MASTER

Modeling the linear viscoelastic behavior of entangled linear and star polymer systems

Mandagi, N.S.

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Modeling the Linear Viscoelastic Behavior of Entangled Linear and Star Polymer Systems

by

N. S. Mandagi

Under supervision of:
Dr. Ir. Jaap den Doelder (Dow)
Ir. Tom Verbrugge (Dow)
Dr. Ir. Fons van de Ven (TU/e)

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Confidential Report
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Abstract

It is well known that the viscoelastic properties of polymers depend on their molecular architectures. The study of this relationship is of interest for Dow. Currently, Dow is focusing on the enhancement of the existing model for linear polymers to branched ones. One step forward in this direction is performed by considering symmetric and asymmetric star polymers. A model that predicts the linear viscoelastic behavior of entangled linear and star polymer system is constructed in this master thesis project. The constructed model is adapted from existing models in the literature. This model is derived based on the tube model for polymer reptation and retraction. Different architectures of polymers contribute in the relaxation process of the system in different ways. Depending on the architecture, polymers can relax either by reptation or retraction. The resulting model is implemented in Delphi and delivered in user-friendly software. Numerical results are compared with available experimental data, and good correspondence is found.
Nomenclature

\[ a(t) \] Tube diameter
\[ a_0 \] Tube diameter at equilibrium
\[ b \] Kuhn monomer length
\[ D \] Diffusivity of a polymer chain along its tube
\[ D_b \] Diffusivity of a backbone along its tube
\[ G(t) \] Relaxation modulus
\[ G_{\text{fast}}(t) \] Fast relaxation modulus
\[ G_{\text{slow}}(t) \] Slow relaxation modulus
\[ G^*(\omega) \] Complex modulus
\[ G'(\omega) \] Storage modulus
\[ G_{\text{fast}}'(\omega) \] Fast storage modulus
\[ G_{\text{slow}}'(\omega) \] Slow storage modulus
\[ G^*(\omega) \] Loss modulus
\[ G_{\text{fast}}^*(\omega) \] Fast loss modulus
\[ G_{\text{slow}}^*(\omega) \] Slow loss modulus
\[ G_N \] Rubber plateau modulus
\[ Gr \] Graessley number
\[ k_B \] Boltzmann constant
\[ L(t) \] Tube length
\[ L_{eq} \] Equilibrium length of a primitive chain
\[ L_{eq,i} \] Equilibrium length of arm \( i \)
\[ L_i(t) \] Length of arm \( i \)
\[ l \] Length of a primitive chain segment
\[ M \] Molecular weight of a polymer
\[ M_b \] Molecular weight of a backbone
\[ M_e \] Molecular weight between entanglements
\[ M_i \] Molecular weight of arm \( i \)
\[ M_o \] Molecular weight of a monomer
\[ N \] Number of monomer in the polymer chain
\[ N_b \] Number of monomer in the backbone
\[ N_e \] Number of monomers between entanglements
\[ N_i \] Number of monomer in arm \( i \)
\[ n \] Number of branches in a polymer
\[ n_a \] Number of arms contained in a polymer system
\[ p_{\text{env}}(x_i,t) \] Survival probability of relaxation by environment
\[ p_{\text{fluc}}(x_i,t) \] Survival probability of relaxation by fluctuation
\[ p_{\text{rept}}(x_i,t) \] Survival probability of relaxation by reptation
\[ x_i \] Normalized curvilinear variable of primitive chain segment along arm \( i \)
\[ T \] Absolute temperature
\[ t \] Time
\[ U \] Potential energy
\[ Z \] Number of primitive chain segments
\[ Z_b \] Number of backbone segments
\(\alpha\)  Dilution exponent
\(\Phi(t)\)  Unrelaxed polymer fraction
\(\Phi_i(t)\)  Unrelaxed fraction of arm \(i\)
\(\varphi_i\)  Volume fraction of arm \(i\)
\(\eta^*(\omega)\)  Complex viscosity
\(\eta_0\)  Zero shear viscosity
\(\Psi(t)\)  Unrelaxed entanglements fraction
\(\tau_b\)  Reptation time of a backbone
\(\tau_d\)  Reptation time of a linear chain
\(\tau_{d,i}\)  Reptation time of arm \(i\) of a linear chain
\(\tau_e\)  Entanglement time
\(\tau_{early}\)  Early fluctuation time
\(\tau_f\)  Fluctuation time
\(\tau_{f,s}\)  Fluctuation time of the short arm of an asymmetric star
\(\tau_{R,i}\)  Rouse time of arm \(i\)
\(\omega\)  Oscillation frequency
\(\zeta\)  Monomeric friction coefficient
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1 Introduction

1.1 Problem description

The knowledge of the flow behavior of polymers is one of the important issues for polymer industries. Accurate description and classification of the flow behavior is directly useful in polymer processing and characterization. Therefore, polymer industries are always interested in the research topic: Rheology (the study of the flow behavior of viscoelastic materials), in particular the Rheology of polymeric liquids.

As it is known that the viscoelastic properties of polymers depend on their molecular architectures, many models have been developed to describe this relationship. In literature, many systems of linear polymers or branched polymers with a limited and controlled level of complexity have been studied. Some examples of these limited branched polymers are symmetric stars, see [1], [16] and [19], asymmetric stars [7], H-shaped [14] and pom-pom polymers [15]. Simple mixtures of stars or mixtures of stars with linear chains have been studied too. The problem is that these models are valid only for their own simplified branched architecture. One of the challenges is to develop a single model, which is able to predict the viscoelastic properties of a large range of polymers with different architectures: linear or branched, monodisperse or polydisperse. Some recent works, of which we are aware, in developing such a model are presented by Van Ruymbeke et al. [26] and Das et al. [2]. Van Ruymbeke et al. [26] developed a model, which is able to predict the linear viscoelastic behavior of arbitrary mixtures of stars and linear polymers: monodisperse and polydisperse (symmetric or asymmetric) stars or linear polymers and mixtures of linear and star polymers. Das et al. [2] developed a more general model, which is able to handle a wider range of polymer systems (such as H-shaped, combs and tree) than the one developed by Van Ruymbeke et al..

The study of this relationship between the viscoelastic properties of polymers and their molecular architecture is of interest for Dow Benelux B. V. (Dow). Dow produces such polymers and finds profit in an optimal flexibility in the design of different molecular architectures for different manufacture processes and final properties. A model to predict the linear viscoelastic behavior of linear polymers has already been implemented within Dow. Now, Dow is focusing on the enhancement of the existing model for linear polymers to branched ones. The main assignment of this master project is to construct a model that predicts the linear viscoelastic behavior of linear and branched architectures. However, the scope of the discussion is limited to systems of entangled linear and star polymers. This means that the system may consist of arbitrary mixtures of linear and star (symmetric or asymmetric) polymers, which are entangled to each other. The model developed here is mainly adopted from Van Ruymbeke et al. [26] with some modifications, especially in the solution approach of the model. The strong point of this model is that it can be extended into a model that can predict the linear viscoelastic behavior of a more complicated system.

1.2 Problem approach

We use the concept of tube theory in deriving the model that predicts the linear viscoelastic behavior of entangled linear and star polymer system. In the tube model, the motion of linear and star polymers is constrained by a virtual tube. Depending on the architecture, this motion is modeled either as reptation or retraction inside a tube. In the reptation model, two cases are investigated: reptation inside a fixed tube and a dilated tube. The reptation model inside a fixed tube is described by a diffusion equation, which we solve analytically. The reptation model inside a dilated tube is described by a convection-diffusion equation with a moving boundary condition. We solve this equation by using the fourth-order Runge-Kutta method. The retraction inside a tube is modeled as an activated process, which we solve analytically.
In literature, two different formulas for the relaxation modulus are used; see [2], [10], [24] and [26]. Here, we investigate these two formulas. These two different formulas lead to different methods in converting the relaxation modulus to dynamic relaxation moduli. When the first formula is used, which is also used by Van Ruymbeke et al. [26], the dynamic relaxation moduli are approximated by two methods. For the lower frequencies, the relaxation moduli are approximated by using a simple numerical integration, while for the higher frequencies, the relaxation moduli are approximated by using Schwarz relations. When the second formula for the relaxation modulus is used, which is also used by Das et al. [2], Larson [10] and Van den Akker [24], the relaxation moduli are obtained analytically.

1.3 Outline of the report
The structure of the report is as follows. Chapter 2 describes the tube model and introduces the general concept of relaxation mechanisms in a system of entangled linear and star polymers. In Chapter 3, different ways of relaxation are discussed in detail and mathematical formulations for the relaxation behaviors are derived. Chapter 4 describes the relation between the relaxation modulus and the dynamic relaxation moduli. The implementation of the developed model in Delphi is presented in Chapter 5. The numerical results of this implementation are presented and validated in this chapter by comparison to available experimental data obtained from the literature [18] and [26]. Moreover, it is shown here how the developed software can be used to analyze the long chain branching effect in the rheological behavior for polycarbonate systems, which is a specific interest of Dow. In Chapter 6, the conclusions and recommendations are given.

1.4 Results and conclusions
The most important results of this project are that we have succeeded in constructing and implementing a model that is able to predict the linear viscoelastic properties of entangled linear and star polymers systems. The predicted properties, specifically the storage and loss moduli show an excellent agreement with available experimental data, which validates the developed model and the numerical simulations. The implementation itself is delivered in user-friendly software written in Delphi.

1.5 Recommendation
In this project, the constructed model considers only linear and star polymers. In reality, there are more polymer architectures occur in a polymer melt. As mentioned earlier, the model constructed here can be extended to a model that can that can predict the linear viscoelastic behavior of a more complicated system. Therefore, it is recommended to extend this model so that it can also handle more complicated polymer architectures. A step forward is by considering H-shaped and pom-pom polymer.
2 System of entangled linear and star polymers

2.1 Basic concepts and definitions of polymer systems

A polymer is a molecule composed of many repeating smaller chemical units or molecules called monomers. Thus, a single polymer molecule can be thought of as a long chain to which we refer as the polymer chain. The size of a polymer chain is characterized by its molar mass. This molar mass is simply the mass of 1 mole of the polymer and usually is quoted in units of g/mol or kg/mol. However, the term molecular weight is often used instead of molar mass, and we will also use this term.

In general, polymers can be categorized into three different types, regarding their molecular architecture [27]. The first type is a linear polymer. A linear polymer is represented by a chain with two ends. The second type is a branched polymer which has side chains, or branches, of significant length, which are bounded to the main chain at branch points. The final type is a network polymer. This polymer has a three-dimensional structure in which each chain is connected to all others by a sequence of branching points and other chains. In principal, a network polymer is an interconnected branched polymer.

Branched polymers can also be subcategorized into several types, such as star polymers, H-shaped polymers, pom-pom polymers, comb polymers and tree polymers. A star polymer has one branch point and several branches. If a star polymer has \( n \) branches, then it is called as \( n \)-arm star polymer. There are two types of star polymers which are symmetric star polymers and asymmetric star polymers. Each arm of a symmetric star polymer has the same molecular weight as the other arms. An asymmetric star has at least one arm which has different molecular weight from the other arms. H-shaped polymers and pom-pom polymers have two branching points and a main chain on which these branching points are located. This main chain is called a backbone. A comb polymer has more than two branching points on its backbone. When the side chains connected to a backbone have subchains (these subchains might also have their own subchains and so on), the polymer is called a tree polymer. In Figure 1, some examples of linear and branched polymers are depicted.

![Figure 1: Examples of linear and branched polymers. (a) linear, (b) three-arm star, (c) H-shaped, (d) pom-pom, (e) comb and (f) tree.](image)

\( ^1 \) A chemical mass unit, is defined to be \( 6.022 \times 10^{23} \) molecules, atoms, or some other unit. Examples: 1 mole of NH\(_3\) has \( 6.022 \times 10^{23} \) molecules and 1 mole of Cu has \( 6.022 \times 10^{23} \) atoms.

(http://chemistry.about.com/od/dictionariesglossaries/g/defmole.htm)
2.2 Tube model

In an entangled\(^1\) polymer system, the motion of a single polymer is highly constrained. The polymers surrounding a given polymer prevent certain displacements. Therefore, in the tube model, each polymer chain, entangled with other chains, may be regarded as enclosed within a virtual tube made of obstacles from neighboring chains. The motion of this chain is constrained by these obstacles. Because of these constraints, the chain cannot move perpendicular to the tube axis; it can only diffuse out of its tube. An illustration of a tube model is depicted in Figure 2. For a given conformation of a linear polymer, we can draw a primitive chain (a virtual line) that connects the two ends of the polymer chain with the same topology as the polymer chain itself relative to the obstacles \([4]\) (see the bold line in Figure 2).

![Figure 2: Illustration of tube model for a linear chain at equilibrium.](image)

The length scales which are used here are calculated as follows. If the molecular weight of the linear chain, \(M\), and its molecular weight between entanglements, \(M_e\), are known, then the number of primitive chain segments, which are segments between two subsequent entanglements, is \(Z = \frac{M}{M_e}\). Let \(L_{eq}\) represents the contour length of the primitive chain at equilibrium. Then \(L_{eq}\) is defined as

\[
L_{eq} = Z l = \frac{M}{M_e} l,
\]

where \(l\) is the averaged length of a primitive chain segment. This length is related to the Kuhn monomer length\(^2\), \(b\), as \([19]\)

\[
l^2 = \nu N_e b^2,
\]

where \(N_e = \frac{M_e}{M_o}\) is the number of monomers between entanglements with \(M_o\) the monomer molecular weight. Here, \(\nu\) is a constant somewhat less than or equal to one (Van Ruymbeke et al. \([26]\) used \(\nu = 1\), while Milner and McLeish used \(\nu = 4/5\) in \([16]\)). In the following discussion, \(\nu\) is chosen to be equal to one, \(\nu = 1\).

In this tube model, the entanglement system is assumed to be isotropic. Because of this assumption, the tube diameter, \(a\), is equal to the length of the primitive chain segment, \(l\). Thus, (2.2) can be written as

\[
a^2 = \frac{b^2}{M_o} M_e.
\]

By assuming that \(b\) and \(M_o\) are constant, we obtain the following proportionality between the tube diameter and the molecular weight between entanglements:

\[
a \propto M_e^{1/2}.
\]

\(^1\) A system containing of many polymers, where each polymer is entangled to the other polymers.

\(^2\) A material parameter depending on the chemical composition of the polymer \([9]\)
Since the length of the tube, $L$, at equilibrium is equal to the length of the primitive chain, i.e. $L = L_{eq}$, by using (2.1) and (2.2), we have the relation between the tube length and molecular weight between entanglements as

$$L = \left(\frac{1}{M_e}\right)^{1/2} M_b M_e^{-1/2}. \quad (2.5)$$

For fixed $M$, the proportionality between the tube length and the molecular weight between entanglements is thus

$$L \propto M_e^{-1/2}. \quad (2.6)$$

From (2.4) and (2.6), we obtain the following proportionality relations between the tube length, the tube diameter and the molecular weight between entanglements:

$$L \propto M_e^{-1/2} \propto a^{-1}. \quad (2.7)$$

In the case of star polymers, the primitive chain of an arm connects the free end of the arm and the branching point of the polymer; see Figure 3. If $i$ represents the arms of the star polymer, then (2.1) can be rewritten as

$$L_{eq,i} = \frac{M_i}{M_e} l_i, \quad (2.8)$$

where $M_i$ is the molecular weight of arm $i$.

![Figure 3: Illustration of tube model for a three-arm star; $i$ represents the arms of the polymer, $i = 1, 2, 3.$](image)

### 2.3 Relaxation mechanisms

Immediately after the onset of deformation, each polymer chain in the system is in an unrelaxed nonequilibrium state. The stress can only disappear if the chains relax, so we are interested in the different ways of relaxing. At very short times, the chains will relax as if they were in a dilute solution (non-entangled system) [26]. This relaxation mechanism is described by the Rouse model [26]. Very soon, the chains will feel the topological constraints arising from the existence of entanglements. The tube will orient and the chain will progressively lose its memory by three relaxation mechanisms: *reptation*, *contour length fluctuations* and *constraint release*. These mechanisms depend on details of the molecular architecture. In this project, we will not focus on the derivation of the Rouse model; our focus is in the derivation of reptation, fluctuation and constraint release mechanisms. This section discusses the general concepts of reptation, fluctuation and constraint release mechanisms, while the detailed models of each mechanism are discussed in Chapter 3.
2.3.1 Reptation and fluctuations in a fixed entanglement network

Let us assume for a while that the chains are surrounded by a fixed entanglement network, i.e. the obstacles, which constrain the movement of an observed chain, do not change with time. For the linear chains, the relaxation is mainly done by reptation. The reptation model describes linear chain motion much like that of a snake moving in a tube formed by the surrounding chains. The chain is only free to reptate along the curvilinear path of its tube; see Figure 4. The classical Doi and Edwards [4] reptation theory computes the relaxation probability from the curvilinear diffusion of an observed chain, of constant length $L_{eq}$ through a virtual tube. In this classical theory, the fluctuations of the primitive chain are not taken into account. However, in reality, the fluctuations cannot be neglected. Van Ruymbeke et al. [26] treated the effects of reptation and fluctuation in the relaxation process of the linear chain separately. The fluctuation of linear chains is incorporated into the relaxation model by seeing a linear chain as a two-arm symmetric star polymer. This approach is also used in the following discussion.

![Equilibrium and Reptation](image)

**Figure 4: Reptation of a linear chain in a fixed entanglement network.**

In the case of star polymers, which have more than two arms, the chains cannot reptate in the way linear chains do. The motion of a star polymer is constrained by its branch. Instead of reptating, the arms will retract towards the branching point. This branching point will act like a pinning point for the entire molecule. The free end of the arm can retract along its own tube and then explore a new path by extending back in another direction; see Figure 5a. As a consequence, the length of the primitive chain of the arm will fluctuate during the relaxation process, i.e. $L_i = L_i(t)$ such that $0 < L_i(t) \leq L_{eq,i}$, where $L_{eq,i}$ is the equilibrium length of the primitive chain of arm $i$; see Figure 5b. This is what is meant by contour length fluctuation mechanism. As mentioned before, a linear chain is seen as a two-arm symmetric star polymer. This type of chain also experiences the retraction process: the two arms will retract towards the center of the chain.
2.3.2 Constraint release mechanism

The description given in Section 2.3.1, considers the reptation and fluctuation processes in a fixed entanglement network. In the real situation, these obstacles are not fixed. When a chain, let us say chain A, involved in an entanglement that defines a portion of another chain’s tube, let us say chain B, moves (relaxes) so that one of its ends slips past the entanglement, the entanglement disappears. In simpler words, the obstacle of chain B, made by a portion of chain A, disappears. Thus, chain B will feel a dilated tube. This is what is meant by the tube dilation mechanism of constraint release. The dilated tube concept was applied to linear polymers by Marrucci [13]; more detailed explanation is given in Section 3.2.2.

Another approach to describe the constraint release mechanism is by seeing the chains, or parts of the chains that have been relaxed, as solvents. These relaxed chains or parts of the chains then dilute the entanglement network. This approach is called dynamic dilution mechanism of constraint release. Ball and McLeish [1] used this concept in their relaxation model for star polymers.

These two approaches of describing the constraint release mechanism lead to the same conclusion: when some parts of the chains in the system have been relaxed, the unrelaxed parts of the chains will feel a dilated tube. Thus, the tube diameter is no longer constant but increases with time in the following way [13]

$$a(t) = \frac{a_0}{(\Phi(t))^{\alpha/2}}$$

(2.9)

where $a_0$ is the tube diameter at equilibrium as given in (2.3) and $\Phi(t)$ is the unrelaxed polymer fraction at time $t$. The complementary fraction $1 - \Phi(t)$ is usually referred to as the solvent [13]. Here, $\alpha$ is the dilution exponent where $\alpha = 1$ corresponds to the naive scaling for dilution and $\alpha = 4/3$ corresponds to the Colby-Rubinstein scaling [17]. Since the length of the tube and the molecular weight between entanglements are related to the tube diameter as given in (2.7), these parameters need to be rescaled accordingly:
\[ L(t) = L_{eq} \cdot (\Phi(t))^{\alpha/2}, \quad (2.10) \]
\[ M_e(t) = \frac{M_{e0}}{(\Phi(t))^{\alpha}}, \quad (2.11) \]

where \( M_{e0} \) is the molecular weight between entanglements at equilibrium. Note that the scaling given in (2.10) uses that at equilibrium \( L(0) = L_{eq} \).
3 Mathematical models for relaxation mechanisms

In this chapter, we describe the mathematical models for reptation and fluctuation mechanisms. The reptation model is constructed based on the classical theory of Doi and Edwards [4] and Marrucci’s model [13], while the fluctuation model is constructed based on Milner and McLeish’s model [16]. The main assumption in the construction of these two models is that the reptation and fluctuation processes are considered as two independent events. Thus, in the reptation model, the length of the primitive chain is constant.

3.1 Probability function of the relaxation mechanisms

In general, the relaxation processes of the chains are described by their probability functions. If a system contains \( n_a \) arms and \( i, i = 1, 2, \ldots, n_a \), represents the arms of the polymer chains, the location of an arbitrary primitive chain segment along arm \( i \) can be represented by a normalized variable \( x_i \), ranging from 0 at the end of the arm to 1 at the center for a linear polymer or the branching point for a star polymer; see Figure 6. Now, let us introduce the probability functions \( p_{\text{rept}}(x_i, t) \) and \( p_{\text{fluc}}(x_i, t) \). These two functions are the probabilities that the segment at position \( x_i \) at time \( t \) is not relaxed by reptation and fluctuations, respectively.

When these two probability functions are known, the fraction of an arm that, at any given time, has not been relaxed by reptation and fluctuation can be determined by

\[
\Phi_i(t) = \int_0^1 p_{\text{rept}}(x_i, t)p_{\text{fluc}}(x_i, t)dx_i,
\]

(3.1)

where \( i \) represents the observed arm. Thus, the unrelaxed fraction of all the arms contained in the system is given by

\[
\Phi(t) = \sum_i \varphi_i \Phi_i(t),
\]

(3.2)

where \( \varphi_i \) is the volume fraction of arm \( i \). The fine description for \( p_{\text{rept}}(x_i, t) \) and \( p_{\text{fluc}}(x_i, t) \) will be discussed in the following sections.

Figure 6: Normalized curvilinear coordinate \( x_i \) of (a) a linear polymer and (b) a star polymer.

---

1 The term volume fraction is used in literature to describe the weight fraction of the arms; see [2], [7], [17], [18] and [26].
3.2 Relaxation by reptation

3.2.1 Reptation in a fixed tube

In the classical theory of Doi and Edwards, the tube is assumed to be fixed in space. This means that the diameter of the tube remains constant during the relaxation process. Now let us consider four successive situations of a reptating chain; an illustration of these situations is depicted in Figure 7.

Let $s$ denote the location of an original tube segment, which confined the linear chain with the total molecular weight $M$. If $p(s,t)$ is the probability density that the original tube segment $s$ remains at time $t$, then $p(s,t)$ obeys the following one-dimensional diffusion equation [13]:

$$\frac{\partial p}{\partial t} = D \frac{\partial^2 p}{\partial s^2}, \quad 0 < s < L_{eq}, \quad t > 0,$$  \tag{3.3}

with the boundary conditions

$$p(0,t) = p(L_{eq},t) = 0, \quad t > 0,$$  \tag{3.4}

and the initial condition

$$p(s,0) = \frac{1}{L_{eq}}.$$  \tag{3.5}

It has been shown by Doi and Edwards [4] that this probability density function $p(s,t)$ also represents the probability that the primitive chain segment $s$ is in the original tube at time $t$, or in another words the probability that it is still not relaxed by reptation.

In (3.3), $D$ is the diffusivity of the chain along the tube given by [4]

$$D = \frac{k_B T}{N \zeta},$$  \tag{3.6}

where $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $\zeta$ is the monomeric friction coefficient and $N = M/M_n$, the number of monomers in the chain.

Let us introduce the following dimensionless variables:

$$x = \frac{2s}{L_{eq}}; \quad \hat{t} = \frac{t}{\tau_d}; \quad \hat{p}(x,\hat{t}) = L_{eq} p(s,t).$$  \tag{3.7}
In the above formulas, the value $\tau_d$ represents a characteristic time (required) for relaxation of an oriented configuration, or, as we can say otherwise, the time needed for the primitive chain to escape completely from the original tube. It is called the reptation time and follows from

$$\tau_d = \frac{L_c^2}{\pi^2 D}. \quad (3.8)$$

By using (2.1), (2.2) (with $\nu = 1$) and (3.6), we can write the reptation time in terms of the molecular weight $M$ as

$$\tau_d = 3\tau_e \left( \frac{M}{M_e} \right)^3, \quad (3.9)$$

where $\tau_e$ is the entanglement time of a segment defined as

$$\tau_e = \frac{\zeta N_i^2 b^2}{3\pi^2 k_B T}. \quad (3.10)$$

With the introduced dimensionless parameters, the dimensionless system characterizing the motion of a linear chain inside a tube is given by

$$\frac{\partial \hat{p}}{\partial t} = \frac{4}{\pi^2} \frac{\partial^2 \hat{p}}{\partial x^2}, \quad 0 < x < 2, \quad \hat{t} > 0,$$

$$\hat{p}(0,\hat{t}) = \hat{p}(2,\hat{t}) = 0,$$

$$\hat{p}(x,0) = 1.$$  \quad (3.11)

The solution of this initial-boundary value problem is

$$\hat{p}(x,\hat{t}) = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n+1)} \sin \left( (2n+1) \frac{\pi x}{2} \right) \exp \left( - (2n+1)^2 \frac{\hat{t}}{\tau_e} \right). \quad (3.12)$$

Since this probability function is symmetric at $x = 1$, we can easily convert our solution into the coordinate system that is introduced in earlier in Section 3.1. As we can see in Figure 8, $x_i = 0$ is equivalent to $x = 0$ for $i = 1$, and $x = 2$ for $i = 2$, while $x_1 = x_2 = 1$ is equivalent to $x = 1$. Thus, the probability that the segment at position $x_i$ at time $t$ is still not relaxed by reptation is given by

$$p_{\text{rept}} (x_i, t) = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n+1)} \sin \left( (2n+1) \frac{\pi x_i}{2} \right) \exp \left( - (2n+1)^2 \frac{t}{\tau_{d,i}} \right), \quad \text{for } i = 1, 2, \quad (3.13)$$

where

$$\tau_{d,i} = 3\tau_e \left( \frac{2M_i}{M_e} \right)^3. \quad (3.14)$$

![Figure 8: Conversion of coordinate $x$ into coordinate $x_i$, $i=1, 2.$](image-url)
3.2.2 Reptation in a dilated tube

In the previous section, the reptation model is developed under the assumption that the diameter of the tube is constant during the relaxation process. However, because of the mobility of the surrounding chains, obstacles continuously disappear and reform. Some of them move more rapidly (e.g., chain segments close to a chain end), while others move more slowly (e.g., chain segments far away from a chain end) [13]. Consequently, as we shall explain below, the tube diameter will increase in time during relaxation.

The situation described above is illustrated schematically in Figure 9. Around the chain, three kinds of obstacles are considered, which differ in mobility. Those represented by a cross are very mobile, i.e., they disappear and reform in a large frequency $\omega_1$, those represented by a circle have a smaller frequency $\omega_2$, and those represented by a square are very permanent, with the smallest frequency $\omega_3$. At time scale $t$, such that

$$\frac{1}{\omega_3} < t < \frac{1}{\omega_2} < \frac{1}{\omega_1},$$

the circles and the squares obstacles are effective obstacles whereas crosses are not; see Figure 9a. For a longer time scale such that

$$\frac{1}{\omega_3} < \frac{1}{\omega_2} < t < \frac{1}{\omega_1},$$

the circles are no longer effective obstacles and the tube diameter is increased; see Figure 9b.

![Figure 9](image)

Figure 9: Segment of a long chain within obstacles of different renewal frequency [13]. Only the obstacles indicated as squares have the same position in (a) and (b).

Since some of the obstacles disappear, the chains have more freedom to move. This phenomenon will accelerate the relaxation process of the chains. Marrucci [13] argued that the tube diameter increases in a way as given in (2.9). As a consequence, the tube length also shrinks in time according to (2.10):

$$L(t) = L_{eq} \Phi(t)^{\alpha/2},$$

where $\Phi(t)$ is the unrelaxed part of the whole chains. Thus, the chain is now moving in a mobile tube. This motion is described by the following convection-diffusion equation [13]:

$$\frac{\partial p}{\partial t} = D \frac{\partial^2 p}{\partial s^2} - \frac{1}{L} \frac{dL}{dt} \frac{\partial}{\partial s} (sp), \quad 0 < s < L(t), \quad t > 0,$$

with the boundary condition

$$p(0,t) = p(L(t),t) = 0,$$

and the initial conditions

$$p(s,0) = \frac{1}{L_{eq}}.$$
Let us introduce the following dimensionless variables:

\[ x = \frac{2s}{L(t)}; \quad \hat{t} = \frac{t}{\tau_d}; \quad \hat{p}(x, \hat{t}) = L(t)p(s, t); \quad \hat{D}(\hat{t}) = \tau_d \tilde{D}(t), \]  

(3.21)

where \( \tilde{D}(t) \) is defined as

\[ \tilde{D}(t) = \frac{4D}{(L(t))^2} = \frac{4}{\pi^2 \tau_d (\Phi(t))^{\alpha}}. \]  

(3.22)

Hence, the dimensionless system takes the form:

\[ \frac{\partial \hat{p}}{\partial \hat{t}} = \hat{D}(\hat{t}) \frac{\partial^2 \hat{p}}{\partial x^2}, \quad 0 < x < 2, \quad \hat{t} > 0, \]

\[ \hat{p}(0, \hat{t}) = \hat{p}(2, \hat{t}) = 0, \]

\[ \hat{p}(x, 0) = 1. \]  

(3.23)

By introducing

\[ \theta(\hat{t}) = \int_0^\hat{t} \hat{D}(\hat{\tau}) d\hat{\tau} \quad \text{and} \quad q(x, \theta) = p(x, \hat{t}), \]  

(3.24)

the system given by (3.23) reduces to

\[ \frac{\partial q}{\partial \theta} = \frac{\partial^2 q}{\partial x^2}, \quad 0 < x < 2, \quad \theta > 0, \]

\[ q(0, \theta) = q(2, \theta) = 0, \]

\[ q(x, 0) = 1. \]  

(3.25)

The solution of this initial-boundary value problem is given by

\[ q(x, \theta) = -\frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin \left( \frac{(2n+1)\pi x}{2} \right) \exp \left( -\frac{(2n+1)^2}{4} \beta^2 \frac{\pi^2}{\theta} \right). \]  

(3.26)

If we convert back this solution into \( x, t \) coordinates, we arrive at the solution:

\[ p_{\text{rept}}(x_i, t) = -\frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin \left( \frac{(2n+1)\pi x_i}{2} \right) \exp \left( -\frac{(2n+1)^2}{4\tau_d} \frac{\Theta(t)}{\tau_d} \right), \quad \text{for } i = 1, 2, \]  

(3.27)

where

\[ \Theta(t) = \int_0^t \frac{1}{\Phi(\tau)} d\tau. \]  

(3.28)

We can see here that by substituting \( \Phi(\tau) = 1, (3.27) \) reduces to (3.13).

### 3.2.3 Solution strategy of reptation model

In this section, we will discuss only the solution strategy for a simplified system. Here we assume that the solvent coming from fluctuations does not play any role in accelerating the relaxation process. This assumption is consistent with our previous assumption that reptation and fluctuation are two independent events. Hence, the unrelaxed polymer fraction given in (3.1)-(3.2) is simplified to (\( p_{\text{fluc}}(x_i, t) = 1 \))

\[ \Phi(t) = \sum_i \frac{1}{\pi} p_{\text{rept}}(x_i, t) dx_i. \]  

(3.29)
By substituting (3.27) into (3.29), we obtain
\[
\Phi(t) = \frac{8}{\pi^2} \sum_i \varphi_i \left[ \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left( -\frac{(2n+1)^2 \Theta(t)}{\tau_{d,i}} \right) \right],
\]
(3.30)
where \( \Theta(t) \) is a still unknown function that we need to solve with the aid of (3.28), in order to be able to determine \( p_{\text{rept}}(x_i, t) \) from (3.27).

This coupled system, (3.30) and (3.28), is difficult to solve analytically. Therefore, we need a numerical method to compute the solution of this system. By taking the first derivative of (3.28) with respect to \( t \), we have
\[
\Theta'(t) = \frac{1}{(\Phi(t))^a}.
\]
(3.31)
We also know that at \( t = 0 \) none of the parts of the chains has been relaxed, i.e. \( \Phi(0) = 1 \). With \( \Phi(0) = 1 \), it follows from (3.28) that \( \Theta(0) = 0 \). By introducing a function \( F(t, \Theta(t)) \) such that
\[
F(t, \Theta(t)) = \frac{1}{(\Phi(t))^a},
\]
(3.32)
we can summarize the problem as solving an ordinary differential equation with initial condition given by
\[
\Theta'(t) = F(t, \Theta(t)),
\]
\[
\Theta(0) = 0.
\]
(3.33)
The solution of this ordinary differential equation can be computed by a well-known numerical method called the fourth-order Runge-Kutta (RK4) method [8].

Let us discretize time \( t \) with a time step \( h \) such that
\[
h = t_{k+1} - t_k, \quad k = 0, 1, 2, \ldots.
\]
(3.34)
Let us also introduce \( \Theta_k = \Theta(t_k) \). The RK4 method for (3.33) is given by
\[
\Theta_{k+1} = \Theta_k + \frac{h}{6} \left( k_1 + 2k_2 + 2k_3 + k_4 \right)
\]
(3.35)
where
\[
k_1 = F(t_k, \Theta_k),
k_2 = F\left(t_k + \frac{h}{2}, \Theta_k + \frac{h}{2}k_1 \right),
k_3 = F\left(t_k + \frac{h}{2}, \Theta_k + \frac{h}{2}k_2 \right),
k_4 = F(t_k + h, \Theta_k + h\Theta_k).
\]
(3.36)
Thus, at each time step, the probability that segment \( x_i \) is survived from reptation is obtained by substituting (3.35) into (3.27).

In his reptation model, as explained above, Marrucci claimed that the dilated tube is always felt by the reptation process. However, some other investigations showed that this is not necessarily true. For instance, Struglinski and Graessley [22] claimed that in a bidisperse mixture of short and long entangled linear chains, the chain reptates in a dilated tube only if
\[
Gr = \frac{M_f M^2}{M^3_s} > 1,
\]
(3.37)
where \( M_f \) and \( M_s \) are the molecular weight of the short and long chains, respectively. This ratio is known as Graessley number. Some experimental studies have confirmed this rule, but with
different criterion. Those studies showed that the Graessley number should be greater than 0.1 instead of 1.

Based on this argument, we conclude that in a monodisperse system, the reptation always happens in an undiluted tube, while in a polydisperse system, not all molecules contribute in dilating the tube. Thus, in general, the tube length is scaled in the following way

\[ L(t) = L_{eq} \cdot (\Phi_a(t))^{\alpha_2}, \]

(3.38)

where \( \Phi_a(t) \) is the unrelaxed polymer fraction, which actively constrains the relaxation process of the chains. It varies from \( \Phi(t) \) to 1, i.e. \( \Phi(t) \leq \Phi_a(t) \leq 1 \).

For the case when \( \Phi_a(t) = 1 \), which is when the chains reptate in an undilated tube, \( p_{rept}(x,t) \) can be directly calculated from (3.13); the other cases have to be solved numerically by using (3.35). When \( \Phi(t) < \Phi_a(t) < 1 \), there are some solvents which do not contribute in accelerating the relaxation process. Mathematically, this can be written as

\[ \Phi_a(t) = \sum_{i=1}^{N_a} \varphi_i \int_0^1 p_{rept}(x_i,t)dx_i + \sum_{i=N_a+1}^{n_a} \varphi_i, \]

(3.39)

where \( N_a \) is the number of arms that actively accelerate the relaxation process and \( n_a \) is the total number of arms in the system. However, both Van Ruymbek et al. and Das et al. suggested that for a polydisperse system, reptation of each arm occurs in a thin tube instead of a dilated tube. This is due to the fact that either only a small fraction of the chains will reptate in a dilated tube or only a small fraction of the chains contributes in dilating the tube of a specific arm.

### 3.3 Relaxation by fluctuations

#### 3.3.1 Arm retraction model

In a fixed entanglement network, Ball and McLeish [1] consider the relaxation of the primitive chain of an arm from segment \( x_i \) to segment \( x_i + \Delta x_i \) as an activated process so that

\[ \tau_f(x_i + \Delta x_i) = \tau_f(x_i) \exp \left( \frac{\Delta U}{k_B T} \right), \]

(3.40)

with

\[ \Delta U = U(x_i + \Delta x_i) - U(x_i), \]

(3.41)

where \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature. Here, \( \tau_f \) is the relaxation time and \( U \) is the potential energy which is given by (apart from an irrelevant constant)

\[ U(x_i) = \frac{3}{2} k_B T \frac{M_i}{M_\epsilon} x_i^2. \]

(3.42)

Equation (3.40) can also be written in the following form

\[ \ln \left( \frac{\tau_f(x_i + \Delta x_i)}{\tau_f(x_i)} \right) = \frac{\Delta U}{k_B T}. \]

(3.43)

By taking the limit \( \Delta x_i \to 0 \) of (3.43) and substituting (3.42) into it, we come to the differential equation

\[ \frac{d}{dx_i} \ln \tau_f(x_i) = \frac{1}{k_B T} \frac{dU(x_i)}{dx_i} = 3 \frac{M_i}{M_\epsilon} x_i. \]

(3.44)

---

1 A polymer system with a uniform molecular weight, i.e. each polymer contained in it has the same molecular weight as the others.

2 A polymer system with non-uniform molecular weights.
The solution of this differential equation can be easily obtained as

$$\tau_f(x_i) = \tau_0 \exp\left(\frac{U(x_i)}{k_B T}\right),$$

where \(\tau_0 = \tau_f(0)\) is a characteristic waiting time.

From (3.45), we can see that the faster (in a sense of relaxation process) segments, which are near the free end, will not constrain the movement of the very slow segments near the branching point. Therefore, the former will act as solvent, which dilutes the entanglement network, for the slower one. According to [16], in such a diluted network, the molecular weight between entanglements is given by

$$M_x(x_i) = \frac{M_{e0}}{(\Phi(x_i))^\alpha},$$

where \(\Phi(x_i)\) is the unrelaxed polymer fraction if the arm \(i\) has been relaxed up to segment \(x_i\). In the case of monodisperse symmetric stars, the unrelaxed polymer fraction \(\Phi(x_i)\) can be easily defined as

$$\Phi(x_i) = 1 - x_i.$$

The presence of dynamic dilution leads to the new expression for the relaxation time as given in [26],

$$\frac{d}{dx_i} \ln \tau_f(x_i) = 3 \frac{M_i}{M_{e0}} x_i (\Phi(x_i))^\alpha.$$

By solving this differential equation, the potential \(U\), according to (3.45), is expressed by

$$U(x_i) = k_B T \ln\left(\frac{\tau_f(x_i)}{\tau_0}\right) = 3k_B T \frac{M_i}{M_{e0}} \int_0^x (\Phi(\xi))^\alpha d\xi.$$

This formula is the general expression for the potential \(U\), with or without dynamic dilution.

Later on, Milner and McLeish [16] refined the fluctuations model by introducing the early fluctuations. They argued that arm retraction for segments near the arm end is not well described by the potential \(U\). Rather, the motion of these segments occurs by an unconstrained Rouse process. The relaxation time for these segments is expressed by [10]

$$\tau_{early}(x_i) = \frac{9\pi^3}{16} \left(\frac{M_i}{M_{e0}}\right)^2 \tau_{R,i} x_i^4,$$

where \(\tau_{R,i}\) is the Rouse time of the arm defined as

$$\tau_{R,i} = \tau_i\left(\frac{M_i}{M_{e0}}\right)^2.$$

Thus, the relaxation of segments closer to the arm end will occur by the unconstrained Rouse process, while deeper segments will fluctuate in the potential. According to Van Ruymbeke et al. [26], the transition between these processes happens at the transition segment, \(x_{trans,i}\), where the potential is equal to the Boltzmann constant times the absolute temperature, i.e. \(U(x_{trans,i}) = k_B T\). In other words, the fluctuations time for the entire range of \(x_i\) is defined as

$$\tau_f(x_i) = \begin{cases} \tau_{early}(x_i) & \text{for } x_i \leq x_{trans,i}, \\ \tau_{early}(x_{trans,i}) \exp\left(\frac{U(x_i)}{k_B T} - 1\right) & \text{for } x_i > x_{trans,i}. \end{cases}$$

16
The surviving probability of a given segment \(x_i\) of an arm of a star at time \(t\) is calculated by using the formula [26]

\[
p_{\text{fluc}}(x_i, t) = \exp\left(-\frac{t}{\tau_f(x_i)}\right).
\]

### 3.3.2 Mixtures of stars

In the case of mixtures of stars, \(\Phi(x_i)\) has to represent the unrelaxed polymer fraction when the observed arm \(i\) has been relaxed up to segment \(x_i\). In order to compute this value, it is important to be able to determine the relaxation state of the other arms starting from the relaxation state of the observed arm. Let us consider two arms, say arm \(i\) (as the observed arm) and arm \(j\). The relaxation states of arm \(i\) and arm \(j\) are linked by the equality of their potential [26]. If we introduce a new coordinate \(z_i = x_i \sqrt{M_i}\), then the potential \(U\) can be written as a function of \(z_i\):

\[
U(z_i) = 3 \frac{k_B T}{M e^0} \int_0^{z_i} z(\Phi(z)) \mu^\prime dz.
\]

Thus, the potential of arm \(i\) and arm \(j\) are equal if and only if \(z_i = z_j\), or if

\[
x_i \sqrt{M_i} = x_j \sqrt{M_j}.
\]

Now let us start with an imaginary system with only two different types of arm involved. Arm 1 has a molecular weight \(M_1\) with a volume fraction \(\varphi_1\) and arm 2 has a molecular weight \(M_2\) with a volume fraction \(\varphi_2\), where \(\varphi_2 = 1 - \varphi_1\). Here without loss of generality \(M_1 < M_2\). When arm 1 has already relaxed up to segment \(x_1\), according to (3.55), arm 2 has relaxed up to segment \(x_2\) such that

\[
x_2 = x_1 \sqrt{\frac{M_1}{M_2}}.
\]

Thus, the total unrelaxed polymer fraction at this state is given by

\[
\Phi(x_1) = \varphi_1(1 - x_1) + \varphi_2\left(1 - x_1 \sqrt{\frac{M_1}{M_2}}\right).
\]

However, we need to be careful when we define \(\Phi(x_2)\). We need to take into account that at some point, arm 1 has fully relaxed, while arm 2 still has some parts that have not relaxed yet. When both arms still have some unrelaxed parts, it means that

\[
x_2 \leq \sqrt{\frac{M_1}{M_2}}.
\]

The total unrelaxed polymer fraction at this state is coming from the unrelaxed parts of both arms:

\[
\Phi(x_2) = \varphi_1\left(1 - x_2 \sqrt{\frac{M_2}{M_1}}\right) + \varphi_2(1 - x_2), \quad \text{for } x_2 \leq \sqrt{\frac{M_1}{M_2}}.
\]

On the other hand, when all parts of arm 1 have relaxed, the total unrelaxed polymer fraction is coming only from the unrelaxed parts of arm 2:

\[
\Phi(x_2) = \varphi_2(1 - x_2), \quad \text{for } x_2 > \sqrt{\frac{M_1}{M_2}}.
\]
So now we can generalize the definitions of \( \Phi(x_1) \) and \( \Phi(x_2) \) given in (3.57), (3.59) and (3.60) for an arbitrary mixture of stars as follows
\[
\Phi(x_i) = \sum_j \varphi_j f_j(x_i),
\]
(3.61)
where
\[
f_j(x_i) = \begin{cases} 
1 - x_i \sqrt{M_i / M_j}, & x_i \leq \sqrt{M_j / M_i}, \\
0, & x_i > \sqrt{M_j / M_i}.
\end{cases}
\]
(3.62)

3.4 Relaxation by the environment

The tube dilation or dynamic dilation, which accelerates the relaxation process of a chain either by reptation or fluctuation, acts as local constraint release mechanism. Besides this local effect, a global constraint release mechanism, coming from the whole system, also must be considered. In Van Ruymbeke et al. [26], this mechanism is called relaxation by the environment. Let us introduce another probability function \( p_{\text{env}}(x_i, t) \). This probability function describes the survival probability of a non relaxed segment if we consider the influence of the relaxation of its environment on its own relaxation. This is equal to the probability that an entanglement taken at random is still oriented, if we know that the observed segment \( x_i \) is not relaxed either by reptation or fluctuation. The relaxation by environment is a generalization of double reptation ideas to polymers that can be branched.

To describe this mechanism, let us observe one arm, say arm \( i \). When a test segment \( x_i = \tilde{x}_i \) survives from reptation and fluctuation, the segments that are between this test segment and the branching point (or the center point for a linear chain) of the molecule also survive from reptation and fluctuation. Our interest here is to know the relaxation state of the other arms at this moment (when \( x_i = \tilde{x}_i \) is still survived). Based on the assumption that the relaxation states, regarding the fluctuation process, of arm \( i \) and the other arm, say arm \( j \), are linked by the equality of their potential, \( U(x_i) = U(x_j) \), we know that all the segments between the equivalent segment \( \tilde{x}_j \) (i.e. the segment that has identical fluctuation potential as \( \tilde{x}_i \)) and the branching point, where arm \( j \) is attached to, survive from fluctuation too. Since \( j \) is arbitrary, we can write the probability that segment \( x_j \) survives from fluctuation at time \( t \) as
\[
0 \leq p_{\text{fluc}}(x_j, t) \leq 1 \quad \text{for} \quad 0 \leq x_j < \tilde{x}_j,
\]
\[
p_{\text{fluc}}(x_j, t) = 1 \quad \text{for} \quad \tilde{x}_j < x_j \leq 1,
\]
(3.63)
for \( j = 1, 2, \ldots, n_a \), where \( n_a \) is the number of arms in the system. However, the segments between \( \tilde{x}_j \) and the branching point might still be relaxed by reptation; see Figure 10.
The observed arm \( i \) segments that survive from reptation and fluctuation at time \( t = x_i \) are given by

\[
\Phi_i(x_i, t) = \int_0^{x_i} p_{\text{rept}}(x_j, t)p_{\text{fluc}}(x_j, t)dx_j + \int_{x_i}^{1} p_{\text{rept}}(x_j, t)dx_j.
\]  

(3.64)

where \( \Phi_i(x_i, t) \) is the equivalent segment of arm \( i \) such that \( U(\Phi_i) = U(x_i) \) is the unrelaxed fraction of arm \( j \) at the moment when a test segment \( x_j = \Phi_j \) survives from fluctuation and reptation at time \( t \) is given by

\[
\Phi_j(x_j = \Phi_i, t) = \int_{x_j}^{1} p_{\text{rept}}(x_j, t)p_{\text{fluc}}(x_j, t)dx_j + \int_{x_j}^{1} p_{\text{rept}}(x_j, t)dx_j.
\]  

(3.65)

where \( \Phi_j(x_j, t) \) is the equivalent segment of arm \( j \) such that \( U(\Phi_j) = U(x_j) \). This formula is obtained by substituting (3.63) into (3.1). Since \( \Phi_j(x_j, t) \) is arbitrary, we can write \( \Phi_j(x_j, t) \) instead of \( \Phi(x_j, t) \). The entanglements are made by the unrelaxed part of the chains, then it is reasonable to define \( p_{\text{env}}(x_j, t) \) as a function that depends on \( \Phi(x_j, t) \). Van Ruymbeke et al. [26] defined \( p_{\text{env}}(x_j, t) \) in the following way

\[
p_{\text{env}}(x_j, t) = \left[ \sum_j \phi_j \left( \int_{x_j}^{1} p_{\text{rept}}(x_j, t)p_{\text{fluc}}(x_j, t)dx_j + \int_{x_j}^{1} p_{\text{rept}}(x_j, t)dx_j \right) \right]^{-\alpha}.
\]  

(3.66)

where \( \phi_j \) is the volume fraction of arm \( j \) and \( \alpha \) is the dilution exponent, which varies from 1 to \( 4/3 \).

### 3.5 Relaxation by reptation of an asymmetric star

Asymmetric star polymers are star polymers whose arms have different lengths (not necessarily all different). The simplest member of asymmetric star polymers is the three-arm star where two of the arms have the same length and the third arm is shorter. The two long arms together are called the backbone. This type of asymmetric star is the one that will be discussed in this section. In principal, the model that is discussed here can be generalized for any type of asymmetric star.

For asymmetric stars, the short arm has shorter terminal time than the long arms, due to the exponential arm length dependence of the fluctuation time. Thus, once the short arm has fully retracted to its branching point, it is no longer effective at entangling with the remaining unrelaxed portions of the long arms. So now the asymmetric star looks like a linear chain composed of the two long arms and it can reptate; see Figure 11.
Figure 11: Illustration of the relaxation process of an asymmetric star. (a) An asymmetric star in an equilibrium state. (b) All the arms are retracted towards the branch point. (c) The backbone repta in its tube. (d) All the arms are extended back in another direction to a new equilibrium state.

This retracted arm will increase the drag on the backbone as they reptate. The extra friction due to this retracted arm is defined as [26]

\[
\zeta_{arm} = \frac{\pi^2 k_B T}{a^2} \tau_{f,s},
\]

where \( \tau_{f,s} \) is the fluctuation time of the short arm to reach the branch point. Therefore, the total friction coefficient of the reptating backbone is found by adding the friction coefficient coming from the backbone and from the retracted arm:

\[
\zeta_{tot} = \zeta_b + \zeta_{arm}.
\]

The friction coefficient coming from the backbone is proportional to the molecular weight of the backbone \( M_b \) according to

\[
\frac{\zeta_b}{k_B T} = \frac{3\pi^2 \tau_c}{a^2} \left( \frac{M_b}{M_c} \right).
\]

This relation is derived from (3.6), (3.8) and (3.9).

In analogy with (3.8), the backbone reptation time is defined as

\[
\tau_b = \frac{L_{eq,b}^2}{\pi^2 D_b},
\]

where \( L_{eq,b} \) is the equilibrium length of the backbone and \( D_b \) is the diffusion coefficient of the backbone, which incorporates the additional drag coming from the collapsed arm, defined as

\[
D_b = \frac{k_B T}{N_b \zeta_{tot}}.
\]

Here \( N_b = M_b / M_a \), the number of monomers in the backbone. By using (3.66) and (3.68), the reptation time of the backbone can be rewritten as

\[
\tau_b = 3\tau_c Z_b^3 \left( 1 + \frac{\tau_{f,s}}{3\tau_c Z_b} \right),
\]

where \( Z_b = M_b / M_c \). It has to be noted here that the reptation time given in (3.71) is valid only if we assume that the backbone reptates in an undilated tube. The influence of dilated tube on the reptation of the backbone has to be treated in a similar way as in the case of linear chain; see Section 3.2.2.
4 Relaxation modulus and dynamic relaxation moduli

In this chapter, we indicate how we can effectively compute the complex modulus, and from this the storage and loss modulus, from the given models for the relaxation modulus derived in the preceding chapter for different types of polymer molecules, but all for a linear viscoelastic material model. In the evaluation of our computations, we will distinguish between fast relaxation and slow relaxation. The results of the computations and a validation with experimental data will be presented in Chapter 5.

4.1 Relation between the relaxation modulus and the dynamic relaxation moduli

As mentioned earlier in Section 2.3, at very short times, the chains are relaxed by a Rouse mechanism, and at longer times, the chains are relaxed by reptation, fluctuation and constraint release mechanisms. Therefore, the relaxation modulus is considered to be the sum of two different contributions; see [2] and [11]:

\[ G(t) = G_{\text{fast}}(t) + G_{\text{slow}}(t), \]

where \( G_{\text{fast}}(t) \) describes the relaxation by Rouse relaxation and \( G_{\text{slow}}(t) \) the relaxation due to escape of polymer chains from the deformed tube and the relaxation of the tube itself.

In experiments, the relaxation behavior of a polymer system is measured via the storage modulus \( G'(\omega) \) and loss modulus \( G''(\omega) \), where \( \omega \) is the oscillation frequency, rather than being directly measured via \( G(t) \). To be able to compare the computational results with the experimental data, we need to transform \( G(t) \) into \( G'(\omega) \) and \( G''(\omega) \).

Let us introduce a complex function \( G^*(\omega) \), known as the complex modulus, which is related to the relaxation modulus \( G(t) \) by [23]

\[ G^*(\omega) = i\omega \int_{0}^{\infty} G(t) e^{i\omega t} dt, \]

where \( i = \sqrt{-1} \). Detailed review of the derivation can be found in [23]. The storage \( (G') \) and loss \( (G'') \) moduli are defined as the real and the imaginary part of \( G^*(\omega) \), respectively, so

\[ G^*(\omega) = G'(\omega) + iG''(\omega). \]

Substituting (4.1) into (4.2), the complex modulus can also be written as

\[ G^*(\omega) = i\omega \int_{0}^{\infty} G_{\text{fast}}(t) e^{i\omega t} dt + i\omega \int_{0}^{\infty} G_{\text{slow}}(t) e^{i\omega t} dt \]

\[ = G^*_{\text{fast}}(\omega) + G^*_{\text{slow}}(\omega). \]

We will term \( G^*_{\text{fast}}(\omega) \) the fast-mode complex modulus and \( G^*_{\text{slow}}(\omega) \) slow-mode complex modulus.
4.2 Fast relaxation

Since our focus is not in the modeling of Rouse mechanism, we just take the formula for \( G_{\text{fast}}(t) \) as given in [2], viz.

\[
G_{\text{fast}}(t) = G_N^0 \sum_j \varphi_j \left[ \frac{1}{4Z_j} \sum_{q=1}^{Z_j-1} \exp \left( -\frac{q^2}{Z_j} t \right) + \frac{5}{4Z_j} \sum_{q=Z_j}^{N_j} \exp \left( -\frac{2q^2}{Z_j^2} t \right) \right],
\]

where \( G_N^0 \) is the rubber plateau modulus, \( \varphi_j \) is the volume fraction of arm \( j \), \( Z_j \) is the number of primitive chain segments of arm \( j \), \( N_j \) is the number of monomers in arm \( j \) and \( \tau_e \) is the entanglement time of the system. The rubber plateau modulus \( G_N^0 \) is a material constant that can be directly measured.

In (4.4), we see that the fast-mode complex modulus is formulated as follows

\[
G^*_{\text{fast}}(\omega) = i\omega \int_0^\infty G_{\text{fast}}(t)e^{-i\omega t} dt.
\]

By substituting (4.5) into (4.6), \( G^*_{\text{fast}}(\omega) \) can be calculated analytically, yielding

\[
G^*_{\text{fast}}(\omega) = i\omega G_N^0 \sum_j \varphi_j \left[ \frac{1}{4Z_j} \sum_{q=1}^{Z_j-1} \left( f_{qj} - i\omega \right) \frac{\omega^2}{\omega^2 + f_{qj}^2} + \frac{5}{4Z_j} \sum_{q=Z_j}^{N_j} \left( \frac{2f_{qj} - i\omega}{\omega^2 + 4f_{qj}^2} \right) \right].
\]

with \( f_{qj} = q^2 / (Z_j^2 \tau_e) \).

Separating into real and imaginary components

\[
G'_{\text{fast}}(\omega) = G_N^0 \sum_j \varphi_j \left[ \frac{1}{4Z_j} \sum_{q=1}^{Z_j-1} \left( \frac{\omega^2}{\omega^2 + f_{qj}^2} \right) + \frac{5}{4Z_j} \sum_{q=Z_j}^{N_j} \left( \frac{\omega^2}{\omega^2 + 4f_{qj}^2} \right) \right],
\]

\[
G''_{\text{fast}}(\omega) = G_N^0 \sum_j \varphi_j \left[ \frac{1}{4Z_j} \sum_{q=1}^{Z_j-1} \left( \frac{\omega f_{qj}}{\omega^2 + f_{qj}^2} \right) + \frac{5}{4Z_j} \sum_{q=Z_j}^{N_j} \left( \frac{2\omega f_{qj}}{\omega^2 + 4f_{qj}^2} \right) \right].
\]

It has to be noted here that the fast relaxation contributes (to the calculation of \( G(t) \) and \( G'(\omega) \)) significantly only at short times (compared to \( \tau_e \)) or, equivalently, at high frequencies [2]. If we neglect this fast relaxation, the predicted high-frequency behavior will deviate from the real one for the loss modulus. Some authors neglected the contribution of the fast relaxation in their model, for example Van den Akker [24] and Van Ruymbeke et al. [26].

4.3 Slow relaxation

The contribution of the relaxation caused by reptation, fluctuations and constraint release mechanisms to the calculation of relaxation modulus is described by \( G_{\text{slow}}(t) \). In literature, there are two different formulas that are used to calculate \( G_{\text{slow}}(t) \). Van Ruymbeke et al. [26] use the following expression for \( G_{\text{slow}}(t) \):

\[
G_{\text{slow}}(t) = G_N^0 \Psi(t),
\]

where \( \Psi(t) \) is a function which describes the relative amount of unrelaxed entanglements at a given time \( t \), while other authors (for example [2], [10] and [24]) prefer to use the following relation:
\[ G_{\text{slow}}(t) = G_N^0 \int_0^1 e^{-i\tau} d(\Psi(\tau)). \] (4.11)

In this project, both formulas are investigated. Depending on the formula which is used, different methods are required to convert \( G_{\text{slow}}(t) \) to \( G^*_{\text{slow}}(\omega) \), where

\[ G^*_{\text{slow}}(\omega) = i\omega \int_0^\infty G_{\text{slow}}(t)e^{-i\omega t} dt. \] (4.12)

Separating into real and imaginary components

\[ G^*_{\text{slow}}(\omega) = \omega \int_0^\infty G(t)\sin(\omega t) dt + i\omega \int_0^\infty G(t)\cos(\omega t) dt \]

\[ = G'_{\text{slow}}(\omega) + iG''_{\text{slow}}(\omega). \] (4.13)

Before we go into the details of the converting methods, first we need to define \( \Psi(t) \). Van Ruymbeke et al. [26], define this function as

\[ \Psi(t) = \sum_i \int_0^1 p_{\text{repl}}(x_i, t) p_{\text{fluc}}(x_i, t) p_{\text{env}}(x_i, t) dx_i. \] (4.14)

Here, we also use this definition. If we consider only a system of linear polymers and we neglect the fluctuation effect, i.e. we assume \( p_{\text{fluc}}(x_i, t) = 1 \) for any \( x_i \) and any \( t \) (the classical reptation theory [4]), equation (4.14) reduces to the relation that is used to calculate the relaxation modulus in the well-known double reptation theory [3]. In the next section, detailed explanation of converting methods from \( G_{\text{slow}}(t) \) to \( G^*_{\text{slow}}(\omega) \) are discussed.

### 4.4 Solution strategy for slow relaxation

#### 4.4.1 Schwarzl relations and trapezoidal rule of numerical integration

When we use (4.10) to define \( G_{\text{slow}}(t) \), it is difficult to calculate \( G^*_{\text{slow}}(\omega) \) analytically. In their work, Van Ruymbeke et al. [26] propose to use Schwarzl relations [21] to approximate the storage modulus \( G'_{\text{slow}}(\omega) \) and the loss modulus \( G''_{\text{slow}}(\omega) \):

\[ G'_{\text{slow}}(\omega) = G_{\text{slow}}(t) - 0.142(G_{\text{slow}}(4t) - G_{\text{slow}}(8t)) + 0.717(G_{\text{slow}}(2t) - G_{\text{slow}}(4t)) \]
\[ + 0.044(G_{\text{slow}}(t) - G_{\text{slow}}(2t)) + 0.102(G_{\text{slow}}(t/2) - G_{\text{slow}}(t)) \]
\[ + 0.101(G_{\text{slow}}(t/4) - G_{\text{slow}}(t/2)) + 0.0085(G_{\text{slow}}(t/16) - G_{\text{slow}}(t/8)), \] (4.15)

\[ G''_{\text{slow}}(\omega) = -0.470(G_{\text{slow}}(2t) - G_{\text{slow}}(4t)) + 1.674(G_{\text{slow}}(t) - G_{\text{slow}}(2t)) \]
\[ + 0.198(G_{\text{slow}}(t/2) - G_{\text{slow}}(t)) + 0.620(G_{\text{slow}}(t/4) - G_{\text{slow}}(t/2)) \]
\[ + 0.012(G_{\text{slow}}(t/8) - G_{\text{slow}}(t/4)) + 0.172(G_{\text{slow}}(t/16) - G_{\text{slow}}(t/8)), \] (4.16)

where \( t = \omega^{-1} \). Schwarzl [21] claimed that the approximation for \( G'_{\text{slow}}(\omega) \), as given in (4.15), is very accurate, while the approximation for \( G''_{\text{slow}}(\omega) \), as given in (4.16), is accurate only for high frequencies. Therefore, we propose another method to approximate \( G'(\omega) \) and \( G''(\omega) \) at lower frequencies. This method is just a straightforward numerical integration, in which we use the trapezoidal rule to approximate the relaxation moduli.
The relaxation modulus $G_{\text{slow}}(t)$ defined by (4.10) is an exponentially decreasing function with initial value $G_N^0$ and goes to zero when $t \to \infty$, because
\begin{equation}
\begin{align*}
&p_{\text{rep}}(x_i,0) = 1, \quad p_{\text{fluc}}(x_i,0) = 1, \quad p_{\text{env}}(x_i,0) = 1, \\
&\quad p_{\text{rep}}(x_i,\infty) = 0, \quad p_{\text{fluc}}(x_i,\infty) = 0, \quad p_{\text{env}}(x_i,\infty) = 0,
\end{align*}
\end{equation}
and because $p_{\text{rep}}(x_i,t)$, $p_{\text{fluc}}(x_i,t)$ and $p_{\text{env}}(x_i,t)$ are all exponentially decreasing with respect to $t$ for each arm $i$. Let $T_c$ be the time such that $G_{\text{slow}}(t) \leq 10^{-10}$ for every $t > T_c$ and let the time interval $[0,T_c]$ be discretized as $t_0,t_1,\ldots,t_K$, where $t_0 = 0$ and $t_K = T_c$. By applying the trapezoidal rule to (4.13), we have the following approximation for $G_{\text{slow}}'(\omega)$ and $G_{\text{slow}}''(\omega)$:
\begin{align}
G_{\text{slow}}'(\omega) &\approx i \omega \sum_{k=0}^{K-1} \left( t_{k+1} - t_k \right) \left( G_{\text{slow},k+1} \sin(\omega t_{k+1}) + G_{\text{slow},k} \sin(\omega t_k) \right), \\
G_{\text{slow}}''(\omega) &\approx i \omega \sum_{k=0}^{K-1} \left( t_{k+1} - t_k \right) \left( G_{\text{slow},k+1} \cos(\omega t_{k+1}) + G_{\text{slow},k} \cos(\omega t_k) \right),
\end{align}
where $G_{\text{slow},k} = G_{\text{slow}}(t_k)$. The quality of this approximation depends on the degree of discretization of the time interval $[0,T_c]$. The more frequent we discretize this time interval, the better quality we get. It will also result in a wider range of frequencies on which we can apply this approximation.

A combination of both methods, i.e. the direct numerical integration for lower frequencies (say $\omega < 10^{-2}$ s$^{-1}$; our numerical results reveal that this method diverges for higher frequencies; see for instance Figure 13, furtheron), and the Schwarzl method for higher frequencies is used in the next chapter to calculate the complex moduli. An alternative approach will be presented in the next section.

### 4.4.2 Fourier transformation

Differently from the previous case (when (4.10) is used), we use here (4.11) to define $G_{\text{slow}}(t)$ and then $G_{\text{slow}}^*(\omega)$ can be calculated analytically. By substituting (4.11) into (4.12), we obtain
\begin{equation}
G_{\text{slow}}^*(\omega) = \int_{-\infty}^{\infty} d\tau \left( \frac{1}{1 + i\omega\tau} \right) e^{-i\omega \tau} \Psi(\tau),
\end{equation}
The integral within the brackets is the Fourier transform of $e^{-i\tau}$, which we call $f(\omega)$. Here, $\tau$ is a constant parameter for $f(\omega)$. This Fourier transform can be obtained analytically, i.e.
\begin{equation}
f(\omega) = \frac{\tau(1-i\omega \tau)}{1 + (\omega \tau)^2}.
\end{equation}
Substituting (4.21) into (4.20), we find
\begin{equation}
G_{\text{slow}}^*(\omega) = i \omega G_N^0 \left( \frac{1}{1 + (\omega \tau)^2} \right) d\tau \Psi(\tau).
\end{equation}
Since $\Psi(0) = 1$ and $\Psi(\infty) = 0$, (4.22) can be rewritten as
\begin{equation}
G_{\text{slow}}^*(\omega) = -i \omega G_N^0 \left( \frac{\tau(1-i\omega \tau)}{1 + (\omega \tau)^2} \right) \frac{d\Psi(\tau)}{d\tau} d\tau.
\end{equation}
Recalling the definition of $T_c$ and the discretization of the time interval $[0,T_c]$ in the previous section, we rewrite (4.23) as

$$G^*_{\text{slow}}(\omega) = -i \omega G_N^0 \sum_{k=0}^{K-1} \left( \frac{\tau(1-i\omega\tau)}{1+(\omega\tau)^2} \right) \frac{d\Omega(\tau)}{d\tau} d\tau.$$  (4.24)

Now let us approximate $\Omega(t)$ linearly in $[t_k,t_{k+1}]$; that is we write

$$\Omega(t) = \Omega_k + \frac{\Omega_{k+1} - \Omega_k}{t_{k+1} - t_k} (t - t_k),$$  (4.25)

where $\Omega_k = \Omega(t_k)$. Thus, we have

$$\frac{d(\Omega(t))}{dt} = \frac{\Omega_{k+1} - \Omega_k}{t_{k+1} - t_k},$$  (4.26)

for $t \in [t_k,t_{k+1}]$. By substituting (4.26) into (4.24), we get

$$G^*_{\text{slow}}(\omega) = -i \omega G_N^0 \sum_{k=0}^{K-1} \left( \frac{\Omega_{k+1} - \Omega_k}{t_{k+1} - t_k} \right) \frac{\tau(1-i\omega\tau)}{1+(\omega\tau)^2} d\tau.$$  (4.27)

Separating this result in real and imaginary components, we arrive at

$$G^*_{\text{slow}}(\omega) = -G_N^0 \sum_{k=0}^{K-1} \left( \Omega_{k+1} - \Omega_k \right) \left[ 1 - \frac{\arctan(\omega t_{k+1}) - \arctan(\omega t_k)}{\omega (t_{k+1} - t_k)} \right],$$  (4.28)

$$G^*_{\text{slow}}(\omega) = -G_N^0 \sum_{k=0}^{K-1} \frac{1}{2\omega} \left( \frac{\Omega_{k+1} - \Omega_k}{t_{k+1} - t_k} \right) \ln \left( 1 + \left( \frac{\omega t_{k+1}}{t_{k+1} - t_k} \right)^2 \right).$$  (4.29)

The comparison between the computational results of the dynamic relaxation moduli, which are obtained from (4.15)-(4.16) and (4.18)-(4.19) if we use (4.10) for the relaxation modulus, and those from (4.27), if we use (4.11) for the relaxation modulus, is presented in Chapter 5.
5 Results and discussions

The model developed in the preceding chapters has been implemented in Delphi. This implementation is briefly explained in the first part of this chapter. To check the quality of the developed model, we compare its predictions to experimental data. This comparison is discussed in the second part of this chapter. The experimental data for all the samples analyzed here are taken from [26]. We tested the model on polybutadiene (PBD), polyisoprene (PI) and polystyrene (PS) samples with various architectures (linear, symmetric stars and asymmetric stars). In the third part of this chapter, we analyze the rheological behavior of polydisperse polycarbonate (PC) systems by varying the architecture of the chains.

5.1 Implementation

The implementation is called the VeSL software. The graphical user interface is depicted in Figure 12. This software calculates the relaxation function $\Psi(t)$ of given entangled linear and star polymeric systems. The function $\Psi(t)$ is used to obtain the relaxation modulus $G(t)$ and the dynamic moduli $G'(\omega)$ and $G''(\omega)$.

![Figure 12: The graphical user interface of VeSL software.](image)

The input data required by the LVE software are the model parameters and the polymer architectures. The model parameters are the rubber plateau modulus ($G_N^0$), the entanglement time ($\tau_e$), the molecular weight between entanglements ($M_e$), the monomer molecular weight ($M_o$) and the dilution exponent ($\alpha$). These data, except for the monomer molecular weight, can be obtained by fitting the predictions for dynamic moduli of a test sample to its experimental measurements. To define the polymer architectures, the information that are needed are the type of the molecules (linear chain or symmetric star or asymmetric star), the weight fraction of the
molecules and the molecular weight of the arms ($M_i$). For a polydisperse system, the weight fraction of each molecule is known from the molecular weight distribution (MWD) of the system. In Appendix A, the detailed information how to obtain the weight fraction from MWD is given.

## 5.2 Test samples

### 5.2.1 Fast relaxation versus slow relaxation

In Chapter 4, we discussed how the dynamic relaxation moduli ($G'(\omega)$ and $G''(\omega)$) are related to the relaxation modulus ($G(t)$). As we mentioned there, we distinguish between fast relaxation and slow relaxation in the evaluation of our computations. First, we start with the discussion of the computational results for slow relaxation. The sample that we tested here is a monodisperse system containing three-arm symmetric star polymers (polyisoprene: PI). We call this system PI-1 sample. The molecular weight of each molecule is 312000 g/mol. Since these molecules are three-arm symmetric stars, then each arm has molecular weight 104000 g/mol. The model parameters are chosen to be the same as in Van Ruymbeke et al. [26], where

$$G^0_s = 0.49 \text{ MPa}, \quad \tau_c = 1.7 \times 10^{-5} \text{ s}, \quad M_s = 4260 \text{ g/mol}.$$  

We use a dilution exponent of $\alpha = 1.2$ for this sample. Figure 13 and Figure 14 show the comparison between the measurements and the predictions of the storage ($G'_{slow}$) and loss ($G''_{slow}$) moduli, respectively. These predictions are obtained from (4.15)-(4.16) and (4.18)-(4.19), if we use (4.10) for the relaxation modulus, and from (4.28)-(4.29), if we use (4.11).

As one can see in Figure 13, the direct numerical integration according to (4.18) to obtain the storage modulus $G'(\omega)$, based on the model for $G_{slow}(t)$ from (4.10), starts to diverge around $\omega < 10^{-2} \text{ s}^{-1}$. This happens because there are not enough points in one period $2\pi/\omega$ in our discretization of the integral $G'_{slow}(\omega)$ in (4.18). Here, we used 1000 points to discretize the time interval $[0, T_c]$. However, for the lower frequencies for which this computation converged, the results can be used to verify what is claimed by Schwarzl [21], namely that his relation for the storage modulus is accurate even for low frequencies. To this end, one should compare the results from the Schwarzl relation (4.15), the blue dotted line, with those from the direct numerical computation.
integration (4.18), the green starred line, for \( \omega < 10^{-2} \text{ s}^{-1} \). This clearly confirms the claim of Schwarzl.

We can also compare the previous two results for slow relaxation, with those for slow relaxation according to (4.28). The latter results are presented by the red solid line in Figure 13. Although the differences are small, we observe that the latter curve gives an even better agreement with the measurement data (circles) than the combined curve for the slow relaxation.

In contrast to the computation of the storage modulus approximation, the Schwarzl relation for the loss modulus, (4.16), does diverge at low frequencies; see Figure 14. Therefore, we do need here the other computation according to (4.19) for low frequencies. Unfortunately, this computation diverges already at even lower frequencies. Hence, there is a range of frequencies in which there is no proper match between these two approximations, meaning that in this range neither of the two computational methods yields a good prediction for the loss modulus. On the other hand, if we define the relaxation modulus by (4.11), the prediction of the loss modulus can be obtained without any computational problem in the whole frequency range of interest. Thus, we suggest using (4.11) in defining the relaxation modulus \( G(t) \) and we will do so in the following discussion. As one can see in Figure 14, the predictions provide an excellent agreement with the experimental data up to a frequency of \( \omega = 10^2 \text{ s}^{-1} \). Above this frequency, all theoretical results (going downwards) diverge from the measurement data (going upwards). It has to be noted here that we have not include the fast relaxation yet in the computation. In the following discussion, we will discuss the contribution of the fast relaxation in predicting the dynamic relaxation moduli \( G' \) and \( G'' \).

![Figure 14: Comparison between measurements (circles) taken from [26] and the predictions of the loss modulus obtained from (4.16) (blue dotted line), (4.19) (green starred line) and (4.29) (red solid line) for the PI-1 sample.](image)
Figure 15 shows the behavior of the total relaxation modulus $G(t)$ of PI-1 sample, which, according to (4.1), is composed as the sum of $G_{\text{fast}}(t)$ and $G_{\text{slow}}(t)$. As we can see in this figure, the fast relaxation contributes to the relaxation modulus only at short times (short compared to $\tau_c = 1.7 \times 10^{-5}$ s). This verifies what is mentioned earlier at the end of Section 4.2. At these short times, the polymer chains have not felt the entanglements yet. However, very soon thereafter, they feel the topological constraints arising from the existence of entanglements. The tubes orient and the chains progressively lose their memory either by reptation, fluctuation or constraint release mechanisms. Hence, in this phase the relaxation process is dominated by the slow relaxation. All this is strikingly confirmed by the results shown in Figure 16 and Figure 17.

In Figure 16 and Figure 17, we compare the predictions of storage ($G'$) and loss ($G''$) moduli, which are obtained as the sum of the fast and slow relaxation contributions, with the experimental data. The available data of the experiment for the PI-1 sample is within the frequency range between $\omega = 10^{-4}$ s$^{-1}$ to $\omega = 10^{4}$ s$^{-1}$. As one can see in Figure 16, the fast relaxation does not contribute to $G'$ in this frequency range (it only comes into play for $\omega > 10^{5}$ s$^{-1}$). However, it does play an important role in calculating $G''$, as is shown in Figure 17. If we neglect this fast relaxation, the predicted high-frequency behavior deviates substantially from the measurements for the loss modulus $G''$ as we already noticed in Figure 14. The contribution of the fast relaxation corrects this deviation. From the excellent agreement between the computational results and the experimental data, we conclude that the relaxation modulus is well described by the model given in (4.1), where the fast relaxation is modeled as in (4.5) and the slow relaxation as in (4.11).

Generally speaking, we conclude that fast relaxation is relevant for small times and high frequencies, whereas slow relaxation is relevant for large times and low frequencies. In the following discussion, we include both contributions (fast and slow relaxation) in calculating the relaxation modulus $G(t)$.
Figure 16: The fast storage modulus (star line), the slow storage modulus (dotted line) and the total storage modulus (continuous line) of PI-1 sample. The prediction of the storage modulus is compared with the experimental data (circles) taken from [26].

Figure 17: The fast loss modulus (star line), the slow loss modulus (dotted line) and the total loss modulus (continuous line) of PI-1 sample. The prediction of the loss modulus is compared with the experimental data (circles) taken from [26].
5.2.2 Computational results for symmetric stars

Besides the PI-1 sample, which is discussed in the previous section, we also tested two other monodisperse symmetric star systems, the PBD-1 and PBD-2 samples. These samples are four-arm symmetric star systems. The molecular weights of these samples are given in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_{\text{molecule}}$ (g/mol)</th>
<th>$M_{\text{arm}}$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBD-1</td>
<td>121000</td>
<td>30250</td>
</tr>
<tr>
<td>PBD-2</td>
<td>162000</td>
<td>40500</td>
</tr>
</tbody>
</table>

The model parameters for PBD samples are chosen to be the same as in Fetters et al. [6]. These model parameters are

$$G_0^s = 1.15 \text{ MPa}, \quad \tau_e = 5.6 \times 10^{-7} \text{ s}, \quad M_e = 1550 \text{ g/mol}.$$  

By fitting our predictions with the experimental data for PBD samples, we found $\alpha = 1.33$ to be the best fit. The comparisons between the experimental data and predictions are depicted in Figure 18 and Figure 19, for PBD-1 and PBD-2, respectively.

Since the tested samples (including the PI-1 sample) are all symmetric stars systems, only the retraction process plays a role in the relaxation process of the polymers contained in the system. This means that at any given time $t$, $p_{\text{rep}}(x_i, t) = 1$ for each segment $x_i$ of arm $i$. By using this and recalling the definition of $p_{\text{env}}(x_i, t)$ in (3.65), we conclude that the contribution of slow relaxation to the relaxation modulus, according to (4.11) and (4.14), is purely determined by the fluctuation mechanism. In Figure 18 and Figure 19, we see a good agreement between the predictions and the experimental data. Thus, we can conclude that the fluctuation mechanism is described well by the theory presented in Section 3.3.

Figure 18: Comparison between the experimental data (taken from [18]) of PBD-1 sample for the storage (circles) and loss (triangles) moduli with their predictions (blue dotted line for storage modulus and green starred line for loss modulus).
5.2.3 Computational results for linear chains

The samples for the monodisperse linear chain systems are the PI-2 and PS-1 samples. The molecular weight of each sample is given in Table 2. For the PI sample, the model parameters are the same as before. The model parameters for PS samples are chosen to be the same as given in Van Ruymbeke et al. [26]. These model parameters are

\[ G_N' = 0.23 \text{ MPa, } \tau_e = 2.5 \times 10^{-3} \text{ s, } M_e = 16500 \text{ g/mol}. \]

The best fit for the dilution exponent is \( \alpha = 1.33 \). The comparison between the experimental data and our predictions are depicted in Figure 20 and Figure 21.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( M_{molecule} ) (g/mol)</th>
<th>( M_{arm} ) (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI-2</td>
<td>212000</td>
<td>106000</td>
</tr>
<tr>
<td>PS-1</td>
<td>355500</td>
<td>177750</td>
</tr>
</tbody>
</table>

For linear chains, both reptation and arm retraction play a role in the relaxation process. In Figure 20 and Figure 21, we see again that the predictions compare well to the measurements over a large frequency domain, except for the loss modulus of PS sample for higher frequencies. Although for the latter the trend is well predicted, the predicted values are somewhat higher than the measured ones.
Figure 20: Comparison between the experimental data (taken from [26]) of PI-2 sample for the storage (circles) and loss (triangles) moduli with their predictions (blue dotted line for storage modulus and green starred line for loss modulus).

Figure 21: Comparison between the experimental data (taken from [26]) of PS-1 sample for the storage (circles) and loss (triangles) moduli with their predictions (blue dotted line for storage modulus and green starred line for loss modulus).
5.2.4 Computational results for asymmetric stars

The last sample that we tested is the PI-3 sample containing asymmetric star polymers. The molecular weight of these molecules is 253000 g/mol. Each molecule has a short arm with molecular weight 39000 g/mol. Here, we use the same model parameters for PI samples as before. As explained earlier in Section 3.5, an asymmetric star will first relax by retracting its arms. When the short arm is fully relaxed, the backbone will also reptate with an extra friction due to this retracted arm, which is modeled as in (3.66), along its confining tube. The prediction of the storage and loss moduli is based on this idea, and the results are depicted in Figure 22. Again, we observe an excellent agreement with the experimental data.

Figure 22: Comparison between the experimental data (taken from [26]) of PI-3 sample for the storage (circles) and loss (triangles) moduli with their predictions (blue dotted line for storage modulus and green starred line for loss modulus).

5.3 Analysis of the branching effect in Polycarbonate systems

In this section, we analyze how the molecular structure affects the flow behavior of a polydisperse polycarbonate system. We recall that in the preceding section we considered monodisperse samples only. The model parameters for PC samples have been fitted on sample PC-1. This sample is a polydisperse linear chain system. The weight-average molecular weight of this system is 22700 g/mol with polydispersity index 2.35. The best fit values are

\[ G_N = 1.2 \text{ MPa}, \quad \tau_e = 1.1 \times 10^{-4} \text{ s}, \quad M_e = 2500 \text{ g/mol}, \]

and a dilution exponent \( \alpha = 1.33 \). These values compare well with those used in [25].

In Figure 23, the comparison between the predictions and the experimental data is depicted. The predictions of the relaxation moduli \( G' \) and \( G'' \), including the contribution from the fast relaxation, are represented by blue dotted and green starred lines, respectively. We see here that the predicted high-frequency (\( \omega > 10^3 \text{ s}^{-1} \)) behavior deviates substantially from the measurements, especially for the loss modulus \( G'' \). However, if we exclude the contribution of fast relaxation, i.e. we consider \( G'_{\text{slow}} \) and \( G''_{\text{slow}} \) only, we obtain a better agreement between the predictions and the measurements for higher frequencies. Unfortunately, we do not know the reason for this phenomenon; this remains a point of discussion for further study.
To continue, we analyze the effect of different molecular structures on the viscosity of the polymer system. The polymers are contained in polydisperse polycarbonate systems that have weight-average molecular weight\(^1\) between 27000 g/mol and 30000 g/mol with polydispersity index\(^2\) (PDI) between 2 and 3. These ranges coincide with the range of interest within Dow. Three variables are varied: the weight-average molecular weight, the PDI and the molecular architecture of the polymers. First, let us start by evaluating the predictions of the zero shear viscosity \(\eta_0\). This value is computed from \[4\] 
\[
\eta_0 = \lim_{\omega \to 0} \frac{G'(\omega)}{\omega}. \tag{5.1}
\]

The predictions of the zero shear viscosity for monodisperse linear chain systems and symmetric star systems are depicted in Figure 24. This figure shows a linear behavior on a log-log scale of the zero shear viscosity \(\eta_0\) as a function of the molecular weight \(M\) for the linear chains, and an exponentially behavior for the symmetric star polymers. These behaviors look like what we (and Dow) expected. In literature, for example [4] and [12], it is reported that, based on experimental results, the zero shear viscosity for the linear chains is related to their molecular weight according to 
\[
\eta_0 \propto M^{3.4}, \tag{5.2}
\]
implying that 
\[
\ln \eta_0 = 3.4 \times \ln M, \tag{5.3}
\]
apart from an irrelevant constant. From (5.3), the zero shear viscosity of the linear chains is indeed expected to be linearly dependent on a log-log scale, on the molecular weight. For star polymers, even though there is no explicit relation given between the zero shear viscosity and the molecular weight, it is reported in [4] and [12] that the zero shear viscosity should depend exponentially, again on a log-log scale, on the molecular weight; we note that our findings depicted in Figure 24 confirm this expectation.

---

\(^1\) The arithmetic mean of distribution of molecular weights [20]  
\(^2\) Its value is often used as a measure of the width of the molecular weight distribution curve [27].
Figure 24: Prediction of the zero shear viscosity of monodisperse linear (blue starred line) and symmetric star (red dotted line) polymer systems. The molecular weights (of the chain for linear polymers and of the arm for symmetric star polymers) are varied between 5000 g/mol to 100000 g/mol.

In the following figures, the predictions (based on our models and numerical simulations of the preceding chapters) of the magnitude of the complex viscosity $\eta^*(\omega)$ for different polydisperse PC samples are depicted. The complex viscosity $\eta^*(\omega)$ is related to the complex modulus $G^*(\omega)$ by [12]

$$\eta^*(\omega) = \frac{G^*(\omega)}{\omega}. \quad (5.4)$$

Thus, the magnitude of the complex viscosity is calculated from

$$|\eta^*(\omega)| = \left\{ \left[ \frac{G'(\omega)}{\omega} \right]^2 + \left[ \frac{G''(\omega)}{\omega} \right]^2 \right\}^{1/2}. \quad (5.5)$$

From (4.2) and (4.3), we have

$$\lim_{\omega \to 0} \frac{G'(\omega)}{\omega} = 0. \quad (5.6)$$

By taking the limit $\omega \to 0$ in (5.5) and substituting (5.3) and (5.6) into it, we get

$$\lim_{\omega \to 0} |\eta^*(\omega)| = \eta_0. \quad (5.7)$$

The predictions of the magnitude of the complex viscosity $\eta^*(\omega)$ for the observed polydisperse PC samples might not be accurate for high frequencies ($\omega > 10^2 \text{ s}^{-1}$), at least for the linear chain system. This is because, as we described earlier at the beginning of this section, the predicted high-frequency ($\omega > 10^2 \text{ s}^{-1}$) behavior deviates substantially from the measurements, especially for the loss modulus $G''$; see Figure 23.

In Figure 25 to Figure 27, the graphs are for fixed weight-average molecular weight and varying polydispersity index and for linear chains, symmetric stars and asymmetric star systems, respectively. As one can see in Figure 25, as $\omega \to 0$, all predicted values of $|\eta^*(\omega)|$ converge to almost the same value of $\eta_0$. Thus, we conclude that the zero shear viscosity for polydisperse linear chain systems does not strongly depend on the width of the molecular weight distribution. However, this is no longer true for the star polymer systems. As one can see in Figure 26 and Figure 27, the predicted values for $|\eta^*(\omega)|$ do not converge for $\omega \to 0$ to the same value of $\eta_0$. 

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From Figure 25 to Figure 27, one can also see that for each molecular architecture, the predicted $|\eta^*(\omega)|$ for the case where the molecular weight distribution has the broadest range, i.e. the one with PDI = 4 (red solid line), decreases faster than the other two cases. More computation results for polydisperse polycarbonate systems are given in Appendix B.

Figure 25: Prediction of the complex viscosity for polydisperse linear chain systems with different polydispersity index. The weight-average molecular weight of these systems is 28500 g/mol. Blue dotted line, green starred line and red solid line represent the system with polydispersity index equal to 2, 3 and 4, respectively.

Figure 26: Prediction of the complex viscosity for polydisperse symmetric star systems with different polydispersity index. The weight-average molecular weight of these systems is 28500 g/mol. Blue dotted line, green starred line and red solid line represent the system with polydispersity index equal to 2, 3 and 4, respectively.
Figure 27: Prediction of the complex viscosity for polydisperse asymmetric star systems with different polydispersity index. The weight-average molecular weight of these systems is 28500 g/mol. Blue dotted line, green starred line and red solid line represent the system with polydispersity index equal to 2, 3 and 4, respectively.
6 Conclusions and recommendations

The research leading to this report has produced several general conclusions:

- The linear viscoelastic behavior of a polymer system, in particular an entangled system of linear and star polymers, depends on the molecular architectures of the polymers contained in the system. This linear viscoelastic behavior is completely determined by the relaxation modulus of the system.

- The relaxation modulus can be determined by knowing the relative amount of unrelaxed entanglements of the system. Each polymer contained in the system experiences different relaxation mechanisms depending on its molecular architecture. Linear polymers will relax by reptation and retraction, symmetric star polymers will relax by retraction, while asymmetric star polymers will first relax by retraction and after a certain time they will also relax by reptation. The mathematical model for each relaxation mechanism is derived from the tube model.

- Two different formulations for the relaxation modulus proposed in literature have been investigated in this report. The first formulation, based on (4.10), which looks simpler than the second one, based on (4.11), leads to a computational problem in converting the relaxation modulus to the dynamic relaxation moduli. Therefore, we suggest using the second formulation rather than the first one in determining the relaxation modulus.

- The developed models have been validated with data taken from literature. The computational results based on these models show a good agreement with available experimental data.

- The molecular architecture of the polymer contained in polydisperse polycarbonate systems does play a role in determining the flow behavior, in particular the zero shear viscosity and the complex viscosity, of the systems.

We also recommend some issues to be considered in further research:

- In the model developed here, we assume reptation and fluctuation processes to be two independent events. Because of this assumption, the solvent (or the relaxed part of the arms) coming from the fluctuation process is neglected in the derivation of the reptation model in a dilated tube. The same happens in the derivation of the fluctuation model, where the solvent coming from the reptation process is neglected. We recommend further research on this, to see how the solvent coming from another relaxation process influences the relaxaton behavior of the polymers.

- The model developed in this project can be extended into one model, which can predict the linear viscoelastic behavior of a more complicated system, such as H-shaped polymers and pom-pom polymers. In order to do so, the retraction model needs to be improved. In analogy with the model for an asymmetric star, the fully retracted arm will increase the drag on the chain segment on which it is attached to. Thus, the effect of the increasing drag needs to be considered also in the derivation of the retraction model.
References

Appendix A: Molecular weight distribution

As mentioned earlier in Section 5.1, for a polydisperse system, the weight fraction of each molecule is known from the molecular weight distribution (MWD) of the system. Here, in the implementation, the molecular weights of the molecules are generated from the logarithmic normal distribution. The MWD is formulated on a $10^\log$ base:

$$\int_{M=0}^{\to \infty} w(M) d\log(M) = 1,$$

(A.1)

where $w(M) = dW(M)/d\log(M)$ with $W(M)$ is the weight fraction of chains with molecular weight below $M$. An example of such MWD is given in Figure A1.

![Figure A1: An example of a logarithmic normal distribution where $M_w=10000$ g/mol and PDI=4.](image)

The relations for the various distribution moments are

$$M_w = \int_{M=0}^{\to \infty} M \cdot w(M) d\log(M),$$

(A.2)

$$\frac{1}{M_n} = \int_{M=0}^{\to \infty} \frac{w(M)}{M} d\log(M),$$

(A.3)

$$M_{z+i} = \frac{\int_{M=0}^{\to \infty} M^{z+i} w(M) d\log(M)}{\int_{M=0}^{\to \infty} M^{1+i} w(M) d\log(M)}, \quad i \geq 0.$$ 

(A.4)

However, the models derived in this project require the discrete weight fraction instead of the continuous ones ($w(M)$).

Let us say that the continuous MWD is generated by using $N_c$ points. Thus, we know the values of $w(M_k)$ for $k=1,\ldots,N_c$. It has to be noted here that $w(M_k)$ is not the discrete weight fraction; it is still the continuous weight fraction at molecular weight $M_k$. Now, let us introduce $w_j(M)$ as the discrete weight fraction. Here, we set $j = k/2$ for $k=2,4,\ldots,N_d$ where $N_d = (N_c-1)/2$ if $N_c$ is odd and $N_d = (N_c-2)/2$ if $N_c$ is even. This $w_j(M)$ represents the sum of the weight fractions of the chains that have molecular weight between $M_{k-1}$ and $M_{k+1}$, i.e.
Thus, \( w_j(M) \) is the area under the curve \( w(M) \) in the interval \([M_{k-1}, M_{k+1}]\), see Figure A2, or we can write \( w_j(M) \) as

\[
w_j(M) = \int_{M_{k-1}}^{M_{k+1}} w(M) d \log(M).
\] (A.5)

Since we know the values of \( w(M_{k-1}) \), \( w(M_k) \) and \( w(M_{k+1}) \) for \( k = 2, 4, \ldots, N_d \), then we can approximate (A.5) by applying the trapezoidal rule. As mentioned above, \( w_j(M) \) is the weight fraction of an interval. In practice, we use \( M = M_k \) to represent interval \([M_{k-1}, M_{k+1}]\).

![Figure A2: The discrete weight fraction \( w_j(M) \).](image)

So now, we have the discrete MWD such that

\[
\sum_{j=1}^{N_c/2} w_j(M) \equiv 1.
\] (A.6)

The relations for the various distribution moments for the discrete MWD are

\[
M_w = \sum_j w_j M_j,
\] (A.7)

\[
\frac{1}{M_n} = \sum_j \frac{w_j}{M_j},
\] (A.8)

\[
M_{z+i} = \sum_j w_j M_j^{z+i}, \quad i \geq 0.
\] (A.9)

The more points \( (N_c) \) that we use to generate the continuous MWD, the error between the continuous and the discrete MWDs is lesser. However, if we increase \( N_c \), then the computation will become slower. The computation time that is needed to calculate the linear viscoelastic properties of a given polydisperse system will depend on the type of the chains contained in the system and the number of points \( (N_c) \) that are used in generating the MWD. As we can see in Figure A3, higher \( N_c \) results in longer time. For a polydisperse system that contains asymmetric star polymers, the computation time is much longer than a polydisperse system that contains linear or symmetric star polymers. This happens because in a polydisperse asymmetric stars...
system, each molecule is considered to have three arms where two of them have the same functionality and the same arm molecular weight. Thus, if the system contains $N_d$ molecules, then there are $2N_d$ different arms (in the sense of their function and molecular weight) to be considered in the computation process. Differently for a linear chains system and a symmetric stars system. In these types of polymer system, each molecule has two or more arms with the same functionality and the same arm molecular weight. If the systems contain $N_d$ molecules, then there are also $N_d$ different arms to be considered.

Figure A3: Computation time of polydisperse linear chains system (blue dotted line), polydisperse symmetric stars system (green starred line) and polydisperse asymmetric stars system (red circled line) for different number of points in generating the MWD. The sample which are considered here is PC sample with $M_w=27000$ g/mol and PDI=3.
Appendix B: Tables and figures

In this appendix, some computation results for the polydisperse polycarbonate system with different cases are given either in tables or in figures. Here, the weight-average molecular weight being considered is 27000 g/mol, 28500 g/mol or 30000 g/mol, while the polidispersity index is 2, 3 or 4. The first part of this appendix reports calculated average molecular weights for all the cases considered here. The number of points \( N_c \) taken in generating the continuous molecular weight (see Appendix A) is 100. The second part of this appendix reports the prediction of their complex viscosity.

B.1 Comparison between continuous and discrete MWD

Table B1: Calculated average molecular weights from log-normal distribution with input \( M_w=27000 \) g/mol and PDI=2.

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<td>( M_n ) (g/mol)</td>
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<td>( M_z ) (g/mol)</td>
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Table B2: Calculated average molecular weights from log-normal distribution with input \( M_w=28500 \) g/mol and PDI=2.

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Table B3: Calculated average molecular weights from log-normal distribution with input \( M_w=30000 \) g/mol and PDI=2.

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Table B4: Calculated average molecular weights from log-normal distribution with input \( M_w=27000 \) g/mol and PDI=3.

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**Table B5**: Calculated average molecular weights from log-normal distribution with input $M_w=28500$ g/mol and PDI=3.

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**Table B6**: Calculated average molecular weights from log-normal distribution with input $M_w=30000$ g/mol and PDI=3.

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**Table B7**: Calculated average molecular weights from log-normal distribution with input $M_w=27000$ g/mol and PDI=4.

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**Table B8**: Calculated average molecular weights from log-normal distribution with input $M_w=28500$ g/mol and PDI=4.

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**Table B9**: Calculated average molecular weights from log-normal distribution with input $M_w=27000$ g/mol and PDI=4.

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B.2 Prediction of complex viscosity for various cases

- Different molecular architecture

Figure B1: Prediction of complex viscosity for different molecular architecture; blue dotted line: linear chains, green starred line: symmetric stars and red solid line: asymmetric star. The polydispersity index is 2. The weight-average molecular weight: (a) $M_w=27000$ g/mol, (b) $M_w=28500$ g/mol and (c) $M_w=30000$ g/mol.
Figure B2: Prediction of complex viscosity for different molecular architecture; blue dotted line: linear chains, green starred line: symmetric stars and red solid line: asymmetric star. The polydispersity index is 3. The weight-average molecular weight: (a) $M_w=27000$ g/mol, (b) $M_w=28500$ g/mol and (c) $M_w=30000$ g/mol.
Figure B3: Prediction of complex viscosity for different molecular architecture; blue dotted line: linear chains, green starred line: symmetric stars and red solid line: asymmetric star. The polydispersity index is 4. The weight-average molecular weight: (a) $M_w=27000$ g/mol, (b) $M_w=28500$ g/mol and (c) $M_w=30000$ g/mol.
• Different composition of molecular architecture

![Graph B4]

Figure B4: Prediction of complex viscosity for mixture of linear and symmetric star polymers with different composition. Blue dotted line: 100% linear chains, red solid line: 80% linear chains & 20% symmetric stars, black dashed line: 50% linear chains & 50% symmetric star and green starred line: 100% symmetric stars. Here, PDI=3 and $M_w=27000$ g/mol.

![Graph B5]

Figure B5: Prediction of complex viscosity for mixture of linear and asymmetric star polymers with different composition. Blue dotted line: 100% linear chains, red solid line: 80% linear chains & 20% asymmetric stars, black dashed line: 50% linear chains & 50% asymmetric star and green starred line: 100% asymmetric stars. Here, PDI=3 and $M_w=27000$ g/mol.
- Different weight-average molecular weight

Figure B6: Prediction of complex viscosity for linear chain system with different weight-average molecular weight; blue dotted line: $M_w=27000$ g/mol, green starred line: $M_w=28500$ g/mol and red solid line: $M_w=30000$ g/mol. The polydispersity index: (a) PDI=2, (b) PDI=3 and (c) PDI=4.
Figure B7: Prediction of complex viscosity for symmetric star system with different weight-average molecular weight; blue dotted line: $M_w=27000$ g/mol, green starred line: $M_w=28500$ g/mol and red solid line: $M_w=30000$ g/mol. The polydispersity index: (a) PDI=2, (b) PDI=3 and (c) PDI=4.
Figure B8: Prediction of complex viscosity for asymmetric star system with different weight-average molecular weight; blue dotted line: $M_w=27000$ g/mol, green starred line: $M_w=28500$ g/mol and red solid line: $M_w=30000$ g/mol. The polydispersity index: (a) PDI=2, (b) PDI=3 and (c) PDI=4.
Different polydispersity index

Figure B9: Prediction of complex viscosity for linear chain system with different polydispersity index; blue dotted line: PDI=2, green starred line: PDI=3 and red solid line: PDI=4. The weight-average molecular weight: (a) $M_w=27000$ g/mol, (b) $M_w=28500$ g/mol and (c) $M_w=30000$ g/mol.
Figure B10: Prediction of complex viscosity for symmetric star system with different polydispersity index; blue dotted line: PDI=2, green starred line: PDI=3 and red solid line: PDI=4. The weight-average molecular weight: (a) $M_w=27000$ g/mol, (b) $M_w=28500$ g/mol and (c) $M_w=30000$ g/mol.
Figure B11: Prediction of complex viscosity for asymmetric star system with different polydispersity index; blue dotted line: PDI=2, green starred line: PDI=3 and red solid line: PDI=4. The weight-average molecular weight: (a) $M_w=27000$ g/mol, (b) $M_w=28500$ g/mol and (c) $M_w=30000$ g/mol.