel chains on one hand and fast moving short chains on the other.

In the first estimate, we neglect all relaxation modes of the short chains faster than their longest relaxation time, as determined from their relaxation on top of the gel chains (rheological data is presented in Figure 4.6). Assuming that, at the time scale of the probe chains relaxation, the major part of their entanglements with the gel are permanent, we use equation (4.12) with $\tau_{CR,TT}=60$ for predicting their relaxation time in the ternary blend. In Figure 4.15(a) we superimpose the obtained theoretical predictions with the simulation results, completed with (not shown in Figure 4.7) ternary blend 3-probe/50-short/47-gel. Data point at $\phi_s=0\%$ corresponds to the binary blend of probe chains diluted in excess of the “gel” chains (see Figure 4.6).

In the binary mixtures, concentration of the short chains is kept the same as in the ternary, but a fraction of gel is replaced by probe chains with molecular weight $M_{w,p}$, therefore probe chains are entangled with same fractions of fast moving short chains as in the ternary blends but also with other probe chains.

In order to compare simulation predictions with theory for binary blends, we recognize that constraint release times of entanglements between probe chains are influenced by their respective entanglements with short chains. In order to estimate “effective” values of the constraint release times we apply a self-consistent algorithm. In this algorithm effective constraint release times between probe chains having $i+1$ entanglements with short chain are computed as $\tau_{CR,FT}^{(i+1)} = \tau_{d,binary}^{(i)}$, where $i=1 \dots Z-1$ and $\tau_{d,binary}^{(i)}$ is obtained using eq. 4.15. In the first step of this calculation $\tau_{CR,TT}^{(1)}=60$ and $\tau_{CR,FT}^{(1)}=57544$, which corresponds to the longest relaxation times of the short and probe chains diluted in the gel (see Figure 4.6). In these calculations, we neglect the part of the relaxation spectrum of the short and probe chains which is faster than $\tau_{d,s}$ and $\tau_{d,probe}$, respectively. Thus, $\tau_{CR,TT}$ remains unaffected in all blend compositions.

In Figure 4.15b we compare these theoretical predictions with two sets of simulation data. In the first set, the fraction of slip-links corresponding to entanglements with the short chains has constant lifetime $\tau_{CR,TT}=60$, whereas values of $\tau_{CR,FT}$ are determined by the CR algorithm implemented in standard slip-spring model. Second set of data is obtained from simulations of the binary blend (short+probe), where lifetimes of all entanglements are defined by the standard CR algorithm of the model. The presented

simulation data are completed with the 50/50 binary blend (not shown in Figure 4.8). Data point at $\phi_s=0\%$ corresponds to the relaxation time of monodisperse probe chains.

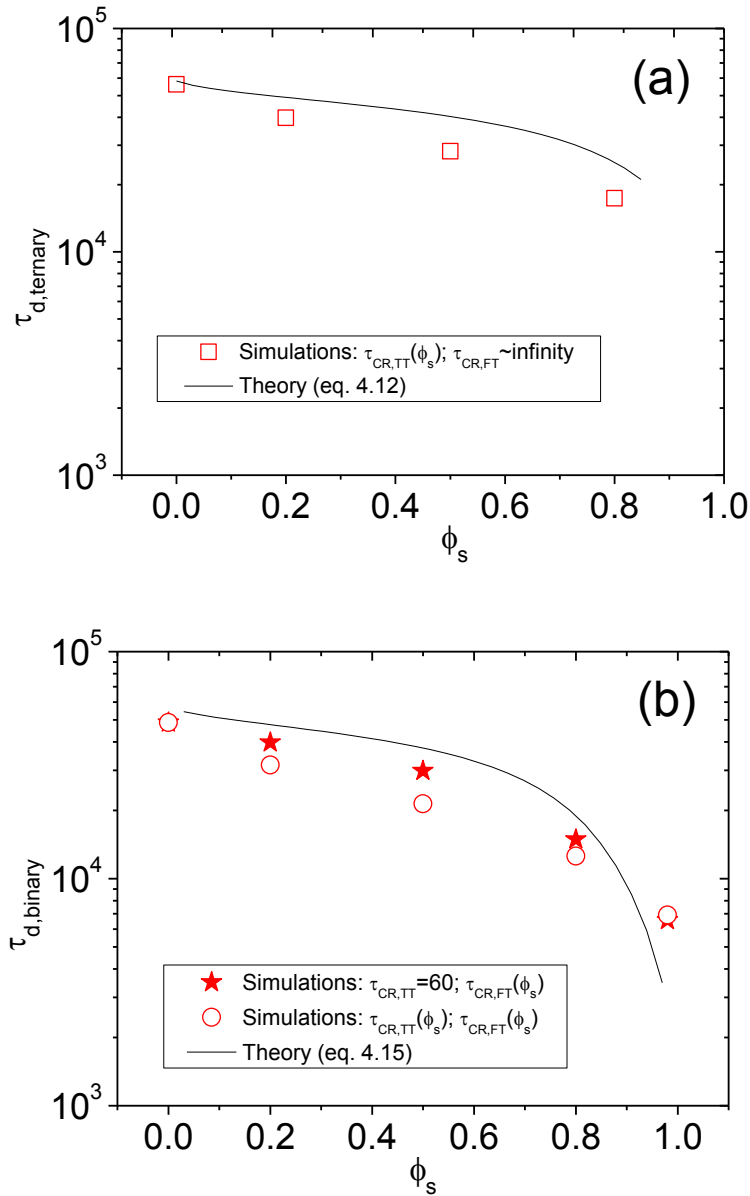


Figure 4.15: Comparison of the theoretically predicted (solid lines) and simulated results (markers) of the probe's end-to-end vector relaxation in the (a) ternary and (b) binary mixtures of probe+short+gel chains and probe+short chains with the same fraction of the short chains, respectively. In the simulated data shown by red stars in (b) fraction of slip-links corresponding to fraction of entanglements with short chains has constant disentanglement rate (1/60), whereas other slip-links disappear and appear again with rate controlled by CR algorithm of the standard slip-spring model. Data points shown by red squares in (a) and circles in (b) correspond to simulation results with the slip-link's life time controlled by CR algorithm of the standard slip-spring model.

The results presented in Figure 4.15 show qualitative agreement. The gradually increasing discrepancy at high ϕ_s is due to the multiple disentanglement rates not accounted for in the theoretical predictions. Too fast relaxation predicted at $\phi_s=0.98$ in Figure 4.15b can be attributed to the very low fraction of the probe chains, which not sufficient to form the fat tube. For predicting this case, eq. 4.5 corresponding to chain relaxation in the sole skinny tube has to be used.

By further analyzing simulation data of the binary and ternary mixtures presented in Figure 4.15 we aim to answer the following questions:

What is the effect of CR on the probe end-to-end vector relaxation time in its monodisperse melt and how does this effect depend on molecular weight? Is longest relaxation time of the probe chains entangled with the same fraction of the short chains different in the binary (probe+short) and ternary (probe+short+gel) mixtures?

In order to answer these questions we plot ratio of longest end-to-end vector relaxation times of the probe and short chains in their ternary and binary blends. In Figure 4.16 data points corresponding to 0 and 100% concentration of the short chains represent the effect of CR in monodisperse melts of the probe and short chains, respectively. The figure shows that the effect of CR in monodisperse melts of short chains (with approx. 4.5 entanglements) is stronger by approximately 50% with respect to that in monodisperse probe chains (with approx. 33 entanglements).

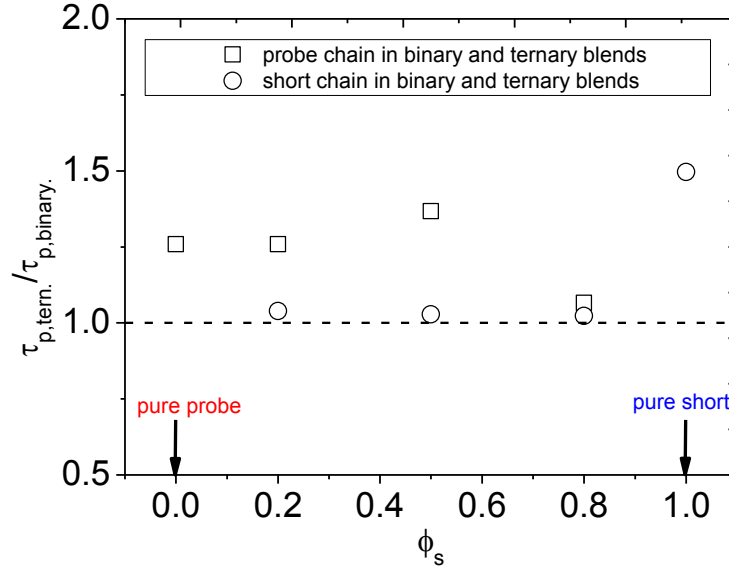


Figure 4.16: Ratio of the simulated longest relaxation times of the short chain ($N=18$) and probe chain ($N=132$) diluted in the binary short chain/probe chain and ternary short/probe/gel ($N=804$) blends. In the binary and ternary blends fraction of short/probe entanglements $\phi_s=0, 0.2, 0.5, 0.8, 1$. Fraction of probe chains in the ternary blends $\phi_p=0.03$.

In section 4.5.3 and 4.5.4 we have shown that if $\phi > 0$ the longest relaxation time of the probe chains with respect to the time of CR can be reduced only if $\tau_{CR} < \tau_{rept,probe}$, where $\tau_{rept,probe} \sim (M_{w,p}/M_e)^3$. If $\tau_{CR,TT} < \tau_e$ probe chains relax by reptation in the fat tube of diameter $a/\phi^{0.5}$ and by reptation in the skinny tube of diameter a when $\tau_{CR,TT} \geq \tau_{rept,probe}$. Thus, the biggest effect on the longest relaxation time can be observed for the larger fraction of entanglements with the highest CR rate ($\sim 1/\tau_e$).

The longest end-to-end vector relaxation time of probe chains in the binary blends (the rheological data are shown in Figure 4.8) can be reduced by two effects, namely, the entire fraction of short chains ϕ_s and the fast-relaxing fraction of other probe chains $\phi < \phi_p$ with $\tau_{CR} < \tau_{rept,probe}$, where τ_{CR} is the lifetime of any entanglements. It should be noted, that distribution of relaxation times of other probe chains is also affected by the same fraction of short chains and therefore respective contributions from these two accelerating effects vary in different composition of the blends. The effect from other probe chains in the binary blends only slightly depends on their fraction and remains comparable to the monodisperse case if $\phi_s < 0.5$ (see square markers in Figure 4.16). However, this behavior is non monotonous, and above $\phi_s=0.5$ the effect from increasing

fraction of the short chains starts to prevail over the influence from other probe chains and becomes comparable to that in the ternary blends.

Following the same reasoning, the reduced relaxation time of short chains in the binary and ternary blends is only due to broad distribution of CR times of other short chains and in the case of the binary blends, the contribution is partially from the small fraction of fast relaxing probe chains with $\tau_{CR} < (M_{w,s}/M_e)^3$.

4.7 Conclusions

In this study we have proposed and verified a method for predicting the effect of CR environment on the relaxation of the end-to-end vector of probe chains in well controlled “model systems” containing unrelaxing chains and/or fast relaxing chains. Experimental data have been confronted with simulations by the slip-spring model, which was later used as a benchmark for validating predictions by a very detailed tube model. For the latter, we follow the CR picture reported in *Viovy et al., 1991* and implement (and refine) the effective chain friction in the fat tube based on ideas of *Read et al. (D.Read et al., 2012)*. The main results are as follows:

- The slip-spring model was successfully validated by simultaneous predictions of the viscoelastic and dielectric relaxation of the monodisperse and binary melts of linear polymers;
- We have found that the longest relaxation time of the end-to-end vector of the probe chain is in fact affected by dynamics of all topological constraints with a lifetime shorter than its own reptation time in the skinny tube.
- Based on an analysis of the effective friction coefficient in the skinny and fat tubes we have proposed an analytical equations for predicting the longest end-to-end vector relaxation times of the probe chain in any monodisperse and binary

environment of topological constraints. In this equation, an adjustable parameter A_{CR} is used and is related to the chain segment jumping amplitude in the event of constraint release. This parameter is determined by fitting the simplest system where all entanglements are blinking at the same frequency and later it is used without adjustment for more complex CR environments. This equation has been validated by comparison with simulation data of mean square displacement of the chain center of mass and longest relaxation time of the end-to-end vector.

- The longest relaxation time of the end-to-end vector of probe chains in a binary blend with short chains is determined by a competition between independent relaxations of the chain in the skinny tube and effective CR motion of the skinny and fat tubes. However, due to the complex combination of different relaxation modes, it seems barely possible to effectively separate dominant relaxation mechanisms responsible for the terminal relaxation.
- In agreement with recent experimental observations in ref (*Matsumiya et al., 2012*) we have found that CR accelerates the end-to-end vector relaxation time in monodisperse melts. Moreover, the effect of CR in monodisperse melts of short chains of $M_w=7.5k$ ($Z=4.5$) is larger with respect to that in the probe chains of $M_w=51k$ ($Z=33$) by approximately 50%. We attribute this to the broader spectrum of disentanglement rates of the short chains.

Finally, the methodology developed in this work can be systematically extended to include a larger number of disentanglement rates. Implementation of the obtained results to tube models could be used for improving predictions of the tube survival fraction and zero shear viscosity in the systems with complex constraint release environments, i.e. polydisperse in chain length and even architecture.

Chapter 5:

THE EFFECT OF MOLECULAR WEIGHT DISTRIBUTION OF INDUSTRIAL POLYSTYRENE ON ITS MELT EXTENSIONAL AND ULTIMATE PROPERTIES.

Abstract.

In most processing operations, the polymer undergoes complex combinations of shear and elongation over a broad range of deformation amplitudes and rates. Understanding and predicting rheological properties during processing as well as the ability of the melt to undergo the applied stresses without catastrophic failure or instability is thus of primary importance. In previous chapters we have extensively discussed the effect of constraint release (CR) and its relationship with molecular structure on linear viscoelastic and dielectric relaxation of model polymer melts characterized by well-defined molecular structure. In this chapter, we try to use some of these molecular rheology concepts in situations relevant to industrial processes dominated by extensional deformation.

Results of this study are currently being prepared for the publication.

5.1. Introduction

Generally, it is very challenging to mimic material behaviour during complex processing operations using commercially available rheometric setups. However, some operations are dominated by a single type of deformation. This is, for instance, the case of fibre spinning, film tenting or film blowing, where the process is controlled by (non isothermal) uniaxial or biaxial deformation. It is therefore of primary importance to understand the rate and temperature-dependent extensional properties of polymers to predict behaviour in processing operations. Although true rheometers capable of controlling biaxial extension kinematics and measure the resulting stresses are practically unavailable, the situation is fortunately different for uniaxial extension which is qualitatively related to biaxial extension. Indeed, since a few years, additional fixtures

for measuring extensional viscosity at different extension rates are available in commercial rheometers (besides the limited availability of a handful of dedicated extensional rheometers).

5.2. Literature review and objectives of the chapter.

Previous attempts to understand a link between rheological properties of polymer structures and different morphological characteristics of the end product show that polymer melts characterized by enhanced strain hardening (or extensional-thickening) and high strain-at-rupture provide better extensibility with more homogeneous morphology (*J.Wang, PhD report, 2009*).

In references (*Spitael, Macosko, 2004; Naguib and Park, 2002*), the authors study extensional behavior of linear and branched polymers by comparing different structural characteristics of the final product. Results of their experimental correlation between uniaxial extension and biaxial extension dominated processes demonstrate that a linear polymer matrix exhibiting no strain hardening is also characterized by worse morphological characteristics in comparison with branched polymers with pronounced strain hardening.

On the other hand (*Stange and Münstedt, 2006*) argue that different molecular structures characterized by similar strain hardening behavior, lead to comparable extensional behavior. Besides, the authors also show that the existence of strain hardening itself is an important but not sufficient characteristic for extension dominated processes. Namely, the dominating factor is the correspondence between the characteristic processing strain rate and the strain rate at which hardening occurs. Moreover, the uniformity of deformation in the strain hardening phase is also a critical parameter.

Strain hardening, also known as extensional thickening, can be described as the resistance of the polymer melt to stretching. This is defined as steep increase of

elongational viscosity at large strain which deviates from the linear viscoelastic envelope. This material characteristic is related to the molecular entanglements of the polymer and resistance to disentangling under applied strain at a given strain rate. The polymer properties affecting the resistance to disentangling are molecular architecture (long-chain branching) (*Spitael, Macosko, 2004; Gotsis, et al., 2002; Wagner, et al., 2000*), molecular weight, molecular-weight distribution (MWD) (*Ye, Sridhar, 2005; Sugimoto, et al., 1999; Sugimoto, et al., 2001*), effective entanglement molecular weight (*Huang et al., 2013*).

This chapter builds on observations and predictions that dilution of an entangled polymer by an unentangled diluent can dramatically increase strain hardening.

The extensional flowing behavior of entangled and unentangled polymer solutions has been extensively studied by (*Bhattacharjee et al., 2002 ; Bhattacharjee et al. 2003; Ye, Sridhar, 2005; Gupta et al., 2000 ; Doyle et al., 1998*). Experimental observations of steady-state extensional viscosity as function of Hencky strain rate revealed fundamental difference between the behavior of polymer solutions and melts (*Bach et al., 2003; Wagner et al., 2005; Luap et al., 2005*). In particular, when the Hencky strain rate $\dot{\epsilon}_H$ increases above the reciprocal disentanglement time of melts and solutions of entangled linear chains $\sim 1/\tau_d$ the steady-state extensional viscosity was shown to scale as $\eta_{E,steady} \propto \dot{\epsilon}^{-1/2}$. However, when further increasing the extensional rate, steady state extensional viscosity of entangled solutions shows an upturn at extension rates above reciprocal Rouse time of the whole chain $\sim 1/\tau_R$, whereas $\eta_{E,steady}$ of melts does not show this hardening behavior and keeps decreasing roughly as $\eta_{E,steady} \propto \dot{\epsilon}^{-1/2}$. Besides, a recent study of linear shear and uniaxial extension flow of concentrated polymer solutions by (*Huang et al., 2013*) shows that polymer melts and entangled solutions having the same number of entanglements are characterized by similar behavior under small angle oscillatory shear. However, characterization in strong extensional flow reveals that strain hardening behavior of solutions is markedly enhanced as compared to melts. The explanation of this behavior can be partially attributed to increased chain extensibility.

Recently (*Yaoita et al., 2012; Ianniruberto et al., 2012; Masubuchi et al., 2014*) have employed stochastic simulations to propose a more detailed picture explaining the difference in strain hardening behavior of solutions and melts. The idea is based on reduction of monomer friction which mitigates chain stretch and consequently strain hardening as a result of strong Kuhn segment orientation induced by fast elongational flow. In melts this orientation is much stronger by comparison with solutions, where isotropic solvent molecules reduce the average orientation in the system, which leads to enhanced strain hardening as compared to melts.

The specific objective of this chapter is thus to investigate the effect of poorly entangled and unentangled diluents on the viscoelastic properties of well entangled linear PS matrix. We will study the influence of diluents and molar mass distributions on those characteristics.

The chapter is organized as follows: In section 5.3 we describe the materials and methodology used in this study. This section includes details of sample preparation, small angle oscillatory shear and uniaxial elongation measurements. In section 5.4 we discuss results of the conducted experiments and end with conclusions.

5.3. Materials and methods.

5.3.1. Materials.

We test mixtures having monomodal and bimodal molecular weight distributions. The bimodal systems are prepared by mixing a well entangled PS matrix (PSM) with an unentangled styrenic diluent, referred to as “D1”. A monomodal mixture is prepared by mixing the same PS matrix with a fraction of poorly entangled PS referred to as D2.

We also analyze the effect of concentration of D1 in mixtures, referred to as “PSD20” and “PSD44”. As we want to avoid significant reduction of T_g or phase separation upon dilution, the diluents (D1 and D2) have full miscibility with, and close T_g to the matrix.

All mixtures have been prepared by blending in a Brabender twin-screw extruder at $T=220^{\circ}\text{C}$. In order to verify that these conditions will not lead to the degradation of the mixture prior to blending both components have been extruded and no changes in MFI have been detected.

The glass transition temperatures are measured using Mettler Toledo DSC 821e at heating rate $10^{\circ}\text{C}/\text{min}$.

The table below summarizes the description of all the materials used.

Table 5.1: Description of the materials.

SAMPLE	DESCRIPTION
<i>PS-matrix</i>	
PSM	Pure PS matrix ($T_g \sim 105^{\circ}\text{C}$)
<i>Diluents</i>	
D1	Styrenic oligomer ($T_g \sim 95^{\circ}\text{C}$)
D2	Poorly entangled PS ($T_g \sim 102^{\circ}\text{C}$)
<i>Effect of diluent's M_w</i>	
Monomodal	65/35 D2/PSM
PSD60	60/40 D1/PSM
<i>Effect of diluent concentration</i>	
PSD44	44/56 D1/PSM
PSD20	20/80 D1/PSM

5.4. Molecular characterization.

The characterization of the samples with respect to the molecular weight distribution was carried out by size-exclusion chromatography (SEC) coupled with a multiangle laser light scattering (MALLS) detector, and a refractive index detector. This method allows determination of the absolute mass average molecular weight of each SEC fraction.

5.5. Rheological measurements in shear.

All measurements of small angle oscillatory shear are conducted using a parallel plate 8mm fixture at constant temperatures of 130, 150 and 170°C in the frequency range 0.01-100 rad/s. For constructing master curves we used the REPTATE software (Ramirez, J.; Likhtman, A.E. <http://reptate.com>, 2009). The time-temperature superposition principle has been used with shift factors determined from WLF parameters: $C_1=8.57$, $C_2=-46.65\text{K}$ for $T_{ref}=120^\circ\text{C}$. The temperature effect on density is taken into account according to the expression $G(T_0)=G(T)/b_T$, where

$$b_T = \frac{\rho(T)T}{\rho(T_{ref})T_{ref}} = \frac{(\rho_0 - T.C_3 10^{-3})(T + 273.15)}{(\rho_0 - T_{ref}.C_3 10^{-3})(T_{ref} + 273.15)}$$

was introduced with values of the parameters characteristic for PS $C_3=0.69$, and $\rho_0=\rho(T=0^\circ\text{C})=1.05\text{g/cm}^3$.

5.6. Rheological measurements in elongation.

Extensional viscosity measurements are conducted using an ARES-rheometer with extensional viscosity fixture (EVF) (see Figure 5.1) at five Hencky strain rates: 0.01, 0.03, 0.1, 0.3, 1.0 s^{-1} and $T_{ref}=120^\circ\text{C}$.



Figure 5.1: Extensional viscosity fixture consists of a fixed and rotating drum, which winds up the sample at constant Hencky strain rate, while measuring the force generated in the sample. Since the torque measurement is decoupled from the motor, no bearing friction correction is required. The picture is adapted from <http://www.tainstruments.com/>.

All samples for the extensional rheology measurements are prepared from granular material using a hot press. Material is compressed during 25-30 min at temperature 150°C. The long molding time is important to obtain stress-free equilibrated samples. Homogeneous rectangular plates made in this way are cut manually using a razor blade to produce strips with dimensions (20mm(length) x 3mm(width) x 1mm(thickness)) appropriate for uniaxial extension.

It should be noted that all measurements of stress growth in this study are limited by the design features of the EVF fixture used. Thus, when strain reaches an approximate value of 2.9-3.1 the sample starts to overlay on itself thus causing discontinuity of measured data.

5.7. Results and discussions.

5.7.1. Molecular characterization.

The weight average molecular weight, M_w , and polydispersity index, $PDI=M_w/M_n$ are presented in Figure 5.2 and summarized in Table 5.2 for all materials described in Table 5.1.

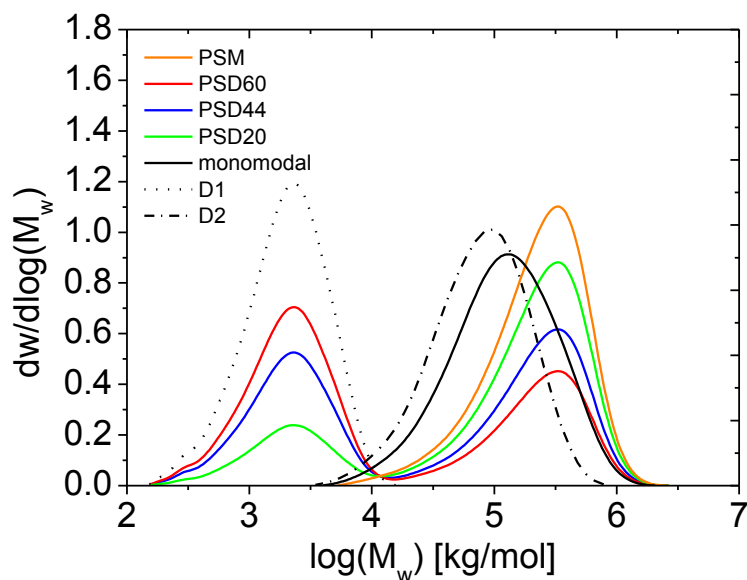


Figure 5.2: Molecular weight distributions for all the materials.

From the results of SEC-MALLS analysis, two well separated MWD's corresponding to unentangled D1 (on the left) and well entangled matrix PSM (on the right) can be distinguished. It must be noted that major fraction of D1 is below entanglement molecular weight, which for PS is about $M_e \sim 13\text{-}16$ kg/mol. On the other hand, MWD of "monomodal" is obviously broader by comparison with that of PSM.

Table 5.2: Results from the SEC-MALLS analysis of all materials.

Material	M_w , kg/mol	PDI
PSM	306.5	2.45
Monomodal	182	2.64
PSD60	-	-
PSD20	-	-
PSD44	-	-
D2	116.7	2.22
D1	2.6	1.86

5.7.2. Linear shear rheology.

As mentioned above, linear shear rheology measurements are conducted at different temperatures and later shifted according to TTS in order to construct master-curves at $T_{ref}=120^{\circ}\text{C}$.

In this section, we measure and compare main linear rheological properties of all the materials. *Viscosity* is represented by the complex viscosity of the sample, $\eta^*(\omega)$ and the zero shear rate viscosity, η_0 , which according to Cox-Merz rule can be determined as (Cox, Merz, 1958):

$$\eta^*(\omega) = \eta(\dot{\gamma}) \Big|_{\dot{\gamma}=\omega}$$

Elasticity is represented by the entanglement modulus of the sample, $G_e=\rho RT/M_e$, where ρ is a density, R – universal gas constant; T – absolute temperature; M_e – entanglement molecular weight. It must be noted that G_e is about 20% higher than G_N^0 (plateau modulus), which can also be observed as a visual plateau of $G'(\omega)$. However, in the case of polydisperse systems this plateau is not well distinguished. Thus for simplicity in future discussions we will refer to G_e as the plateau modulus.

The linear rheology measurement results for all materials are presented in Figure 5.3 and Figure 5.4.

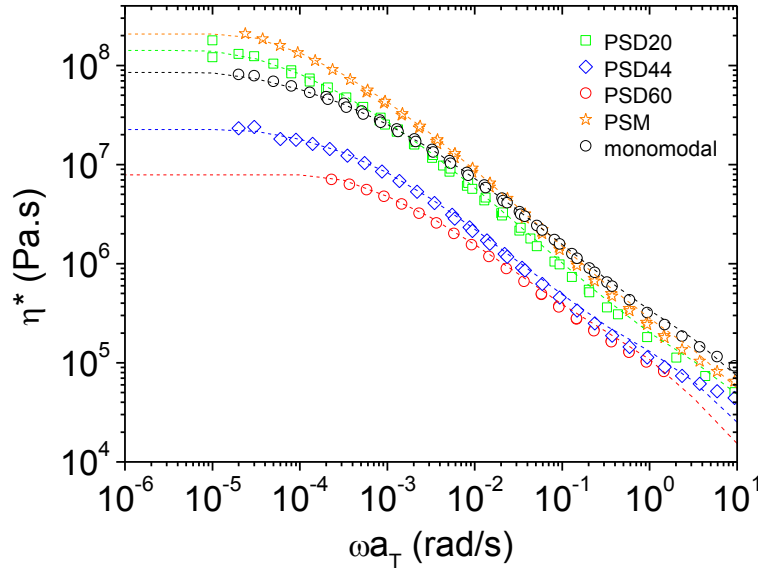


Figure 5.3: Dynamic shear viscosity (open symbols) obtained at $T_{ref}=120^{\circ}\text{C}$ for all materials. Dashed lines show Maxwell model prediction.

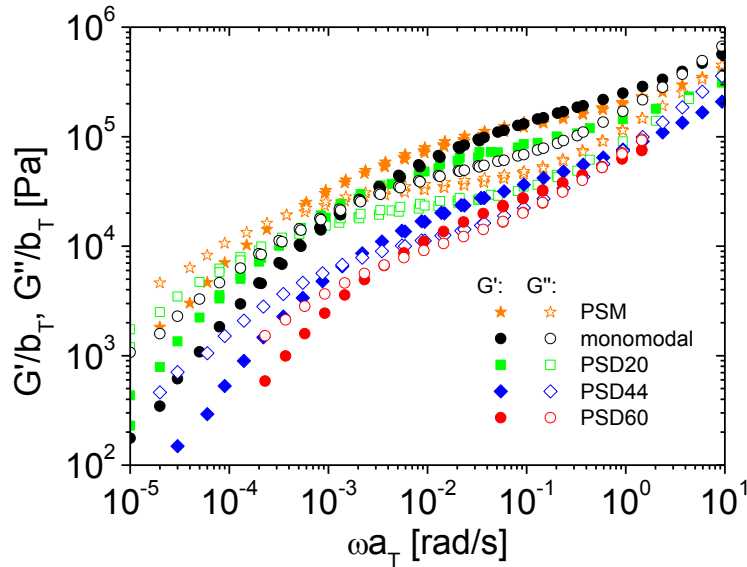


Figure 5.4: Master curves for the dynamic shear modulus for all materials (reference temperature 120°C).

In the table below we present numerical values of the plateau modulus and zero shear viscosity obtained from data in Figure 3 and Figure 4. The values of G_e are determined as modulus corresponding to the high-frequency cross-over between $G'(\omega)$ and $G''(\omega)$. The frequency corresponding to this cross-over determines entanglement Rouse time, τ_e , of the respective material.

It can be noticed that the high-frequency cross-over of every material is shifted with respect to PSM and “monomodal” towards lower frequencies proportionally to the fraction of oligomeric diluent. Thus the largest shift with respect to that of PSM and “monomodal” is that of PSD60. This shift can be attributed to the combined effect of different T_g of the materials and dilation effect on entanglement molecular weight, resulting in different entanglement Rouse time. This effect will be discussed with more details later.

The zero shear viscosity data is determined from extrapolated by Maxwell model constant values of $\eta^*(\omega)$.

Table 5.3: Linear viscoelastic material parameters for all studied materials measured at $T_{ref}=120^\circ\text{C}$.

	$G_e [Pa]$	$\eta_0 [Pa.s]$
PSM	3.3E5	2.1E8
PSD60	0.5E5	7.9E6
PSD44	0.97E5	2.2E7
PSD20	2.33E5	1.4E8
Monomodal	3.7E5	8.5E7

The results in Figure 5.3 and Table 5.3 show that the effect of a bimodal distribution of molecular weights is pronounced in both linear viscoelastic characteristics. On the other hand, mixing with a comparable fraction of even poorly entangled diluent D2 has milder effect on G_e and η_0 .

In terms of the tube picture, the observed differences in material behavior can be explained using tube dilation theory (*Marucci, 1985; Viovy, 1985*). According to this theory, right after the load has been applied the lateral motions of the probe chain are constrained by the imaginary tube formed by all types of entanglements (with chains of all M_w from the distribution). The tube has a diameter a and length L . Relaxation of fast relaxing fraction of the mixture’s MWD causes tube dilation followed by effective increase of the tube diameter $a=a_0/\phi^{d/2}$ and thus corresponding increase of effective

entanglement molecular weight $M_e = M_{e,0}/\phi^d$, where ϕ is the weight fraction of the polymer matrix in the solution and d is the dilution exponent whose value is close to unity. Therefore the effect of mixing well entangled PSM with "instantaneously" relaxing unentangled diluent D1 becomes obvious already at the high-frequency range. On the other hand, average molecular weights of PSM and D2 are not well separated, i.e. their longest relaxation times have comparable orders of magnitude ($\sim M_w^3$). Therefore the effect of D2 on relaxation of PSM can only be observed in the terminal relaxation zone after complete relaxation of the diluent.

The observed discrepancy between the plateau moduli of "monomodal" and PSM is in the range of $\sim 12\%$, close to experimental error. It is clearly not related to CR and can only be explained by differences in sample loading during the measurements.

In the figure below we plot G_e and τ_d for mixtures with different fraction of D1. The longest relaxation time, τ_d , is determined as time inverse to the low-frequency cross-over between $G'(\omega)$ and $G''(\omega)$ in Figure 5.4.

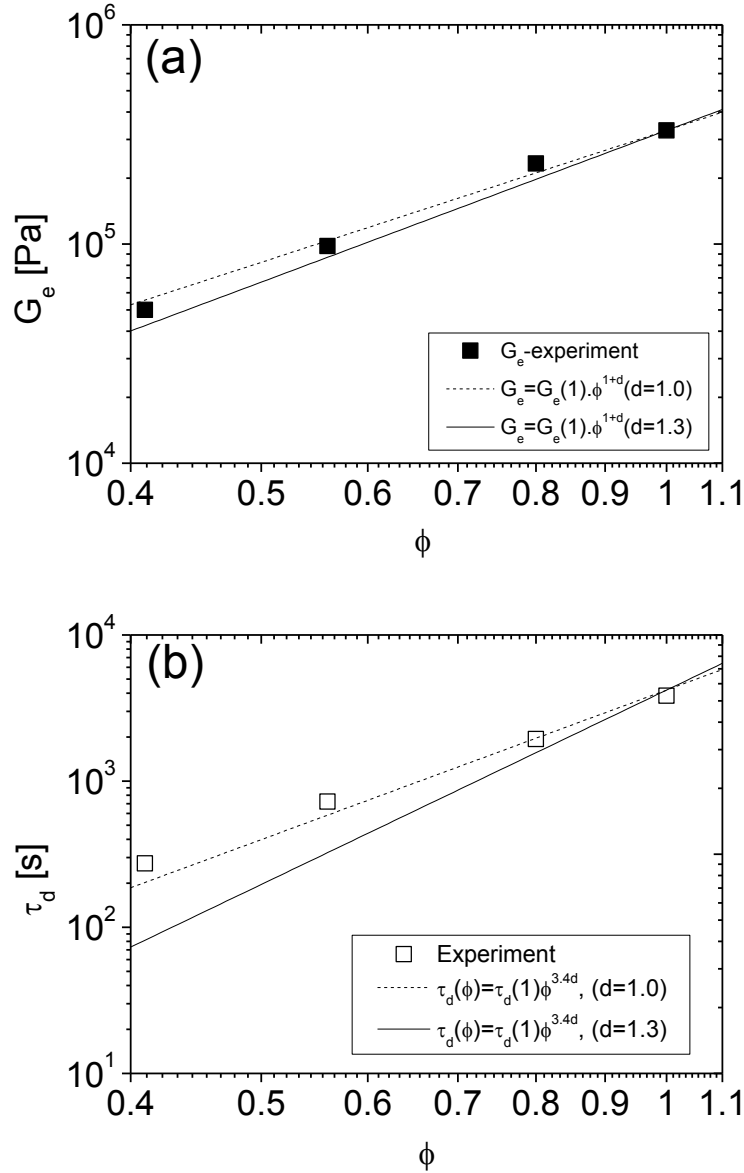


Figure 5.5: Determination of the dilution exponent, d . (a) Scaling of the plateau modulus G_e as function of PSM fraction in the solution $\phi=1-\phi_{DI}$. Numerical values of G_e are determined as corresponding to the high-frequency cross-over between $G'(\omega)$ and $G''(\omega)$; (b) The longest relaxation time, τ_d , as function of ϕ is determined as time inverse to the low-frequency cross-over between $G'(\omega)$ and $G''(\omega)$. Solid lines on both plots correspond to $d=1.3$, dashed lines correspond to $d=1.0$.

For analysis of the dilution exponent we anticipate $G_e \sim \phi^{1+d}$ and $\tau_d \sim \phi^{3.4d}$. From the curves plotted in Figure 5.5 it can be concluded that the best predictions of the diluting effect on G_e and τ_d are obtained with $d=1.0$. This value of the dilution exponent is in accordance with earlier published results for well-defined polymer systems, where $d=1.0$ or 1.3 depending on the model used to analyze the data (*Bhattacharjee et al.*

2002; Larson, 2001; Park; Larson, 2003) and (Auhl, et al., 2009; Watanabe et al. 2004).

5.7.3. Extensional rheology.

In Figure 5.6, results for extensional behavior of all the materials are presented as time-dependent stress growth coefficients, defined as

$$\eta_E^+(t) = \sigma_E(t) / \dot{\epsilon}_H$$

where Hencky strain is defined as $\epsilon_H = \ln(L(t)/L(0))$, with L – length of the sample.

As can be clearly seen from the divergence from their respective linear viscosity envelopes, all studied materials are characterized by strain hardening behavior at every measured Hencky strain rate. This means that applied extension rates are all above the reciprocal effective stretch relaxation time (Auhl et al., 2009). This relaxation time is related to the lowest deformation rate for strain hardening in steady elongational flow. For well-defined linear mixtures of nearly monodisperse short and long chains, this time has been determined as $\sim \tau_R / \phi^d$, where the Rouse time of the pure long chains is defined as $\tau_R = \tau_e Z^2$ with Z - total number of entanglements per long chain and τ_e is the Rouse relaxation time of a single entanglement segment (Auhl et al., 2009). It would be of interest to analyze the effect of polydispersity on the concentration dependence of the effective stretch relaxation time, however we leave this for future studies.

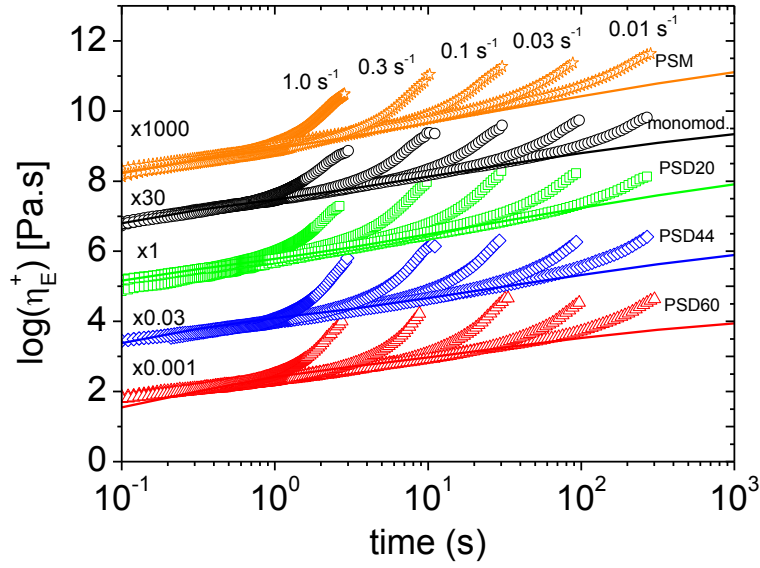


Figure 5.6: Stress growth coefficient η_E^+ as a function of time, t , at different Hencky strain rates, $\dot{\epsilon}_H$, obtained at $T_{ref}=120^\circ\text{C}$ for all materials. Curves are shifted in vertical direction for a better visualization according to the numbers indicated. Linear viscosity in extension for every material is shown by solid lines of respective color.

Quantitative differences between strain hardening behavior of the materials are best seen in Figure 5.7, where so-called strain hardening coefficients are plotted.

The strain hardening coefficient is defined as the stress growth coefficient normalized by linear extensional viscosity:

$$X_E(t, \dot{\epsilon}_H) = \eta_E^+(t, \dot{\epsilon}_H) / \eta_{E,0}(t)$$

The linear extensional viscosity envelope can be obtained from measured complex shear modulus $G'(\omega)$, $G''(\omega)$ and decomposition into Maxwell modes:

$$\eta_{E,0}(t) = 3 \sum_i g_i \tau_i (1 - e^{-t/\tau_i})$$

Where g_i and τ_i are the modulus and relaxation time of the i^{th} Maxwell mode.

In order to avoid data perturbation due to overlaying of the sample on itself (due to experimental limitation of the EVF fixture) maximum X_e has been taken at “safe” Hencky strain $\epsilon_H=2.7$. The strain rate dependence of this “safe maximum X_e ” is shown in Figure 5.7.

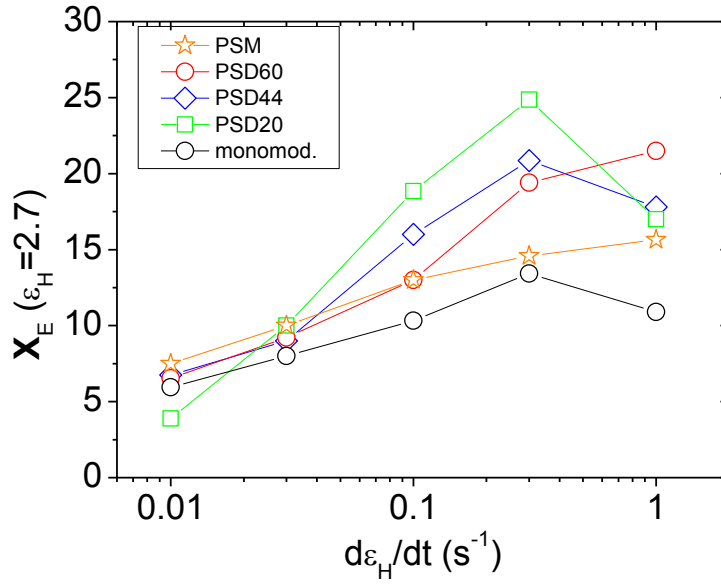


Figure 5.7: Strain hardening coefficient X_E at a Hencky strain of 2.7 as a function of Hencky strain rate, $\dot{\epsilon}_H$, obtained at $T_{ref}=120^\circ\text{C}$ for all materials. The error bars of the data points are within size of the markers. Lines are drawn for directing the reader's eye.

As can be seen in Figure 5.7, in the range of extension rates ($<0.1 \text{ s}^{-1}$), all materials demonstrate similar strain hardening behavior. By contrast, at higher rates, all diluted samples demonstrate remarkable growth of X_e with respect to pure PSM. Surprisingly, the highest growth at $\dot{\epsilon}_H < 1.0 \text{ s}^{-1}$ is shown by the less diluted sample PSD20. On the other hand, the highest diluted sample PSD44 demonstrates the best gradual increase of X_e with extension rate. Further, at the highest rates, a downturn is observed for all samples. Finally, at the highest extension rate values of safe maximum X_e are proportional to the diluent concentration. The strain hardening behavior of the PS with monomodal MWD is very similar to pure PSM except for the downturn at the highest extension rate.

By comparing PSD60 with “monomodal” samples having similar diluent fractions but very different diluent molecular weights, it can be clearly seen that molecular weight of the diluent dramatically affects the strain hardening behavior of the PS matrix in particular at high extension rates. Moreover, a bimodal molecular weight distribution of PSD60 results in enhanced strain hardening behavior in contrast to the monomodal material. This observation is in accordance with results presented in ref. (Huang *et al.*,

2013). According to Huang et al., nematic interactions in the diluted polymer mixtures impose anisotropy in the system and thereby reduce their strain hardening. They argue that nematic interactions between polymer matrix and diluents are proportional to the molar mass of the diluent and therefore mixtures with shorter diluents strain harden more.

In the next section we analyze the ultimate properties in extension of all materials in order to highlight differences observed in Figure 5.7.

5.7.4. Failure behavior in uniaxial elongational flow.

Although the processability of polymeric materials is primarily governed by their viscoelastic properties, the processing parameters are also constrained by the ultimate load that can be handled by the polymer melt without loss of integrity. Therefore in this section we analyze the failure behavior of the samples upon extension.

According to terminology of (Malkin and Petrie, 1997) one has to distinguish between failure and rupture as a reason of loss of integrity.

Strain-at-failure is a dynamic instability determined as a strain at which ‘necking’ appears and progressively develops until complete breakage of the sample. This homogeneity limit is predicted from the *Considere* condition (McKinley, Hassager, 1999; Considere, 1885). This condition states that viscoelastic material under transient extension is homogeneously deformed only if engineering stress (force/initial area) is an increasing function of extension.

$$\frac{d\sigma_E}{d\varepsilon_H} \geq 0$$

Equivalently, this condition states that for homogeneous elongation Trouton ratio ($Tr=3X_E$) should increase at least exponentially in order to overcome exponential decrease in the cross section area:

$$\frac{d \ln Tr}{d \varepsilon_H} \geq 1$$

Extensional viscosity can be measured even beyond the onset of ‘necking’ instability.

In our experiments we measure strain until the sample is completely separated in two parts (this is indicated by the measured torque decreasing below $1e^{-3}$ N.m). We refer to this limiting strain as *strain-at-rupture* and we measure it at different $\dot{\varepsilon}_H$.

Figure 5.8 shows the dependence on $\dot{\varepsilon}_H$ of the Hencky strain-at-failure. It is obvious that for all materials diluted by the oligomers the strain corresponding to the onset of necking instability has a maximum at $\dot{\varepsilon}_H \sim 0.1 \text{ s}^{-1}$ followed by the downturn at higher extension rates.

On the other hand, for pure PSM, except at the lowest extension rate, maximum *strain-at-failure* is effectively independent on $\dot{\varepsilon}_H$. The “monomodal” diluted sample shows similar behavior to PSM but with slightly lower absolute values at all extension rates.

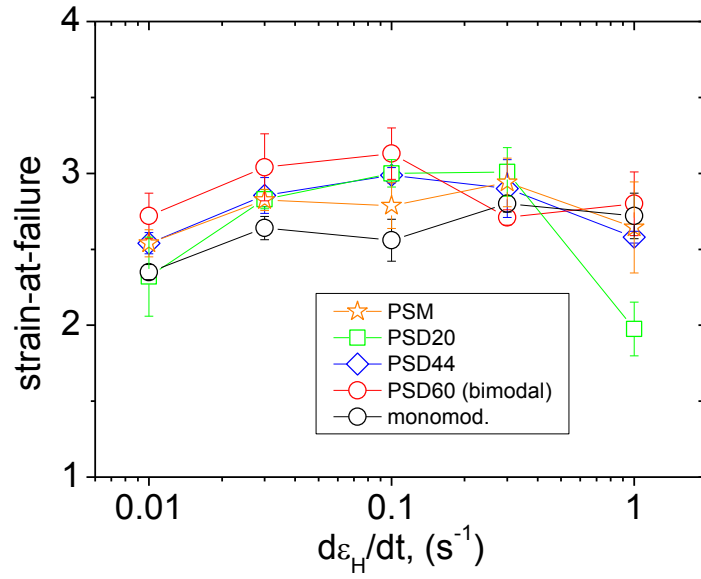


Figure 5.8: Dependence on Hencky strain rate of the Hencky strain-at-failure measured at $T_{ref}=120^{\circ}\text{C}$, for all materials. Lines are drawn for directing the reader's eye. The error bars represent standard deviation from the average value obtained from 3-5 measurements. Not shown error bars are of the size of the markers.

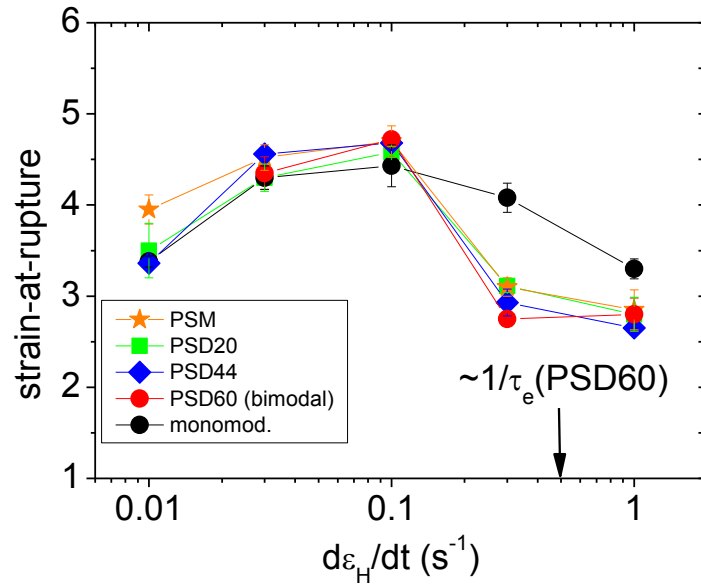


Figure 5.9: Dependence on Hencky strain rate of the Hencky strain-at-rupture obtained at $T_{ref}=120^{\circ}\text{C}$, for all materials. Lines are drawn for directing the reader's eye. The error bars represent standard deviation from the average value obtained from 3-5 measurements. Not shown error bars are of the size of the markers. Arrow shows inverse Rouse time per entanglement segment of PSD60. This time corresponds to the high frequency cross-over of G' and G'' .

In Figure 5.9 the dependence of the Hencky strain-at-rupture on $\dot{\epsilon}_H$ is shown. A clear step-like profile can be observed around a critical extension rate of 0.1 s^{-1} for all materials with bimodal molar mass distribution. This is characterized by an abrupt decrease (by $\sim 50\%$) of the ultimate Hencky strain from the plateau value observed at lower $\dot{\epsilon}_H$. According to ref. (*Malkin and Petrie, 1997*) this transition can be attributed to a change of the ultimate strain regime from viscoelastic at low rates (i.e a direct consequence of strain at failure following the Considère criterion) to brittle failure (i.e. solid-like crack propagating failure) characterized by lower limiting strains at high rates often occurring even before loss of homogeneity. This is why failure behavior demonstrated in Figure 5.8 and Figure 5.9 becomes equivalent at high rates.

The characteristic extension rate corresponding to the change of rupture mode seems to be in the order of inverse entanglement Rouse time, τ_e , of the most diluted material PSD60. All other samples due to smaller effective entanglement molecular weight have smaller values of $\tau_e \sim \phi^{2d}$, where ϕ – matrix fraction in the mixture. In order to approximately estimate value of τ_e (PSD60) we invert value of frequency corresponding to the high-frequency cross-over between respective G' and G'' .

Interestingly, this abrupt transition is slightly smoother for materials with lower fraction of D1. The especially smooth transition is shown by the “monomodal” material.

By comparing Figure 5.8 and Figure 5.9, we can conclude that the processing window governed by the ability of the material to withstand a given load without loss of homogeneity during elongation (strain-at-failure) and loss of cohesion can be affected differently if blended with the diluents of different molecular weight. However, no pronounced effect of concentration of unentangled diluent on the strain corresponding to the loss of cohesion is observed for all “bimodal” mixtures.

As can be seen from Figure 5.7, all diluted samples show enhanced strain hardening. However with increasing entanglement molecular weight upon dilution, the linear extensional viscosity envelope is shifted down. Therefore in order to estimate the effect of diluent molecular weight and concentration on melt strength, we show stress-strain

curves for the highest and lowest Hencky strain rates in Figure 5.10. Due to the limitation imposed by the EVF ($\varepsilon_{H,max} \sim 3.0$) the maximum stress can not be reached for most of the materials, therefore, only qualitative analysis of melt strength can be performed.

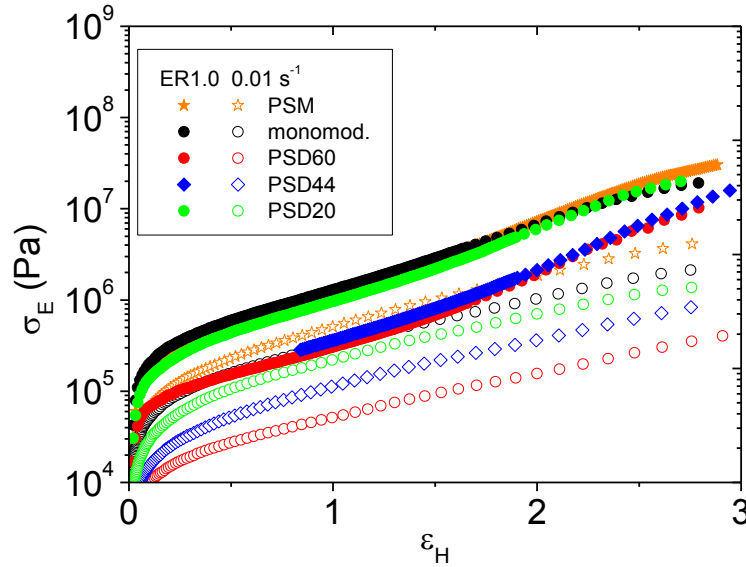


Figure 5.10: Stress as function of applied strain ε_H for all materials as determined by uniaxial elongational experiments with Hencky strain-rate 1.0 s^{-1} (closed markers) and 0.01 s^{-1} (open markers).

The melt strength at $\dot{\varepsilon}_H = 0.01 \text{ s}^{-1}$ is reduced proportionally to the fraction of oligomeric diluent (D1) but for the diluent with higher molecular weight (D2) the effect is milder. On the other hand, at high extension rate, the melt strength seems less sensitive to the oligomeric fraction.

5.8. Conclusions.

In this chapter, we have studied the linear and nonlinear extensional behavior of industrially relevant PS. Analyzed materials comprised different compositions of binary mixtures of matrix and unentangled diluent with well separated M_w 's as well as a monomodal mixture with broad MWD.

The presence of unentangled diluent in the binary mixtures influences the dynamic linear elastic and viscous responses starting from very high frequencies, whereas the effect on the monomodal mixture becomes obvious only in the terminal relaxation zone.

The constraint release effect on G_N^0 and η_0 induced by adding D1 is found to be in accordance with theoretical value of dilution exponent d ($=1$).

The effect of diluent molecular weight and concentration producing very different CR environments is clearly seen from the stress growth coefficient. Contrary to the monomodal diluted sample, mixtures with well separated M_w 's show pronounced buildup of X_e proportionally to the diluent concentration at all covered extension rates.

In relation to the ultimate behavior, we have demonstrated that the processing window governed by the ability of the material to withstand a given load without loss of homogeneity during elongation and finally loss of cohesion can be affected differently if blended with the diluents of different molecular weight. As for example, it was shown that mixtures with “bimodal” molar mass distribution demonstrate more pronounced strain-rate dependence of their ultimate properties.

The effect of diluent on melt strength at $T_{ref}=120^\circ\text{C}$ has been shown to be strong at low $\dot{\epsilon}_H$ but milder at high $\dot{\epsilon}_H$.

In summary, we have shown that existence of strain hardening behavior is not sufficient for complete characterization of extension dominated operations. Obtained in this study results demonstrate that enhancement of strain hardening achieved by adding small- M_w diluents often leads to trade-off with respect to other important extensional characteristics (e.g. strain-at-failure, strain-at-rupture, melt strength).

With respect to linear viscoelastic properties the effect of molecular structures is equivalent to the effect of different constraint release environments discussed in previous chapters. Fundamental understanding of these effects could perspectivevely be linked with the nonlinear properties.

Chapter 6:

SUMMARY

In this thesis we have investigated multi-chain effects on the dynamics of entangled polymers. The main part of the thesis consists of 5 chapters which can be ranked from the increasing complexity of CR environment, represented by the distribution of relaxation times of neighboring chains. Even though, at the end of every chapter we have already presented corresponding conclusions and perspectives, here we summarize the key results contributing to the main objectives highlighted in the introduction chapter of the thesis.

- We have developed a systematic methodology for testing different relaxation mechanisms. For this purpose we have used a stochastic single chain slip-spring model which quantitatively predicts chain dynamics at long time scales. In this model all relaxation mechanisms are naturally integrated. In order to test different assumptions related to respective contributions of different relaxation mechanisms we used a set of simplified slip-spring “toy” models, where different relaxation modes are systematically deactivated, analyzed and later reassembled in a controlled way.
For testing existing CR theories we have analyzed different mixtures of linear and simplest branched polymers.
- In particular, in chapter 3 the effect of adding short linear chains on stress relaxation dynamics of long star-branched polymers was investigated. We found that the effective friction of stars diffusing in the fat tube is larger than its bare friction. Additional friction was found to originate from the blinking nature of entanglements with shorter chains. We investigated dependence of this extra friction from blend composition and proposed an analytical equation for predicting its effect on the terminal relaxation zone dominated solely by relaxation of star chains. Conclusions made in this chapter were further developed in chapter 4, where we further investigated the effect of topological constraints with various mobilities on orientational relaxation of the probe chain.

First, we recognized that the stress relaxation dynamics of the chain originates from a combination of CR dynamics and sliding dynamics of the chain, where for “type-A polymers” the global relaxation effect of the sliding dynamics can be measured by dielectric spectroscopy and simulated as chain end-to-end vector autocorrelation function.

After validating the standard slip-spring model by simultaneous comparison with published rheological and dielectric data of binary melts of linear PI we have systematically analyzed the CR effect from each component of the binary blend on relaxation of the end-to-end vector. We found that the longest relaxation time of the end-to-end vector of the probe chain is in fact affected by dynamics of all topological constraints with a lifetime shorter than its own reptation time in the skinny tube. Furthermore, we proposed an analytical equation for predicting the longest relaxation times of the probe chain in any monodisperse and binary environment of topological constraints. We verified the derived equations by comparison with the simulation data.

- Further, in chapter 3 we have addressed some difficulties related to different approaches combining relaxation mechanisms in tube models. As suggested in the hierarchical algorithm we separated total stress relaxation of a star in three time zones according to dominant relaxation mechanism. Next, we verified that arm-retraction is not interrupted and only slightly influenced by CR from short chains in the time zone dominated by CR motion of the skinny tube. Finally, by recognizing that up to the fat tube zone all relaxation mechanisms are independent and simultaneously contribute to the total stress relaxation, we have proposed a simple multiplicative law for combining all relaxation zones as done in the time marching algorithm.
- Finally with respect to the industrially relevant polystyrene (PS) systems experimentally analyzed in chapter 5 we have shown that: materials with bimodal molar mass distribution demonstrate more pronounced strain rate dependence of the extensional properties with respect to the monomodal ones. Enhancement of strain hardening (achieved by adding small- M_w miscible diluents) often leads to trade-off with respect to the failure behavior characteristics.

The results obtained in this thesis could be implemented in advanced tube models to correct some of their present deficiencies. In particular, an accurate account for the effect of topological constraints on different stress relaxation components remains an unresolved issue for predicting linear rheological properties of complex industrially relevant polymers. The methodology developed in this work (chapter 4) can be systematically extended to include a larger number of disentanglement rates. Implementation of the obtained results to tube models could be used for improving predictions of all stress relaxation components in the systems with complex constraint release environments, i.e. polydisperse in chain length and even architecture.

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