Dynamics and Rheology of Model Branched Polymers

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Abstract

There is an intimate relationship between the molecular structure of industrial polymers, their rheological properties and their final processing and mechanical properties. The tube model of Doi, Edwards and de Gennes (Doi and Edwards, 1986; de Gennes, 1971) enables a molecular understanding of this relationship. The linear rheology data of linear and star polymers can be quantitatively predicted by adaptations of the original tube model. All parameters can be determined self-consistently from the chemistry except for the dilution exponent α and friction parameter p² whose exact values are still being debated (van Ruymbeke et al., 2012). However, the inherent problems of the tube model theory arise with predictions of complex branched structures and with predictions of these polymers in complex non-linear shear and extensional flows. One of the reasons for this is due to the uncertainty related to relaxation mechanisms such as constraint release. Moreover, it is also a problem of obtaining well-defined mondisperse branched polymers, accurate characterization of the branching structure and developing reliable non-linear flow experiments where experimental artificats are avoided. This is the exact goal of this work, to combine well-defined anionic synthesized polymers, state-of-the-art characterization tools such as TGIC and systematic rheological studies in both the linear and non-linear regime in order to validate and improve existing current tube model theories.

More specifically, our study focuses on the determination of the physical origin of chain stretch in complex branched polymers. We use the Sentmanat Extensional Rheometer fixed to a strain controlled rheometer to perform uniaxial extensional rheology. Uniaxial extensional rheology is difficult to measure in experimental set-ups but is a crucial experiment for introducing chain stretch. We investigate three types of architecture from order of branching complexity: linear, H, comb polymers. The uniaxial extensional rheology of linear polymers is highly rate dependent and the onset rate of experimental strain hardening (the macroscopic consequence of chain stretch) is equivalent to the theoretical prediction of the inverse Rouse time. Moreover, even linear polymers will stretch considerably under high deformations until they reach finite extensibility. The molecular dynamic picture becomes more complicated when introducing two or more branch points and two or more relaxation

times. We study H polymers, which have been anionically synthesized by (Roovers, 1984) and characterized recently by state-of-the-art TGIC. We discover that due to the hierarchical relaxation scheme of the H polymer, there is a greater degree of chain stretch and an earlier onset rate. We determine that as the experimental extensional rate is increased, the chain stretch is increased until it is no longer entropically favourable to do so, and branch point withdrawal occurs. Contrary to linear polymers, the maximum stretch is independent of stretch rate and only depends on architecture such that $\lambda = q$ where q is the number of arms on each branch point. This can be explained by the simple rationale that the backbone segment is not free to relax until the branches have full retracted (McLeish and Larson, 1998). When increasing the number of entanglements of the arms and backbone of the H polymer, the effect of chain stretch is magnified. Moreover, we study well-defined comb polymers (Roovers, 1979) with long molar mass of backbone M_b and rather short arm ends. When doubling the number of entanglements of the arms systematically while keeping the M_b constant, the onset of chain stretch occurs at earlier rates. This can be rationalized by accounting for the effect of dynamic tube dilution and extra drag from the arms that results in an effectively slower stretch relaxation time. We modify the original differential pom-pom model of (McLeish and Larson, 1998) with the recently added modification to include drag strain coupling (Blackwell et al., 2000) by specifying the coupling of stretch between adjacent backbone segments. The model is validated successfully by comparison with a wide variety of combs (with different molecular features) and a wide range of extensional rates. At high rates, the maximum stretch condition is reached and branch point withdrawal occurs, when arms are first oriented and then withdrawn into the stretched backbone tube segments, first from the free ends and then gradually progressing towards the center. By studying the internal dynamics of the backbone segments, we discover that at this maximum stretch condition, the central backbone segment has a stretch factor equal to $\lambda = n_s/2$ and that the stretch factor decreases by a value of 1 at each adjacent backbone segment. At these high rates, the addition of drag strain coupling smoothens the transition to maximum stretch and allows for better predictions.

Moreover, our study focuses on the effects of the environment on the reptation and fluctuations of model H and comb polymers. By systematically varying the length of the linear chains, we study the acceleration factor related to the arm and backbone relaxation times. The acceleration factor has a strong dependence on the length of the linear chains. The shorter the chains, or the larger the difference between the relaxation times of the linear

matrix and the branched polymer, the more enhanced is the acceleration factor. For the study of bidisperse linear blends, there is the Struglinksy-Graessley parameter which is often invoked to explain the transition from static dilution of the short linear chains in a dilated tube to reptation in a skinny tube. There is no similar interpretation for blends of branched polymers and linear chains. We model the SAOS data using the Time Marching Algorithm by estimating a priori whether the linear polymer would be taken as a theta solvent or whether the reptation occurs in a skinny tube. The criterion for this estimation is based on the relaxation timescale separation between the linear matrix and the H or comb. In addition, the BOB model is used to model the SAOS data of the mixtures and is shown to match the data moderately well. The second diluted plateau modulus is overpredicted, indicating that the full dilution is not taken into account.

Chapter 1

Introduction

This chapter provides a summary of the industrial significance and motivation of the study of the dynamics of model polymers. Also, the existing experimental and theoretical challenges in the field are discussed. Moreover, the following sections explain the basic concepts of polymer physics related first to the motion of one single test chain, then to the dynamics of short polymer chains and finally the extension of theoretical models to larger length scales to explain the dynamics of long-entangled chains. The tube model is discussed in depth first for linear chains and then for more complicated branched structures such as stars, H and comb polymers in order of branching complexity. The chapter concludes with some recent progress and limitations in the field. Lastly, it enlists the prime objectives and the structure of this thesis.

1.1 Scientific challenges, industrial significance and motivation

Ever since the development of the tube model (Doi and Edwards, 1978), the field of entangled polymers has fascinated scientists. The dramatic influence of purely entropic topological constraints on polymer dynamics has opened the route for designing new polymers and improving their processability. Moreover, the fact that macromolecular architecture provides the means to control viscosity via branching distribution (McLeish, 2002), say, increasing total molecular weight, can result in viscosity reduction of a star polymer in comparison to a linear polymer, has significant implications in technology. The topology of complex polymers plays a significant role in understanding their processing and final properties. The key to solving complex industrial processing problems and the design of new products is the intimate link between the topology of polymers and their melt properties. An example of a common industrial problem is the so-called shark skin, observed during deformation of a molten polymer upon passing a critical flow rate due to flow instabilities such as melt fracture and wall slip.

The study of both linear viscoelasticity and non-linear shear and extensional properties of model polymers are crucial in closing the industrial design loop as shown in Figure 1.1. Linear viscoelasticity is very sensitive to details of the molecular structure and offers direct information about relaxation times of branching and blend components, as well as the respective moduli. Well-controlled non-linear shear and extensional rheology simulate more closely real processing conditions.

Most industrial processes such as extrusion, blow molding and film blowing consist of complex flows and are often a combination of strong shear and extensional flows at rates much higher than the inverse characteristic polymer relaxation time. Hence, the polymer chains undergo significant orientation and stretching. In effect, the extensional component plays a key role in industrial processes, however the majority of the experimental studies are focused on shear flow. Moreover, the behavior of one polymeric system under shear is not necessarily reflective of the behavior of the same system under extension. For example, common industrial grades linear density polyethylene (randomly branched) and high density polyethylene (mostly linear) have the same shear thinning response although LDPE is considerably more strain hardening than HDPE due to the the presence of long-chain branching (LCB) in the structure of the former (McLeish, 2002). Therefore, the design of well-controlled non-linear rheology experiments in both shear and extension as well as the extension of molecular viscoelastic models also in the non-linear flow regime are of great industrial interest.



Figure 1.1: Graphical diagram of the industrial motivation of this study. Rheology is instrumental in linking the molecular structure with the processing behavior and vice-versa.

Moreover, although model systems are far from industrial polymeric materials since the former have low polydispersity, are amorphous homopolymers and are well defined in terms of their branching content, their study is really the first step in understanding the effect of topological interactions of polymers on the dynamic response. Without the experimental rheology data generated with these well-defined systems, it would be impossible to further test and develop any of the latest-state of the art molecular models (Larson et al., 2001; Likhtman and McLeish, 2002; van Ruymbeke et al., 2006). Graessley was the pioneer of this type of work, he was the first to systematically study the rheological properties of model polymers (Graessley et al., 1976; Graessley and Roovers, 1979; Graessley et al., 1980).

The ultimate goal of these molecular models is to be used as a tool to predict microstructural information from viscoelastic and non-linear data of industrial resins (Shanbhag, 2011). Linear density polyethylene is an example of an ill-defined industrial blend polymer material, highly polydisperse in both molecular weight and branching content.

The topology of LDPE is a combination of several branched structures such as Caylee trees, combs, H, star and linear polymers. Thanks largely to the advances in computational models such as Branch on Branch polymers (BOB) (Das et al., 2006), Reptate (Likhtman and McLeish, 2002), Time Marching Algorithm (TMA) (van Ruymbeke et al., 2006), Hierarchical Model (Larson, 2001; Park et al., 2005), the mystery behind the structure of LDPE is one step closer to being solved. These computational models include all of the most recent and state-of-the art theoretical treatments in the field. A new term coined computational rheology allows one to match the rheological response of an industrial polymer to a complex branched ensemble. These new computational tools have strengthened the collaboration between industry and academia and have allowed for significant advancements in the field. In this study, we use BOB, Reptate and TMA and verify their applicability, strengths and weaknesses for model polymers.

Evidence of the major effect of the topology of polymers on the physical properties of molten polymers is long-chain branching (LCB) in randomly branched polymers. A very small amount of LCB provides for optimum final product properties which include a large amount of shear thinning and high zero shear viscosity. The enhanced shear thinning ensures reduced energy consumption at the same output rates. The high zero shear viscosity contributes to improved mechanical properties and reduced sag.

However, the analysis of long-chain branching is extremely difficult and often rheology on its own is not a powerful enough characterization method. Usually, a combination of techniques are needed in addition to rheological methods, such as melt-state C-NMR spectroscopy, size exclusion chromatography (SEC), temperature rising elution chromatography (TREF) and light-scattering (by g-factor). One of the reasons why rheology is not sufficient to detect LBC is the fact that, whereas it is such a powerful quantitative tool sensing any microstructural change, it lacks qualitative resolution, as needed for example in the case of different microstructural characteristics which give rise to the same macroscopic response. For example, it has been shown that the effects of polydispersity and the effects of long-chain branching act in the same direction, say with respect to nonlinear shear and extensional viscosity (Münstedt, 1980; Hatzikiriakos, 2000; Lohse et al., 2002; Milner, 1996; Doerpinghaus and Baird, 2003; Auhl et al., 2009; Stadler et al., 2009; van Ruymbeke et al., 2010b). Note that industrial polyolefins, even when produced using metallocene catalysts, have a minimum polydispersity index of 2. Hence, it is important to separate the effects of polydispersity and architecture. One of the main goals of the thesis, is to elucidate the role of branching features such as the length and number of branches on the rheological response. This is only possible with the use of well-defined model branched systems. We comparatively study model systems by increasing the level of branching complexity. For example, we study the rheological effects of a single branch point by comparing a linear polymer to a star polymer. Moreover, we study the effect of multiple branch points by studying the macroscopic response of model H and comb polymers.

In the following sections of the introduction, we will begin with a short description of the polymer physics related to a single polymer chain and then proceed to larger length scales and finally discuss the dynamics of long entangled chains. Most of the introduction will be focused on a description of the tube model and its elaboration for branched and polydisperse structures and for more complex shear and extensional flows.

1.2 Linear flexible chains: Kuhn model

In order to understand the macroscopic dynamic response of topologically complex polymers, it is important to first understand the fundamental polymer physics of a single polymer chain. (Kuhn, 1934) first described the configuration of polymer chains using the random coil model. A polymer chain is assumed to be a Gaussian freely jointed chain as shown in Figure 1.2. In addition, the following assumptions are made: it is a phantom chain (two chain segments cannot occupy the same space); and the chain is not extended by external forces such as flow (Dealy and Larson, 2006). The chain consists of N_f freely jointed segments of length b_f (Kuhn length). A molecule will move by Brownian motion through many equally probable conformations (random walk) at a single point in time and the mean-square end to end distance is given by:

$$\left\langle R^2 \right\rangle_0 = b_f^2 N_f \qquad 1.1$$



Figure 1.2: Random walk polymer chain statistics

1.3 Dynamics of short unentangled chains

Short unentangled polymer chains can be modeled using a Rouse model (Rouse, 1953), the simplest of the molecular dynamic models. The polymer chain (Figure 1.3) can be represented as a series of N beads (monomer being the degree of polymerization) with monomeric friction coefficient ζ_0 , connected to Gaussian entropic springs. The friction is considered equidistributed in the chain such that $\zeta=N\zeta_0$.



Figure 1.3 Sketch of the Rouse model applied to a single polymer chain which is represented by N beads connected to entropic springs

The Rouse model accounts for the chains in an inert non-interacting environment of other chains, hence it excludes hydrodynamic interactions and excluded volume effects. Although, there are many simplifications inherent in the Rouse model, it has been shown to be useful in modelling entangled polymer dynamics in the melt and in semidilute concentration regimes (Doi and Edwards, 1986). Also, for long entangled chains, the Rouse theory is valid at very short times of the chain relaxation within the tube (see below). The longest Rouse relaxation time is proportional to M^2 , where M is the molecular weight of the polymer chain. In a frequency sweep curve, the characteristic features of the Rouse model include a slope of $\frac{1}{2}$ at intermediate frequencies for both the storage and loss modulus and at terminal frequencies a slope of 2 and 1 for the storage and loss modulus respectively.

$$G'(\omega), G''(\omega) \sim \omega^{1/2} \text{ for } \frac{1}{\tau_{R}} < \omega < \frac{1}{\tau_{0}}$$

$$G'(\omega) \sim \omega \text{ and } G'(\omega) \sim \omega^{2} \text{ for } \omega < \frac{1}{\tau_{R}}$$
1.2

Polymers consist of a large number (hundreds or thousands) of repeating monomers convalenty bonded together. An oligomer is composed of only few monomers. The smaller the number of monomers in a molecule, the more significant is the effect of the local monomer chemistry. For instance, amorphous polymers and oligomers have different glass transition temperatures, which is known to vary significantly with molar mass. Therefore, all viscoelastic data needs to be compared not at the same temperature but at the same distance to T_g (Graessley, 2004).

1.4 Dynamics of long entangled chains

Due to their size, the macroscopic properties of long, entangled flexible polymers depend only on topological interactions. Evidence of the universality of the melt properties for the same monomer chemistry is observed in both the viscosity scaling and the elastic plateau modulus. Below a critical molecular weight where $M_c \sim 2$ times M_e , the viscosity of a polymer is proportional to the M_w but above M_c it follows a steep power law behavior where $\eta \sim M^{3.4}$ (Ferry, 1980; Berry and Fox, 1968).

The high-M regime is known as the entanglement regime. Here, these long chains cannot cross each and are topologically constraint by their neighbors as seen in Figure 1.4. The characteristic molecular weight between them is M_e and has a characteristic relaxation time of a sub-chain between two consecutive entanglements τ_e . These entanglements are similar to chemical crosslinks such as those found in rubber networks except that the physical entanglements are transient and are only measured over a limited frequency range. The molecular model which explains the physical picture of chain statistics preserved within an entanglement segment (blob) is the tube model which will be explained further below.



Figure 1.4: Sketch of physical picture of entanglements. The polymer chains which are contained within their theoretical tube are overlapping with other polymer chains

The molecular weight between entanglements is universal for the same chemical microstructure and is derived from the rubber-elasticity theory (Green-Tobolsky, 1980; Doi and Edwards, 1986):

$$M_e = \frac{\rho RT}{G_N^0}$$
 1.3

At an earlier stage, before entanglements are active, 1/5 of the tension along the chain is relaxed by longitudinal monomer rearrangements along the tube (Likhtman and McLeish, 2002) and therefore, the plateau modulus is reduced by 4/5 of its value.

$$M_{e} = \frac{4\rho RT}{5G_{N}^{0}}$$
 1.4

1.5 Tube model

The scientific breakthrough which made possible the understanding of the link between molecular structure and polymer dynamics was the tube theory (Doi and Edwards, 1986) and reptation (de Gennes, 1971), concepts which were expanded more recently by (Milner and McLeish, 1998; Likhtman and McLeish, 2002) and others (van Ruymbeke et al., 2006). The tube model was first introduced to explain the dynamics of rubbers by (Edwards, 1967) and then elaborated by de Gennes to include the theory of reptation. (Doi and Edwards, 1978) were the first to develop a constitutive equation based on the elaborated tube concept and reptation of entangled linear chains. The topological constraints caused by the presence of other long, flexible entangled chains, also trapped within their respective tubes restricts the motion of the test chain inside a theoretical tube (Figure 1.5). The parameters which define the tube include the tube diameter a and the length of the tube l_{eq} (primitive path or contour length). The latter is equal to:

$$L_{aq} = \frac{N}{N_e} l$$
 1.5

where N represents the total number of Kuhn segments in the chain, N_e is the total number of Kuhn segments between two entanglements and 1 is the length of a segment between two entanglements. The tube diameter a (following Graessley's definition) is equivalent to:

$$a^{2} = \frac{4M_{e}b^{2}}{5M_{e}}$$
 1.6

with b as the random-walk parameter derived by equation 1.1 where R^2 is the end to end distance of the tube.



Figure 1.5: Sketch of the tube and the parameters which define the tube

1.6 Linear polymers and reptation

In the linear viscoelastic regime, long linear entangled polymers will undergo three relaxation mechanisms in order to relax their tube conformations from an imposed stress or strain 1) reptation 2) contour length flunctuations and 3) constraint release.

The test chain trapped within its theoretical tube can only relax its stress by diffusing (thermal Brownian motion) along the curvilinear distance of its tube, a term known as

reptation. It is the main mechanism of relaxation of linear polymers and becomes progressively less important, the more heavily branched the polymer system. Figure 1.6 illustrates the steps in the reptation process. The analogy most often used as representative of the reptation process is the diffusion of a snake.



Figure 1.6: Reptation process (Rubinstein and Colby, 2003) a) at one end of the snake, formation of a loop b) loop propagates along the tube c) release of the loop and creation of new section of the tube

The original Doi and Edwards model was further developed by the incorporation of contour length flunctuations (Doi, 1981; Milner and McLeish, 1998) and thermal constraint release (de Gennes, 1975; Rubinstein and Colby, 1998). With these modifications, the model was able to explain more quantitatively terminal viscoelastic properties of flexible linear polymers such as the 3.4 power law of the zero shear viscosity.

The chain ends of linear polymers will relax by a faster process known as contour length fluctuations, (Doi, 1981) spring-like chain fluctuations, as seen in Figure 1.7, which will act to decrease the viscosity with respect to the reptation prediction. Chain-end fluctuations are more predominant in short chains and by increasing chain length, they progressively lose importance.



Figure 1.7: Illustration of contour length fluctuation relaxation process. The ends of chains pull away from the tube, previous tube segments vanish and new tube conformations are created.

Additionally, due to the non-permanent nature of the tube, tube motion (thermal constraint release) will also act to speed up the reptation process. The release of multiple constraints due to relaxation of surrounding chains, will act to change the conformation of the tube (vertical hops of the tube). These vertical tube hops are modeled by "Rouse motion" of connected tube sections (Likhtman and McLeish, 2002). In Figure 1.8, the steps in the constraint release relaxation process are illustrated.



Figure 1.8: Illustration of constraint release rouse process. Constraints from surrounding chains are removed, new constraints are formed and the conformation of the tube changes (also called tube renewal or tube re-configuration).

1.7 Star polymers dynamics

Reptation is not possible for the most simple branched architecture, the star polymer due to the presence of a branch point which makes it impossible for the chains to slide along the tube. Rather, stars relax their stress by fluctuations, similarly to the chain ends of linear polymers. More specifically, initially, the chain ends will relax by rapid Rouse motion (Pearson and Helfland, 1984; Milner and McLeish, 1997) and later, this rapid chain end motion will crossover to an exponentially slow activated diffusion of the deeper arm segments. Meanwhile, the relaxed arms segments will act as a dynamic solvent (Marrucci, 1985; Ball and McLeish, 1989) for the remaining arm segments and the effective tube grows throughout the relaxation process. This is not an entropically favorable process and is exponentially dependent on the length of the arms (de Gennes, 1979). In figure 1.9, the viscosity dependence on span M_w for a linear polymer is compared to that of a data set of star polymers (Fetters and Pearson, 1983). As discussed in Chapter 1.1, the linear entangled polymer follows a 3.4 power-law dependence whereas the star polymer follows a much steeper exponential dependence on the number of arm entanglements.



Figure 1.9: Star viscosity data versus span M_w showing the exponential dependence on M_{arm} and the comparison between the power law-dependence of linear polymers (Fetters and Pearson, 1983).

Star polymers have both a very broad and slow relaxation time spectrum. This is clearly evident in the linear rheology curve where a shoulder in seen in the loss modulus G" (Frischknecht et al., 2002). Additionally, the number of arms has no effect on the relaxation time, up to a functionality of about 30. At higher functionalities, the central core of the star has more of a colloidal nature than a polymeric one (Vlassopoulos et al., 2001).

1.8 H polymer dynamics

The next most complicated branched structure is the H polymer. The H polymer consists of two arms attached to each end of a central backbone. The relaxation mechanism is primarily governed by a hierarchical process from the outer parts with free ends (here branches) to the inner without free ends (here backbone) (McLeish, 1988). As seen in Figure 1.10, initially, the H polymer backbone remains frozen until the final retraction of the arms. Similarly to stars, the H polymer arms will relax by exponentially slow contour length flunctuations (Roovers, 1984; McLeish et al., 1999). Additionally, the backbone will act as a type of permanent network for the relaxing arms, and hence slow down the relaxation even further. The longest relaxation time is then not only exponentially dependent on the number of entanglements of the arms but also on the arm fraction. The relaxed fraction of the arms will act as a solvent for the unrelaxed fraction (backbone) and hence, reduce the effective number of entanglements of the backbone and dilate the tube. Experimental evidence of dynamic tube dilation is determined from the value of the second plateau modulus which is equal to $G_N^0 \phi_b^{\alpha+1}$ where $\alpha=1$ or 4/3 (Graessley, 2008; Rubinstein and Colby, 1990).

All the effective friction of the arms is concentrated on the branch points. On time scales shorter than τ_{arm} , the branch points are localized and cannot move. The branch points begin to hop between neighboring cells of the entanglement net on the time scale of arm retraction τ_{arm} . The length scales of these hops are of the order of the tube diameter a. Figure 1.10 illustrates the three major relaxation mechanisms associated with the H polymer.



Figure 1.10: Illustration of the three step process in the hierarchical relaxation of H polymers. First, the star arms will retract while the backbone remains immobile. Second, the tube will expand and the arms will act as a dynamic solvent. Third, the branch points will perform diffusive hops. Image of branch point hopping (Bacova et al., 2013) of a star polymer with three arms.

The H polymer is the most simple branch polymer which exhibits strain hardening, the macroscopic consequence of chain stretch, experimentally seen as an upturn in the tensile stress growth coefficient compared to the linear viscoelastic prediction, in extensional flow. The condition for strain hardening is that a segment is contained within two branch points. There has been significant progress in understanding the dynamics of H polymers thanks to the seminal work of (McLeish et al., 1999) which incorporates in one model the linear relaxation mechanisms (reptation, CLF, hierarchical relaxation) and the non-linear chain stretch parameter in order to predict linear, non-linear rheology and neutron scattering experimental data. Moreover, the pom-pom model of (McLeish and Larson, 1997) provides a molecular framework for the understanding the non-linear rheology of H polymers and other more complicated pom-pom structures. The pom-pom model will be discussed in more depth in Chapter 3.

1.9 Comb polymer dynamics

The comb polymer is a structure with a higher level of complexity than the H polymer due to the presence of multiple branch points. For the comb structure, the friction is distributed at each of these branch points and not localized on the chain ends as is the case of H polymers or other structures with two branch points and multiple arms attached to these such as the pom-pom molecule. There are two types of comb polymers which have been investigated previously, the ones with a linear backbone (Roovers and Graessley, 1981; Ahmadi et al., 2011; Chambon et al., 2008; Daniels et al., 2001, Kapnistos et al., 2005) and the ones with a star backbone (Kapnistos, 2006). Attached to the linear or star backbone, there are an equal number of branches which are distributed randomly along the branches. However, the majority of molecular models assume equidistant distribution of comb branches, however, they account separately for polydispersity and uncertainty and position of branches (Daniels et al., 2001; Kapnistos et al., 2005). The dynamic relaxation of comb polymers with linear backbone are similar to H since, they both consist of two separate hierachical mechanisms governed first by the arms through fluctuations and second by the backbone, through dynamically diluted reptation. Also, similarly to the H polymers, the segments between branch points lead to chain stretch and strain hardening. However, the comb cannot be modelled using the same physical concepts as used for the H and pom-pom but rather can be rescaled as a dynamic diluted linear polymer with the effective friction concentrated at the branch points (Lentzakis et al., 2013). The extensional rheology behaviour of comb polymers will be discussed in more depth in Chapter 3.

1.10 Industrial branched polymers dynamics

The ultimate goal of all the rheological work on model polymers is to develop the expertise needed to understand the relaxation mechanisms of more complex branched systems which are similar to those found in industrial applications. For highly randomly branched structures, it is known from modeling and from rheological data, that relaxation proceeds hierarchically (Chen et al., 2010; Das et al., 2006; Read et al., 2011). The relaxation will proceed from the outer most segments (chain ends between branch points or a dangling end) to the deeper inner most segments. In order to follow the relaxation of the branching segments, each segment is given a seniority or priority value (Figure 1.11) and its value is

determined by the number of segments connected to the dangling ends (Read et al., 2011, Rubinstein et al., 1990; McLeish, 2002).

All variables in these computational models (BOB and Hierarchical Model) are predetermined from the chemistry (M_e , τ_e and melt density) and tube-model theory parameters (α and p^2). However, there are still some uncertainties related to the choice of tube-model theory parameters (Park and Larson, 2003; van Ruymbeke et al., 2012). Despite this, these hierarchical models are able to predict semi-quantitatively the rheology of complex randomly branched polymers (Read et al., 2011).



Figure 1.11: Seniority or priority values of each chain segment in a randomly branched polymer (Read et al., 2011). The relaxation proceeds from the free ends, assigned a seniority value of 1 to the inner most segments, which are assigned the highest seniority value (4 in our diagram).

1.11 Extension of viscoelastic models to branched and blend structures

While the linear rheology of monodisperse linear and star polymers is well described by adapted versions of the Doi-Edwards model, other more complicated branched structures (H, combs, Caylee trees) and blends of these still present a challenge. Although, there have been groups who have been successful in the predictions of H (McLeish, 1988), comb (Daniels et al., 2001; Kapnistos et al., 2005; Ahmadi et al., 2011) (as mentioned in the previous sections), asymmetric star polymers (Frischknecht et al., 2002), Cayley-trees (Blackwell et al., 2001; van Ruymbeke et al. 2007, 2010) there still remains open challenges and the need for a unified approach.

For instance, one open problem is how to account for polydispersity in both branching content and molecular weight distribution. In polydisperse systems, it becomes important to understand the incorporation of thermal constraint release into the existing theoretical models. For polydisperse melts of short and long chains, constraint release is important since fast relaxation of short chains remove topological constraints and allow partial relaxation of long chains (Struglinsky and Graessley, 1985; Watanabe et al., 1984, 1985, 2004; van Ruymbeke, 2010). Several models and interpretations of constraint release exist in the literature. Example of the latter include, the Rouse-like motion of the tube (Graessley, 1982), tube dilation (Marrucci, 1985), double reptation (Tsenoglou, 1987; des Cloizeaux, 1988) and dual constraint model (Pattamaprom and Larson, 2001). Due to uncertainty around the interpretation of constraint release, even the linear viscoelasticity of simple bimodals blends of linear-linear and linear-star still presents a challenge (Viovy et al., 1991; Park and Larson, 2006; Read et al., 2012).

1.12 Extension of viscoelastic models to non-linear rheology

The tube model of Doi, Edwards and de Gennes (1986) with the added relaxation mechanisms of CLF and contraint release has been successfully implemented in predicting the linear viscoelasticity of entangled solutions and polymer melts. Also, in the case of non-linear step-strain relaxation, the experimental damping function superimposes well with the predicted damping function for entangled linear and star chains (review by Osaki, 1993). Moreover, taking into account the theory of dynamic tube dilation, the model also can quantitatively predict the weaker damping function of more complex branched structures such as combs which have additional modes of relaxation (Kapnistos et al., 2009). However, in other cases, the Doi and Edwards model cannot quantitatively and at times, qualitatively predict the experimental data in the non-linear regime.

For example, start-up transient shear data of linear and branched polymers as a function of shear rate shows a plateau for shear rates between the inverse Reptation time and inverse Rouse time. The Doi and Edwards model shows a stress maximum (overshoot) in this region which suggests a shear banding instability (Ravindranath et al., 2008). (Marrucci, 1996) proposed an additional relaxation mechanism, convective constraint release (CCR) at high rates, which acts to remove entanglements due to the effect of convective flow on the surrounding chain. (Ianniruberto and Marrucci, 1996; Mead et al., 1998; Ottinger, 1999;

Graham et al., 2003) have developed non-linear constitutive models in which the influence of CCR and stretch is incorporated.

Moreover, the Doi-Edwards model also fails to predict the negative $\frac{1}{2}$ slope (Bach et al., 2003) found experimentally using the state-of the art filament stretching rheometer of the transient steady stress growth coefficient plotted versus extensional rate (rates between $1/\tau_D$ and $1/\tau_R$). Rather, the Doi-Edwards model predicts a slope of -1. In figure 1.12 (Marrucci and Ianniruberto, 2004), the difference between the theoretical prediction and the experimentally determined slope is visualized. In addition, for the experimentally determined data of the group of Hassager, at high rates, there is no upturn of the tensile stress growth coefficient for linear entangled polymer melts. However, for entangled polymer solutions, this upturn is experimentally observed (Huang et al. 2013). Therefore, more experimental data and theoretical investigations are needed in the non-linear regime in order to be able to make more quantative predictions.



Figure 1.12: Comparison of experimentally determined data of (Bach et al., 2003) and Doi and Edwards theoretical prediction (Marrucci and Ianniruberto, 2004).

1.13 Structural probes and non-linear rheology

Rheology is an indirect probe of chain and tube motion. From rheological methods, it is impossible to extract tube parameters such as tube length and tube diameter. The latter can only be extracted indirectly from tube theory calculations. More microscopic probes of polymer dynamics include neutron-scattering, neutron-spin echo (Wischnewski et al., 2002; Zamponi et al., 2010), NMR (Cormier et al., 2001), dielectric spectroscopy (Watanabe et al.

2004, 2005) and molecular dynamic simulations (Kremer and Grest, 1990; Auhl et al., 2003; Everaers et al., 2010; Zhou and Larson, 2010; Wang et al., 2010; Bacova et al., 2013).

In order to have fully quantatitive tube model theories, microscopic probes are needed in addition to rheological methods. For example, the combination of rheology and Neutron Scattering experiments (McLeish et al. 1999, Ruocco et al. 2013) or Neutron Spin Echo Spectroscopy (Zamponi, 2010), allow the direct observation of the short-time stress relaxation of entangled polymer chains. Selectively labelling parts of the structure of complex polymers, for example labelling chain ends, allows the distinction between the stress relaxation of each of the chain segments. One open problem which can only be investigated by microscopic probes is the validity of the assumption of affine deformation of the tube (Read, 2004). These questions can only be properly addressed with microscopic probes although theorists have proposed different explanations in order to understand deviations of non-linear rheological data (Read, 2003; Marrucci and Ianniruberto, 1999).

Conventional commercial rheometers can be used for standard linear viscoelastic measurements. However, in the nonlinear regime at high shear rates and/or shear amplitudes, modifications to conventional commercial rheometers are needed. The problems arise due to various instabilities such as edge fracture, wall slip and elastic instability (McKinley et al., 1991). Edge fracture is an instability which is specific to cone-plate and parallel-plate shear flows of viscoelastic materials at high shear rates (Hutton, 1963; Tanner and Keentok, 1983). It is characterized by the formation of a crack or indentation at a high shear rate on the free surface of the liquid. By the combination of flow visualization techniques and methods to delay melt fracture such as for example the cone-partitioned plate (Meissner, 1989; Schweizer 2002; Snijkers et al. 2011), more reliable non-linear data can be achieved. The flow visualization techniques include particle image velocimetry (Ravindranath et al., 2008; Li et al., 2013) neutron scattering (Heinrich et al., 2004; Ruocco et al., 2013) or confocal microscopy (Lam et al., 2003). These techniques are essential to both isolate the effects of each of the flow instabilities but also in the experimental design of non-linear rheological experiments which are for the most part, free of these flow instabilities. Moreover, it is important to understand that rheological properties are measured and tested by models based on the assumption that the flow and deformation is homogeneous. Therefore, the models are as robust as the design and execution of the experiments.

1.14 Progress in the field

Important progress has been made in the field of polymer dynamics mainly due to three contributing factors. First, the availability of well-defined monodisperse branched polymers (Roovers, 1979; Pitsikalis, 1998; Hadjichristidis, 1999). Second, the development of state-of the art characterization techniques in both chromatography (TGIC) and extensional (Bach, 2003) and shear rheology (Meissner, 1989; Schweizer, 2002). Third, the advancement in coarse-grained tube-model theories (Likhtman and McLeish, 2002; Larson et al., 2002; van Ruymbeke et al., 2006) and "slip-link" models (Schieber et al., 2003; Likhtman, 2005; Khaliullin and Schieber, 2009, 2010; Masubuchi et al., 2008).

Although nearly monodisperse polymers can be produced (by high-vacuum anionic polymerization), when it comes to branched polymers their architectural dispersity could be a problem. Recent advances in characterization combining Temperature Gradient Interaction Chromatography, TGIC (Chang, 2005) and modeling have shown that the targeted anionic synthesis of a specific branched architecture can lead to a range of side products which may affect the final rheological properties (Snijkers et al., 2011; Chen et al., 2011, Chambon et al. 2008; Li et al. 2011; Hutchings et al., 2012). In order to account for the presence of these side products in the analysis of the rheological response, Larson has developed a rheological methodology named combinatorial rheology (Chen et al., 2011). First, they characterize the anionically synthesized branched polymer with the state-of the art TGIC method and perform fractionation to remove any and all side-products. Next, the sample is blended with its precursor, characterized once again by TGIC and finally they analyze the rheology of both the sample and its blend using the latest state-of-the art theories. The idea is to be able to control the polydispersity and then model the system and not model the system based on the assumption that the polymers are wrongly monodisperse.

As a short summary of the Introduction, we present a table which presents the characteristic dynamic features of the most simple polymeric structure of unentangled linear chains extending to the more complicated branched structures such as H, comb and pom-pom models.

Table 1.1: Characteristic dynamic and rheological features of unentangled linear, entangled linear, star and H, combs and pom-pom structure.

Types	Unentangled linear	Entangled linear	Stars	H, combs and pom-pom
Molecular Architecture	~	\langle	S	5
Main Mechanism of Motion	- Rouse model	- Reptation: center of mass diffusion	- CLF: arm retractions which becomes less entropically favourable as branchpoint is reached.	- Combination of CLF (at high frequency) and reptation at low frequency
Additional Modes of Relaxation		 Constraint Release Rouse (tube motion) CLF of chain ends DTD in polydisperse 	- DTD - CR	 Dynamic tube dilution of backbone CR Branch point hopping
Characteristic features of linear rheology curve	- No plateau modulus	- The longer the length, the more extended the rubber plateau modulus in frequency	 Logarithmic plateau modulus Broad relaxation time with extended shoulder in G" 	- Two plateau moduli, a universal plateau modulus and a second plateau modulus of diluted backbone
Non-linear features	 No overshoot seen in non-linear start up shear, except at high rates Shear thinning due to finite extensibility 	 Overshoot seen in non-linear start- up shear at intermediate and high rates Strain hardening only at rates higher than 1/T_R due to retraction of chain within the tube 	 Shear thinning No increased strain hardening except in asymmetric stars 	 Shear thinning Increased strain hardening due to stretch of backbone contained within two branch points.

1.15 Objectives

Listed below are the objectives of this work pertaining to the viscoelastic response of branched polymers undergoing linear and non-linear deformation.

- 1. Study of experimental linear and non-linear rheology of well-defined complex branched polymer systems.
- 2. Validate and improve current tube-model theories.

Organization of the thesis

This Thesis has been structured in five chapters as follows.

Chapter 1 provides a brief introduction and background literature on polymer dynamics. The discussion in this chapter sets the motivation and objective of this study.

Chapter 2 gives a detailed description of the model branched polymers systems used in the thesis and the experimental techniques and the methods used to investigate the structure and rheology of these systems.

Chapter 3 presents the results on the tensile stress growth coefficient of the simple linear, H and finally more complex comb polymer systems and how the molecular features affect the tensile stress growth coefficients and the modeling results on these comb systems.

In **Chapter 4**, the influence of constraint release and contour length fluctuations in a dilute blend of model H and comb polymer is presented. We use the TMA (Time-Marching Algorithm) to fit the linear rheology data and try to understand the effects of the environment (length of linear chains) on the dynamics of the model branched polymer.

Chapter 5 summarizes the salient conclusions from each chapter enriching the literature on dynamics of polymers and further ends with the recommendation for future investigations in this field.

Chapter 2

Systems and Characterization

This chapter provides a detailed procedure used for the rheological characterization and also gives background information on the experimental protocols and methods that are pertinent to the results presented in the subsequent Chapters. It begins with a brief description of all the model systems used. Next, the experimental methodology used is explained. Finally, a detailed description of the various characterization techniques is presented such as Size Exclusion Chromatography (SEC), Temperature Gradient Interaction Chromatography (TGIC), Differential Scanning Calorimetry (DSC), Dynamic light scattering (DLS), and finally Linear and Non-Linear Rheological Methods.

2.1 Polymer Systems

All polymer systems used in this study are well-defined, nearly monodisperse and amorphous homopolymers. We have used two different chemistries, polyisoprene (1,4 addition) and polystyrene. The anionic synthesis of the combs (Roovers, 1979, Kirkwood et al., 2009) and H polymers (Roovers and Toporowski, 1981) is described in the literature. The linear polymers were either purchased commercially from Polymer Source (Montreal, Canada) or Polymer Standard Service (Mainz, Germany) or synthesized by synthetic chemists in Athens or Mainz. Their molecular characteristics are listed in Table 2.1, 2.2, 2.3 and 2.4. In all cases, the polydispersity index (PDI= M_w/M_n) where the subscripts w and n refer to weight- and number- average molar mass) was less than 1.1. Hence, the samples can be considered as model polymers. However, the true confirmation of their quality at the architectural level comes from the temperature gradient interaction molecular chromatography analysis (TGIC). In order for a polymer to be considered well-defined, it becomes imperative to control all the following molecular parameters:

- Molecular weight
- Microstructure, in the case of polyisoprene, rich in 1,4 addition (>90%)
- Polydispersity (less than 1.1, preferably less than 1.05)
- Chain end (branch) functionality
- Homogeneity of branching architecture (architectural dispersity)

2.1.1 Linear Polymers

Both un-entangled and entangled linear monodisperse polymers were used in this study. The aim of the rheological experiments on the linear polymers was twofold. First, as a reference for the model branched polymers and second, as a blend component in the mixtures. The molecular characteristics of the linear polymers use in this study are found in Table 2.1.

The rheological response of linear model polymers is well understood and can easily be predicted by their molar mass. The larger the molar mass, the more extended the frequency range of the plateau modulus, although its value is independent of the M_w . The plateau modulus is inversely proportional to M_e and can be determined from equation 1.4. At lower frequency, the chains are no longer in their pseudo-equilibrium state, they undergo a relaxation process and the relaxation modulus G(t) drops quickly. The relaxation time for monodisperse entangled linear polymers has a 3.4 power-law dependency on the molar mass (same as the zero-shear viscosity).

Code	$M_w \left(kg/mol\right)^1$	PDI
PS 5k ⁴	5.1	1.08
PS 22k ⁴	22.2	1.07
PS 51k⁴	50.8	1.06
PS 129k ⁴	129	1.04
PS 182k ⁵	182	1.03
PS 262k ⁶	262	1.1
PS 483k ⁵	483	1.05
PS 1M ²	1000	

PI 22k ³	22.2	1.05
PI 96k ²	96	1.02
PI 1.5M ³	1500	

1 The molar masses mentioned are weight-averaged

2 from Athens

- 3 from MPI (Mainz Polymer Institute) Polymerforschung
- 4 from Polymer Source
- 5 from Polymer Standard Service
- 6 from BASF

2.1.2 H polymers

The polystyrene H polymers were recently characterized by TGIC in order to determine their quality and polydispersity since they were synthesized a long time ago by (Roovers, 1981) and kindly donated. Both H polymers have the same molar mass of backbone and arms and a large volume fraction of arms of approximately 81%.

Table 2.2: Molecular characteristics of model H polymers used

Polystyrene	$M_b (kg/mol)^1$	$M_a (kg/mol)^1$	$M_{total}(kg/mol)^1$
H2A1 ²	44	46	228
H3A1 ²	123	132	651

1 The molar masses mentioned are weight-averaged

2 from (Roovers 1981)

2.1.3 Comb polymers

Three series of comb polymers were used in this study, two of which are polystyrene and the other one is 1,4 polyisoprene. The PS combs were synthesized by (Roovers, 1979) and the PI combs by Driva (Kirkwood et al., 2009) and kindly donated. The combs were also recently characterized by TGIC.

The PS combs consists of two series classified by the molecular weight of the backbone. The C6 series have an M_b of 275k, a constant number of arms (q~30) and an average $M_{seg} < M_e$, where M_{seg} is the molar mass between the backbone branch points as well

as the molar mass between the chain ends and their respective branch point. The C7 series have a larger M_b of 860k, a constant number of arms (q~30) and an average $M_{seg} > M_e$.

The PI series has roughly the same average $M_{seg}>M_e$, varying number of branches (4.6-17.6), varying M_a (from less than 1 to 3 entanglements) and varying M_b (14-62 entanglements assuming $M_e=6kg/mol$) (Fetters et al., 2006).

Code	$\mathbf{M}_{\mathbf{b}}$ (kg/mol) 1	$\mathbf{M}_{\mathbf{a}}$ (kg/mol) 1	q (number of branches)	$\mathbf{M}_{\mathbf{total}}$ (kg/mol) ¹
PI472k ²	370	5.8	17.6	472
PI254k ²	120.5	18.8	7.1	254
PI211k ²	157	6.3	8.6	211
C622-PS ³	275	11.7	30	624
C642-PS ³	275	47	29	1630
C712-PS ³	860	6.5	30	1055
C722-PS ³	860	11.7	28	1190
C732-PS ³	860	25.7	26	1530
C742-PS ³	860	47	29	2530

Table 2.3: Molecular characteristics of model comb polymers used

1 The molar masses mentioned are weight-averaged

2 from (Kirkwood et al., 2009)

3 from (Roovers, 1979)

2.1.4 Mixtures

Two series of mixtures were used. In the first series, the H polystyrene H3A1 was blended with a series of varying M_w linear polymers. The second blend consisted of the comb polyisoprene PI254k blended with different M_w linear polymers.

The linear monodisperse PS samples were blended with 1.5%, 3% and/or 10% volume fraction of H polymer (Table 2.4). The samples were carefully weighed, enough tetrahydrofuran (THF) or toluene was added in order to completely dilute the mixture and the blend was slowly mixed (for a minimum of one full day). Toluene was used as a solvent instead of THF in the case of the high M_w PS samples since it was shown to be a more

appropriate solvent. The use of a stirrer and THF solvent lead to degradation, more specifically chain scission, of high M_w PS samples during sample preparation. Therefore to ensure the high quality of the sample, the mixing of these samples was performed using a tumbler and THF was replaced with toluene. After mixing, the solvent was then evaporated slowly at first and then gradually more quickly as the temperature was increased above the glass transition temperature (above 100°C) in a well-sealed vacuum oven in order to evaporate the last remaining drops of solvent. In order to ensure that all the THF was evaporated, the weight of the mixture was monitored. The linear monodisperse PI samples were blended with 10% by vol. fraction of PI254k comb polymer, mixed with cyclohexane and the evaporation process followed was the same as for polystyrene.

CODE	Vol fr. H or comb	M _{total} (kg/mol)
PS 5k ⁻¹	10%	70
PS 22k ¹	1.5%, 3%, 10%	32, 41, 85
PS 51k ¹	1.5%, 3%, 10%	60, 70, 111
PS 129k ⁻¹	3%, 10%	147, 181
PS 182k ¹	1.5%, 3%, 10%	189, 199, 229
PS 483k ¹	10%	500
PS 1 M ¹	10%	965
PI 22k ²	10%	45
PI 96k ²	10%	51
PI 1.5 M ²	10%	1380

Table 2.4: Molecular characteristics of mixtures used.

The molar mases mentioned are weight-averaged except for PS 483k, whose molar mass corresponds to a peak M_w

- 1 Linear PS blended with H polymer H3A1
- 2 Linear PI blended with comb polymer PI254k

2.2 Methodology

The global objective of the thesis is to link the molecular characteristics of model polymers to their dynamic response. In order to achieve this goal, a systematic methodology is needed and each step is critically important. The polymers are first synthesized and separately characterized by the synthetic chemists both during and/or after the synthesis.
Complex branched polymers need to be characterized during synthesis due to the procedure inherently involved in anionic synthesis. For example, to synthesize a model H polymer, in a first step, the arms and backbone are both polymerized and characterized separately and in a second step, they are polymerized together via a linking agent. The standard characterization techniques used by the synthetic chemists are Size Exclusion Chromatography (SEC) coupled with Multiple-Angle Light Scattering for obtention of the molecular weight distribution, ¹H-NMR spectroscopy for analysis of microstructure content and Differential Scanning Calorimetry (DSC) for determination of glass transition temperature.

Before performing any linear rheology experiments, first computational programs are used such as tube-based BOB (Das et al., 2006) and Reptate (Likhtman and McLeish, 2002) in order to predict the rheological response. Due to the limitations inherent in the study of model polymers such as low sample quantity and sample degradation even at moderately high temperatures, it is imperative to have a first estimation of the linear rheological response. This will enable first to establish the experimental conditions, such as measurement temperatures and the approximate time needed for sample equilibration and second, as a problem-solving tool in case of any technical problems related to the measurement. Especially in the case of linear and star entangled polymers, these computational tools are indispensable since they offer exceptional viscoelastic predictions. After performing a linear rheology experiment, the linear viscoelastic envelope is calculated and the appropriate conditions for non-linear rheology measurements are determined. A final step after performing measurements in the non-linear regime is the comparison with appropriate theoretical molecular models. However, due to the quantitative and often qualitative differences between non-linear rheological models and experimental data, this is often not possible. Therefore, there are two alternatives, either a development or modification of tubebased molecular models or a systematic phenomenological analysis.



Figure 2.1: Schematic of methodology followed in this thesis

2.3 Anionic synthesis of model polymers

The anionic synthesis of the systems mentioned in Chapter 2.1 was not performed by us but by synthetic chemists. Therefore, only a brief description of the method will be explained.

Living anionic polymerization under high vacuum conditions has been demonstrated to be an ideal method to synthesize well-defined polymers with low degrees of compositional heterogeneity and with control of the major structural parameters that affect polymer properties. This method involves chain reaction polymerizations that proceed in the absence of the kinetic steps of chain termination and chain transfer. It is possible to determine and control the number average molecular weight (M_n) of the final polymer via the stoichiometry since one initiator molecule generates one final polymer molecule.

Anionic synthesis is a very difficult synthetic method to perform since the presence of a trace amount of impurities will lead to undesirable termination reactions. As a consequence,

most often fractionation is needed to remove by-products. Therefore, model polymers synthesized using this technique are often prepared in very small sample quantities which becomes a considerable limitation for further rheological measurements.

One example of anionic synthesis of stars using chlorosilane chemistry is shown in Figure 2.2. The synthesis was performed by Kedar Ratkathwar (Ratkanthwar et al., 2013). First a narrow M_w linear living polyisoprene was prepared in benzene with sec-BuLi as an initiator. Each of the arms were removed by termination with degassed MeOH. Next, each of the living polyisoprene arms were end-capped with 4-5 units of butadiene before the final reaction with the linking agent tetrachlorosilane to obtain the 4 star arm.



Figure 2.2: Steps of the four arm star PI living anionic polymerization (Ratkanthwar et al., 2013)

2.4 Characterization of Molar Mass

Traditionally, the method of choice for characterization of M_w was Size Exclusion Chromatography (SEC) since it was both a quick and efficient method. However, there are inherent limitations to SEC as will be discussed in the following section. The advent of the TGIC method allowed for a more accurate characterization tool, with the only limitations of larger amount of sample and time needed for each measurement.

2.4.1 Size exclusion chromatography (SEC)

The systems described in Chapter 2.1 were characterized by Size Exclusion Chromatography (SEC) to assess their quality and level of polydispersity. It is a technique which separates molecules based on differences in hydrodynamic volume (size), in order to obtain information about the average molecular weight and molecular weight distribution. The polymer is dissolved in a solvent and pumped through columns packed with porous beads. The largest molecules will flow easily and quickly through the column and will be detected first, while the small molecules will move a longer distance through all beads and will be detected last.

For linear polymers, molecular weight is proportional to molecular size, which is defined by the mean square radius of gyration. Standard commercial calibrations are available for linear polymers which convert elution volume to molecular weight. However, for branched polymers, characterization is not as straight-forward since the branches can lead to a more compact structure which decreases the hydrodynamic volume. Otherwise, different architectures may be of the same size but have different molecular weights. Therefore, in order to detect the actual M_w distribution, the setup needs to be equipped with a Multi Angle Light Scattering Detector. Another limitation of SEC is observed for high molecular weight polymers which are difficult to characterize due to plugging and chain scission during the measurement.

For SEC analysis of the PS samples, two columns (Agilent, Mixed-B two-column set, $300 \times 7.5 \text{ mm i.d.}$) were used at a column temperature of 40 °C. Eluent was THF (Samchun, HPLC grade) at a flow rate of 0.8 mL/min. SEC chromatograms were recorded with a light scattering (LS)/refractive index (RI)/viscometer (DP) (Viscotek TDA 302) and a UV absorption detector (TSP, UV2000 at 260 nm wavelength) for on-line determination of absolute molar mass of polymers. The dn/dc value for PS in THF is 0.185 mL/g. Polymer samples were dissolved in THF at a concentration of ~1 mg/mL, and the injection volume was 100 µL.

2.4.2 Temperature gradient interaction chromatography (TGIC)

Although all the monodisperse branched polymers in this study have been prepared using high-vacuum anionic synthesis, they cannot be considered to be entirely pure since there are still very small fractions of other species present (as discussed in the Introduction). Size exclusion chromatography may reveal a polydispersity index as low as 1.03, but this is not fully accurate because of the inherent limitations of the technique. The main problem is the co-elution of analytes with similar hydrodynamic volumes. The effect of these impurities can be negligeable but in some cases, can have very important rheological implications. Such is the case of ring polymers, where very small fraction of linear polymer contaminants (1%) can produce drastic changes in the rheological response (Kapnistos et al., 2008). The challenge is both the characterization and the removal of these impurities.

Temperature Gradient Interaction Chromatography (Chang et al., 1999) offers a solution to the limitations of SEC. It does not separate based on molecular size but rather on molecular weight and has better resolution and sensitivity to branching components of complex polymers than SEC. It is a type of high performance liquid chromatography method which controls the retention of polymer molecules during isocratic elution by a programmed variation of temperature of the columns.

For reversed phase (RP) TGIC analyses of PS combs, a C18 bonded silica column (Nucleosil C18, 7 μ m, 500 Å pore, 150 × 4.6 mm i.d.) was used. The mobile phase was a CH₂Cl₂/CH₃CN mixture (57/43, v/v, Samchun, HPLC grade) at a flow rate of 0.5 mL/min. The temperature of the column was controlled by circulating fluid from a programmable bath/circulator (ThermoHaake, C25P) through a homemade column jacket. The sample solutions (~5 mg/mL) were prepared by dissolving the polymers in a small volume of the eluent and the injection volume was 100 μ L. The chromatograms were recorded with a LS detector (Wyatt, Tristar) and UV detector (Younglin, UV730D).

2.5 Dynamic light scattering (DLS)

Dynamic light scattering measures fluctuations in scattered light intensity due to particles diffusing by Brownian motion. In our study, dynamic light scattering was performed on a dilute polystyrene H polymer in a good solvent (THF) in order to determine the overlap concentration c* (as explained in Figure 2.3).



Figure 2.3: Polymer chains as they pass from dilute regime $c < c^*$, where the distance between the chains is larger than their size, to the overlap concentration $c=c^*$, where the chains overlap and at higher volume fraction $c>c^*$, to the semi-dilute regime where there is considerable overlap and chain interactions.

The setup is a standard goniometer light scattering setup by ALV (Langen, Germany), which uses a PM (photo multiplier) tube as a detector and a ALV-5000 correlator which correlates intensity with time and determines the auto correlation function. Dynamic light scattering was performed at five angles (30, 60, 90, 120 and 150 degrees).

A beam of monochromatic light (laser of wavelength 532 nm) hits the particles in the sample and light gets scattered in all directions. The scattering vector q is defined as the difference between incident beam vector K_i and the scattered beam vector, K_f in equation 2.1

$$q = K_{\rm i} - K_{\rm f} = 4\pi n \frac{\sin\theta/2}{\lambda}$$
 2.1

where n = refractive index of the solvent, λ = wavelength of the laser of 532 nm.

The autocorrelation function (time-dependent fluctuation in the scattering intensity which contains the dynamic information of the particles), obtained was analyzed typically with an exponential fit to determine the decay rate.

$$\Gamma(q) = D_{l}(q)q^{2} \qquad 2.2$$

In our case, the sample is monodisperse and therefore the decay rate can be fit with a single exponential function. The decay rate divided by the diffusion coefficient is plotted against q^2 (at various angles). The extrapolation of this curve to q = 0 which in our case is not necessary since a straight line (another indication that the sample is monodisperse) is obtained will allow the determination of the diffusion coefficient. The hydrodynamic radius is then related

to the diffusion coefficient and η the viscosity of the solvent by the Stokes-Einstein-Sutherland equation 2.3

$$R_{H} = \frac{k_{B}T}{6\pi\eta D_{t}}$$
 2.3

where k_B the Boltzmann constant and η the viscosity of the solvent.

From the hydrodynamic radius, it was then possible to calculate the critical chain overlap concentration c^* , the crossover concentration between the dilute and semi-dilute concentration (when chains interpenetrate) regime using equation 2.4.

$$c^* = \frac{3M}{4\pi R_{H}^{3} N_{AVG}}$$
 2.4

where M corresponds to the molar mass and N_{avg} corresponds to Avogrado's Number.

2.6 Differential scanning calorimetry (DSC)

Differential Scanning Calorimetry was used to determine the glass transition temperature of the amorphous polymers. A standard calorimeter (PL-DSC from TA) was used and all the samples were heated at a rate of 10 °C/min.

The value of the glass transition temperature is important to measure for the model polymers since it influences the entanglement time τ_e . Its value is dependent on the flexibility of the chains and their interactions. For linear polymers, the Fox-Flory equation relates the number-average molecular weight M_n, to the glass transition temperature T_g by the following equation:

where $T_{g,\infty}$ is the maximum glass transition temperature and K is a material specific constant. This relationship is mostly valid at low molecular weights since the reduction of T_g is due to the free volume contribution of chain ends and at high molecular weights, there is a levelling off to a plateau value.

2.7 Linear rheology

Rheology is the study of flow and deformation of matter. More specifically, it describes how stress or strain develops in a sample when a well-defined stress or deformation (shear or extension) is imposed. For complex polymers melts, rheology is an ideal characterization method since the molecular structure and viscoelastic properties are intimately linked to the rheological characterization (described in Chapter 1.1).

First, the basic concepts of rheology are introduced by considering the most simple shear flow condition of two parallel plates separated by a distance d as shown in Figure 2.4. The top plate slides with a velocity v and a force F_{xy} applied while the bottom plate is stationary (v=0), creating a gradient dv_x/dy which is constant throughout the gap h. This gradient is known as the shear rate calculated as the ratio of the velocity v and the plate-plate distance h.

$$\dot{\gamma}_0 = \frac{v}{h} \tag{2.6}$$

The deformation (strain) is dimensionless and is defined by the deflection d divided by the plate-plate distance h.

$$\gamma = \frac{d}{h}$$
 2.7

Moreover, the shear stress is defined as the ratio of the F_{xy} and the cross-sectional area.

$$\sigma_{xy} = \frac{F_{xy}}{A}$$
 2.8

In practice, this is not the preferred rheological method and rather rotational rheometers are more commonly used. Although there are some groups which have designed novel sliding plate rheometers for oscillatory measurements, notably JM Dealy's group (Giacomin et al., 1989).



Figure 2.4: Shear flow created by an upper plate which moves with a velocity v and force F while the bottom plate is stationary.

Linear rheology measurements give valuable information on viscoelastic properties, structure, relaxation times and MWD information. Small amplitude oscillatory shear, stress relaxation and creep are all examples of linear rheology measurements. An experiment is assumed to be linear if the deformation or stress imposed is sufficiently small that the polymer chains remain in the equilibrium state.

2.7.1 Small amplitude oscillatory shear

The most commonly used linear rheology experiment is SAOS (Small Amplitude Oscillatory Shear). In a strain controlled rheometer, the strain imposed is a sine wave.

$$\gamma_{xy} = \gamma_0 \sin(\omega t) \tag{2.9}$$

If the strain amplitude is sufficiently small to generate a linear response, the stress response is also sinusoidal but shifted horizontally by a phase angle δ (Figure 2.5). From an SAOS experiment, the storage modulus G' (elastic response) and the loss modulus G'' (viscuous response) are the outputs of interest and they can be determined from the stress response.





Figure 2.5: Sinuisodal strain imposed and corresponding stress response in a SAOS experiment

SAOS experiments were performed for the monodisperse and blend PS and PI samples on an ARES 2KFRTN1 strain-controlled rheometer (TA Instruments, USA) at temperatures ranging from 110°C to 190°C for PS and -60°C to 80°C for PI with an Invar (copper-iron alloy with low thermal expansion coefficient) parallel plate geometry of 8, 13 and 25 mm diameter. The lower limit is determined by the glass transition temperature of the sample and the upper limit is determined by the final relaxation time of the sample and the accuracy of the transducer. The temperature control was achieved with a convection oven yielding an accuracy \pm 0.1°C and the measurements were always performed in a nitrogen environment in order to reduce the risk of degradation. Although SAOS experiments are relatively easy to perform, they can still be problematic if a well-defined methodology is not performed which include the following steps:

- Sample preparation: High M_w PI and PS samples were press-molded in a vacuum oven into diskotic shape of 8,13 or 25 mm diameter and thickness between 0.7 and 1.5 mm at temperatures much higher than the glass transition temperature. Low M_w PS and PI samples were loaded directly in the rheometer.
- 2. **Sample loaded** and trimmed in order to fill entire gap and create a homogeneous spherical (bulge) shape at the ends



Figure 2.6: Correct sample loading shape in the parallel plate geometry

- 3. **Time sweep and strain sweep** measurements were performed at the loading temperature in order to ensure proper thermal equilibration of the sample and to determine the conditions needed (percentage of strain) to remain in the linear regime.
- 4. Frequency sweep (FS) measurement at loading temperature.
- 5. Steps 3 and 4 are repeated at different temperatures, minimum of three FS measurements needed.
- 6. The final FS measured is again at the loading temperature. If the final FS is different than the initial FS than this is a sign of sample degradation and/or inhomogeneous sample shape between the parallel plates.
- 7. Time-temperature superposition was performed (as explained below)

Time-temperature superposition (TTS) (Ferry, 1980; Dealy and Plazek, 2009) is necessary in order to extend the frequency sweep to a broad range of frequencies and times. TTS was performed at a reference temperature of 130°C and 170°C for PS and 0°C and 25°C for PI and the WLF parameters were calculated in order to generate a complete mastercurve which captured all the relevant viscoelastic parameters ie entanglement time τ_e , plateau modulus G_N^0 and reptation time τ_D . The entanglement time corresponds to the high frequency crossover of G' and G'', the plateau modulus is extracted from the G' at the minimum of tan δ = G''(ω)/G'(ω) and the reptation time corresponds to the low frequency crossover.

For the melts, the vertical shift factors b_T were calculated from the density compensation [Ferry (1980)]:

$$b_{T} = \frac{\rho(T_{REF})(T_{REF})}{\rho(T)(T)}$$
 2.11

with ρ the density and T the temperature [K]) where for PS:

$$\rho(T) = 1.2503 - 6.05 \times 10^{-4}(T)$$
 2.12

and for PI (ρ in g/cm³, T in K, Zoller and Walsh 1995)

$$\rho(T) = 0.918 - 5.34 \times 10^{-4} T - 4.70 \times 10^{-8} T^{2}$$
 2.13

are hence not fitted. The horizontal shift factors a_T follow from a two dimensional minimization procedure. They can be fitted with the WLF-equation (Ferry 1980):

$$\log(a_{T}) = \frac{-C_{1}(T - T_{REF})}{C_{2} + T - T_{REF}}$$
 2.14

For the PS samples, the following parameters result: $C_1=8.4$ and $C_2=80^{\circ}C$ at a reference temperature T_{REF} of 130°C. In addition, the data was also time-temperature superimposed at T_{REF} of 170°C to obtain the following shift factors $C_1=5.6$ and $C_2=120^{\circ}$ C which is consistent with other literature values when compared to the same reference value (Kapnistos et al., 2005; Kapnistos et al., 2008; Ferry, 1980). In Figure 2.7, a plot of the shift factors obtained for various PS architectures is depicted.



Figure 2.7: Horizontal (a_T) and vertical shift factors (b_T) for polystyrene comb, H, star, linear and blend mixtures.

For the polyisoprene, the following WLF parameters are found at 0°C, C_1 =5.5 and C_2 =110°C consistent with other works (Snijkers et al., 2013, Kirkwood et al., 2009, Auhl et al., 2008).

In addition, the data was also time-temperature superimposed at T_{REF} of 25°C to obtain the following shift factors C_1 =4.5 and C_2 =132° C, again consistent with other literature values when compared to the same reference value. In Figure 2.8, a plot of the shift factors obtained for various PI architectures is shown.



Figure 2.8: Horizontal (a_T) and vertical shift factors (b_T) for polyisoprene comb, star, linear and blend mixtures.

2.7.1.1 Experimental Challenges of SAOS

In the specific case of FS measurements at low frequencies, high phase angle values (approaching 90°) and when the G'' is much higher than the G' value, the G' values are associated with a large amount of error and are therefore considered unreliable. The problem is that only a small amount of the total signal comes from the response associated with the G' modulus. Therefore the characteristic G' slope equal to 2 which is representative of the terminal relaxation of a monodisperse polymer sample is difficult to obtain. Instead there is a bending of the G', which is characterized by a higher value of G' and a tan delta value that varies with strain%. A way to counteract this and obtain a reliable G' measurement is to continuously increase the strain amplitude as the frequency decreases and thus obtain higher values of torque. In this case, it is important to monitor carefully the transition to non-linear behavior which may arise at high strain amplitudes. In order to achieve the right balance, a high enough strain amplitude needs to be applied in order to have a clear G' signal but not too

high which would result in the transition to non-linear behavior. A good methodology to use is to run strain sweeps at varying frequencies and find the minimum strain amplitude which results in a constant tan delta value (Velankar, 2007).

In addition to the limitations associated with the instrument, there are also sample considerations which may lead to this G' bending effect. Even anionic synthesized polymers contain some polydispersity, which is often hard to detect even by SEC (Size Exclusion Chromatography) (Snijkers et al., 2011). Even a very small fraction of high M_w contaminants (less than 1%) which relax at these low frequencies would add extra elasticity. Another potential problem is the existence of small bubbles in the polymer samples. Although the samples were not loaded with bubbles, it is possible that during the measurement, small bubbles were formed which are invisible to distinguish by eye (Figure 2.9). These bubbles are most likely created by the adsorption of water despite the fact that the polystyrene is not hygroscopic.



Figure 2.9: Small bubble in the PS sample which are not visible by eye

The bubbles which cause an extra relaxation process may be wrongfully mistaken for a structural relaxation but rather is due to the slow relaxation of the interfacial tension at the low frequencies (Mundstedt, 2013). The action taken to counteract this effect is to anneal the sample overnight in a vacuum oven before the rheological measurement.

2.7.2 Stress relaxation and creep measurements

Another type of linear rheology experiment is a stress relaxation experiment where the strain is increased instantaneously from 0 to a constant strain value γ_0 . The ratio of shear stress to the strain imposed corresponds to the relaxation modulus G(t). An example of a stress relaxation curve for an entangled linear polymer is seen in Figure 2.10 where the sample transitions from a glassy regime to a temporary permanent network (plateau modulus) to a liquid-like flow regime.



Figure 2.10: Stress Relaxation Curve

Therefore as explained in 2.7.1.1, due to the problems which may be related either to instrument or sample limitations, it becomes necessary to find another method in which to measure the viscoelastic response at low frequencies. Therefore, in addition to FS measurements performed in the ARES rheometer, we also performed stress relaxation and creep measurements on the Physica MCR 501 (Anton Paar, Austria) stress-controlled rheometer (with an efficient feedback control loop for precise strain-control measurements as well) with 8 mm parallel plates. The temperature control of $\pm 0.1^{\circ}$ C was achieved with a Peltier system, under nitrogen atmosphere. The Anton-Paar Physica can be used for stress relaxation experiments since it has a an efficient feedback control loop feedback mechanism to enable it to function in strain controlled mode. Moreover, the Anton Paar has a better low torque resolution than the ARES, which enables the measurement of stress relaxation at long times.

Stress relaxation and creep measurements can provide for more accurate measurements at long times and low frequencies because they are both faster and can be performed at lower more safe temperatures. However, there are also many considerations to take into account such as conversion methods from stress relaxation G(t) and creep compliance J(t) to dynamic storage $G'(\omega)$ and loss modulus $G''(\omega)$. Also, it is very important to ensure that the strain and stress imposed is in the linear regime. In order to verify this, the G(t) and J(t) curves should superimpose on each other at different magnitudes of strain and stress.

For the purpose of comparing with simulation data, it would be preferable to measure stress relaxation for a wide range of times and frequencies. However, it is very difficult to obtain complete and accurate G(t) for a very wide range of times, specifically, at short times (transducer response time) and long times (poor torque resolution). In order to obtain a higher torque response typically the strain magnitude could be increased but this can potentially lead to wall slip and edge fracture, two of the most common artifacts of step strain experiments (Venerus, 2005). The conversion from stress relaxation G(t) to G'(ω) and G" (ω) and vice versa can be performed using programs such as TA Orchestrator software, NLREG (Nonlinear Regression Analysis Programme) software and Reptate. In order to make sure that our G(t) is in fact reliable we superimpose the converted G'(ω) and G" (ω), using the TTS shift factors.

To probe the lowest frequency range, the ideal linear rheology method is creep compliance since unlike SAOS the torque does not decay with time. However, creep experiments are not accurate at short times since the stress needs some time to reach its desired value. Another problem related to this type of measurement is that the build of strain with time might cause a shift from the linear to the non-linear regime. In creep compliance measurements, the stress is increased from 0 to a constant stress value of σ_0 (as shown in Figure 2.11). The creep compliance J(t) measured corresponds to the ratio of the transient strain and σ_0 .



Figure 2.11: Creep Compliance Curve

There are many numerical methods which can be used to convert from J(t) to $G'(\omega)$ and $G''(\omega)$. Different methods include the use of NLREG software, TA Orchestrator software, Reptate, Evans et al. program (Evans et al., 2009). However, all these methods involve Fourier transformation of the G(t) data and can be very sensitive to small scattering of data (typically at short and long times) and also become unstable. The Schwarzl approximation uses simple numerical formulae to convert creep compliance data to viscoelastic moduli (Schwarzl et al., 1969). Despite the fact that it is an approximation, it has

been shown to agree well with the above methods in the intermediate time range and is very robust. The procedure followed involved first to ensure to be in the linear regime which implies compliance J(t) constant for different stresses. Second, to find a function that fits the creep compliance data very well in log scale. Third, to perform the formula of Schwarzl to obtain dynamic compliance data and then to convert the J'(ω) and J''(ω) data to G'(ω) and G''(ω). The Schwarzl formulae are described below:

$$J'(\omega) = J(t) + 0.0007(J(32t) - J(16t)) - 0.0185(J(16t) - J(8t)) + 0.197(J(8t) - J(4t)) - 0.778(J(4t) - J(2t)) - 0.181(J(t) - J(t/2)) - 0.049(J(t/4) - J(t/8)) 2.14$$

$$J''(\omega) = -0.47(J(4t) - J(2t)) + 1.674(J(2t) - J(t)) + 0.198(J(t) - J(t/2)) + 0.620(J(t/2) - J(t/4)) + 0.012(J(t/4) - J(t/8) + 0.172(J(t/8 - J(t/16)) + 0.043(J(t/32) - J(t/64)) + 0.012(J(t/128) - J(t/256)) 2.15$$

In order to have a complete picture for slow relaxing samples, a combination of all three linear rheology experiments in their respective frequency domains is needed. Frequency sweeps are the most useful in the high frequency region, stress relaxation in the intermediate frequency region and creep measurements at the very low frequency region. In figure 2.12 below, we combine all three methods for the characterization of a 1 M high molecular weight PS.



Figure 2.12: Combination of frequency sweep, stress relaxation and creep compliance to obtain a final mastercurve of the PS 1 M.

2.8 Non-linear Rheology Measurements

Non-linear rheology measurements are useful to perform since they mimic the conditions found in industrial processes. However, to test entangled model polymeric systems under large, rapid extension and shear deformations is extremely difficult due to the tendency of these systems to deform in a non-homogeneous manner.

2.8.1 Extensional Rheology

First, a small description of the history of extensional rheometers will be presented. Next, a short description on extensional flows and finally, the procedures involved in performing extensional rheology measurements with the Sentmanat Extensional Rheometer (SER) and the Filament Stretching Rheometer (FSR).

2.8.1.1 Short history of extensional rheometers

The studies of the behaviour of polymers and specifically model polymers in elongational flows are rare, due to the difficulty in the design of an experimental setup which generates well-defined extensional flows. In the last few decades, there has been significant progress made, mainly for the development of homogeneous uniaxial extensional flows. The Rheometrics melt extensiometer (Meissner and Hostettler, 1994) is the first commercial extensional rheometer for melts and an adapted version of the original one developed by Meissner in his laboratory (Meissner, 1969). The sample is placed in a silicone oil bath (to remove the sagging effect) and mounted in a horizontal or vertical position and extended by rotary clamps. Due to the large sample quantity needed in this type of setup (approximately 1 gram) (Meissner and Hostettler, 1994), model polymers are very difficult to measure using this technique. However, the sample can be stretched for an extended period of time up to a Hencky strain of 7.

An important milestone occurred with the design of filament stretching rheometer for solutions (McKinley and Sridhar, 2002 review) and melts (Bach et al., 2003), since better control over the sample deformation was possible. This could be attributed to a feed-back control loop and the addition of laser microscopy which enables a direct visualization of the sample. Uniaxial extensional rheology become available to a wider rheological community with the advent of the SER (Sentmanat Extensional Rheometer) and EVF (Elongational Viscosity Fixture) which allowed for a small sample size to be used and consisted of a simple fixture which could easily be mounted on a commercial rheometer.

2.8.1.2 Description of extensional flows

Extensional flow is different than shear flow for two main reasons, the deformation of the sample in extension is in the same direction as the applied flow and extensional flows generate a significant amount of chain stretch in a short period of time. Chain stretch in shear flow is suppressed by the mechanism of convective constraint release at high rates (as explained in Introduction 1.12).

There are three types of extensional flows which are possible to generate, uniaxial extensional, biaxial extensional and planar extension. The most common one and the technique used in our study is uniaxial extensional flow. The general expressions for the velocity in the x, y and z direction are (Equation 2.16).

$$v_{z} = -\frac{1}{2}\dot{\varepsilon}(1+b)z$$

$$v_{y} = -\frac{1}{2}\dot{\varepsilon}(1+b)y$$

$$v_{x} = \dot{\varepsilon}x$$

$$2.16$$

In the case of uniaxial extension, b=0 and integrating the velocity expressions as a function of time results in the following expressions (Equation 2.17).

$$v_{z} = x(t_{2}) = z(t_{1}) \exp(\frac{-\dot{\varepsilon}(t_{2} - t_{1})}{2})$$

$$v_{y} = y(t_{2}) = y(t_{1}) \exp(\frac{-\dot{\varepsilon}(t_{2} - t_{1})}{2})$$

$$v_{z} = \dot{\varepsilon}x = x(t_{2}) = x(t_{1}) \exp(\dot{\varepsilon}(t_{2} - t_{1}))$$
2.17

As seen in Figure 2.13, if a cube is stretched horizontally in the x-direction, its length increases (stretches) exponentially, while its cross-sectional area decreases exponentially (compresses).



Figure 2.13: Cube stretched exponentially in the x direction

The average Hencky strain simply corresponds to the following expression:

$$\varepsilon_{_{H}} = \ln(\frac{L(t)}{L_{_{0}}})$$
 2.18

2.8.1.3 Sentmanat extensional rheometer

We have used the SER fixture (Sentmanat, 2004) mounted on an ARES 2KFRTN1 strain-controlled rheometer (TA Instruments, USA). The measurements with polystyrene

were performed at a temperature of 170°C and with polyisoprene at 0°C, i.e., attempting to keep nearly the same distance from the glass transition temperature T_g . The average measured T_g of the PS and PI combs was 106°C and -61°C, respectively (Kapnistos et al., 2006). These temperatures were carefully chosen in order to allow for the samples to be sticky enough to adhere to the two cylindrical drums and to ensure that the torque levels are sufficiently high to avoid the noise levels that arise at low strain rates. Moreover, the Rouse times (τ_R) of the polymer series were estimated based on the linear rheology curves and the temperature was chosen in order to access extensional rates that fall below and above $1/\tau_R$ (see discussion below). The experiments were always run under a nitrogen environment (liquid nitrogen in the case of PI, gas for PS). To further reduce the risk of degradation, extra effort was made to perform all necessary actions very fast (order of 5 minutes), including sample loading, equilibration and deformation.

Before measurements, the PS film samples were press-molded into a rectangular shape with a thickness between 0.6 and 0.8 mm, a length of 17 mm and a width between 4 and 6 mm. The aspect ratio, defined as the width divided by thickness, was always between 6 and 8. The polymer powder samples were first pressed into shape at room temperature, then placed in between two Teflon disks inserted into a home-made mold and heated in a vacuum oven at 170°C. For the PI samples, a different procedure was used because of their low glass transition temperature. The samples were rolled into cylindrical specimens with an approximate diameter of 1-2 mm and a length of approximately 17 mm at room temperature (Auhl et al., 2009).



Figure 2.14: a) The SER sample shape prepared from a rectangular shape cut out prepared by b) press-molding PS powder in the oven at high temperatures in between two heavy metal pieces

The diameter was kept as low as possible while still bearing in mind practical considerations (e.g., noise levels associated with low torque levels). Results from recent numerical computations (Yu et al, 2011) indicate that when using a cylindrical sample, a diameter greater than 0.5-1 mm may result in large deviations from ideal uniaxial extension. The accurate dimensions of the sample were measured before each experiment. Due to the limited amount of sample available (typically of the order of 100 mg), after the completion of one run, the (usually broken) specimens were reformed and reused. However, if there was any sign of degradation, such as yellowing of the sample and/or a deviation of the low-rate data from the linear viscoelastic envelope, the sample was discarded. Moreover, the homogeneity of the specimen was also considered to be crucially important, and samples with uneven thickness, bubbles or appearance of cracks were not used at all.

Special attention was paid to the temperature control which is important for accurate extensional measurements. The temperature sensor is not located directly on the SER fixture, hence the temperature control is indirect. In order to ensure that the fixture is at the target temperature, a long pre-heating time of the fixture was used (1 hour), and afterwards the sample was loaded as quickly as possible (less than 30 seconds loading). The tensile stress coefficient was corrected for thermal expansion (Sentmanat et al., 2005). Moreover, a prestretch was used for the polystyrene samples in order to correct for any minor sag effects and to ensure better quality data, especially at short times (Sentmanat et al., 2005). The results were always checked against the linear viscoelastic prediction. In the slow-flow regime of transient start-up, the tensile stress growth coefficient is related to the zero shear viscosity by a factor of 3 according to the Trouton ratio.

During the measurement, a constant uniaxial Hencky strain rate is applied which is equal to the sum of the angular velocity of the slave and master drums divided by the distance L_0 between the drums.

$$\dot{\varepsilon}_{\mu} = \frac{2\Omega R}{L_0}$$
 2.19

The transient tensile stress growth coefficient is then calculated from the tangential force (the sample's resistance to deformation) divided by the decreasing cross-sectional area.

$$\eta_{E}^{+} = \frac{F(t)}{\dot{\varepsilon}_{H}A\exp(-\dot{\varepsilon}_{H}t)}$$
 2.20



Figure 2.15: a) The sample is placed between two cylindrical drums separated by a distance L_0 , the drums rotate in opposite directions creating a tangential force in the horizontal direction .b) The SER fixture is fixed onto the ARES rheometer

In order to check whether the specimen deformation was uniaxial when a constant elongational rate was applied, the cross-sectional area was monitored. Under uniaxial conditions, this area should decrease exponentially with time. A Fire- i^{TM} digital camera was used (rate of 30 frames/second) along with an image analysis program (Image J) in order to record the time-varying width at the center of the specimen during the deformation. To test the conditions of uniaxial extension, the measurement of the time-dependent width of the specimen is shown in Figure 2.16 b). The results of the video microscopy show that the deformation of the sample is uniaxial since the width W(t) of the sample during deformation

does follow the following relationship $W(t) = W_0 \exp\left(-\frac{\dot{\epsilon}t}{2}\right)$, with W₀ the original width of the undeformed specimen. From this result we conclude that uniaxial extensional conditions are achieved in our experiments.



Figure 2.16: a) Fire- i^{TM} digital camera attached to rheometer b) Variation of the normalized specimen width, $-2*\ln(W/W_0)$ (to its unstretched value W_0) with t. The linear dependence indicates uniaxial extension and determines the true stretch rate, here 0.097 s⁻¹ (squares), which compares well to the experimentally imposed (circles) 0.1 s⁻¹.

In addition, an alternative approach was used, according to which the experiments were run until a Hencky strain of 3, and subsequently the sample was quenched with nitrogen gas, removed and then the width in the center of the specimen was measured. In both cases the results were very accurate and there was less than 5% deviation from uniaxial prediction. The only discrepancy occurred at the end of the experiments when the samples broke too quickly, which would typically occur at low extensional rates (below 0.01s⁻¹).

The maximum Hencky strain achieved was 4, corresponding to one full rotation of the drums. Often, sample breakage occurred at lower strains. After one full rotation, the polymer film sample will touch the clamps which may lead to a sudden increase of the torque response, resulting in an increase of tensile stress growth coefficient and misleading results. As also reported by (Barroso et al., 2010), at low extensional rates, the polymer film was prone to break prematurely by ductile failure, shortly after reaching the maximum in engineering stress. This can be explained by the Considère criterion which predicts that for a purely elastic material sample failure occurs at the maximum in engineering stress (McKinley and Hassager, 1999). Recent work with entangled polymers relates the breakup to the elastic

breakdown of the entanglement network and associated non-uniform extension (Wang et al 2007).

2.8.1.4 Filament stretching rheometer

The filament stretching rheometer used in this study was the one designed by (Bach et al., 2003b) at the Technical University of Denmark and can be visualized in Figure 2.17. The PS sample was first pre-moulded in a vacuum oven at 160°C into cylindrical specimens with radius of 2.7 mm and length of approximately 1.5 mm. The sample was then placed between two cylindrical parallel plates enclosed in an oven always with a fixed flow of nitrogen gas to avoid degradation. Thereafter, the samples were pre-stretched to a radius of approximately 2 mm at a temperature 20°C higher than the measurement temperature. During the experiment, when a constant Hencky strain rate was applied, the upper plate was pulled at a constant rate (by a step-rate motor) such that the mid-radius of the sample decreased exponentially. An on-line laser micrometer was used to measure the mid-diameter of the filament during extensional deformation and this information is fed back to the feeback controlled loop. If the stretching of the sample deviated from uniaxial extension, hence R(t) is not equal to $R_0 \exp(-\epsilon/2)$ then the end-plate velocity would be adjusted in order to keep stretching and avoid sample failure. Moreover, by using video images, the sample could also be visualized during stretching to monitor any sample inhomogeneities. Also, the axial Force measured on the bottom plate, placed on top of a weight cell was monitored in order to calculate the final transient stress growth coefficient using the following expression:

$$\eta_{E}^{+}(t) = \frac{F(t) - m_{1}g}{\pi R(t)^{2} \dot{\varepsilon}_{0}}$$
 2.21



Figure 2.17: Filament stretch rheometer at DTU equipped with an on-line laser micrometer. Image kindly provided by Hassager's group.

The filament stretching rheometer (FSR) at DTU is considered to be state-of the art for a few reasons. First, the unique feature of the FSR is the ability for the sample to be stretched under homogeneous uniaxial elongation for longer stretch times (reaching a Hencky strain of approximately 6) compared to the standard extensional rheometers. Hence, it is possible for the polymer melt to reach a steady state tensile stress growth coefficient and therefore, to avoid the typical problems which may arise such as necking, ductile failure and brittle failure. Also, since it is assured that steady-state is reached then it also becomes possible to measure reliable stress relaxation data. Second, both polymer melts and solutions can be measured in this experimental setup. Third, it is possible to measure very low extension rates without resorting to time-temperature superposition to shift the data. Due to all these reasons, the FSR is an ideal method to test the current state of the art tube non-linear tube theory models.

However, despite all its advantages, the method also has a few limitations. For example, it becomes very difficult to measure polymer melts with very long relaxation times due to the difficulty of sample equilibration and adhesion to the plates during deformation. The adhesion will improve only slightly with a rise in temperature which may also lead to sample degradation. Also, high rates above $\sim (0.3-0.5 \text{ s}^{-1})$ are also very difficult to measure again due

to the problem of sample adhesion. Therefore, to measure high M_w model polymers and to measure at higher Hencky strain rates, it is advisable to opt for the Sentamanat Extensional Rheometer. The advantages and disadvantages of SER and FSR are summarized in Table 2.5. (Nielsen et al., 2009) also make a detailed comparison of transient extensional measurements performed on the SER, EVF and FSR for an entangled linear polyisoprene melt.

SER		FSR	
Advantages	Disadvantages	<u>Advantages</u>	Disadvantages
- Fast and easy measurements	- Can only stretch to ε=4 and sample usually fails before this strain is reached	 Can stretch for longer time without the sample rupturing due to feedback controlled loop ε=7 	-Must have excellent sample adhesion to the metal plates
- Can measure slow relaxing polymers with high zero shear viscosity	- Require a minimum zero shear viscosity due to sample sagging	-More control over sample, laser micrometer can track sample changes	-Difficult to achieve high rates of extension
- Can reach higher rates, up to 10 s ⁻¹	- Difficulty to measure at low rates due to inhomogeneous sample failure	-Can reach very low rates of stretching	- Slow relaxing polymers such as high M _w polymers difficult to measure
- Small sample quantity required	- Cannot measure polymer solutions	- Can be used also for polymer solutions	

Table 2.5: Advantages and disadvantages associated with the use of the SER and FSR for the purpose of uniaxial extensional rheology experiments

The filament stretching rheometer was used to measure the PS H sample H2A1 and to confirm the reliability of the SER measurements for PS comb sample C712. Specifically for the comb sample, we performed two experiments with the filament stretching rheometer (FSR) of Hassager and coworkers in DTU, Denmark (Hassager et al., 2010, Nielsen et al., 2006). The measured transient tensile stress growth coefficients of the PS comb sample C712 at T_{ref} =170°C at Hencky strain rates of 0.003 s⁻¹ and 0.03 s⁻¹ were in excellent agreement with the respective SER results.

2.8.2 Non-linear start-up and relaxation in simple shear

Non-linear start-up shear involves the application of a sudden step-rate, monitoring the transient shear viscosity and then stopping the flow and following the relaxation. The typical transient shear viscosity diagram for a linear entangled polymer is shown in Figure 2.18 where an overshoot is first seen (due to chain orientation and also chain stretch at high Wi) and subsequently a lower steady-state shear viscosity is achieved, the flow is then stopped and the relaxation proceeds very quickly.



Figure 2.18: Schematic of shear start-up and relaxation experiment

Non-linear start-up shear and subsequent steady state relaxation measurements were performed on select samples using a cone partitioned plate (CPP) fixture. We used the CPP developed by F.Snijkers, explained in detail elsewhere (Snijkers et al., 2011) and based on the original version of (Meissner, 1999) and further elaborated by (Schweizer, 2002). The temperature control of $\pm 0.1^{\circ}$ C was achieved with a home-made ceramic oven custom-made to fit around the CPP. As seen in Figure 2.19, the CPP was composed of a 25 mm cone attached to the bottom of the ARES, a 6 mm diameter Invar parallel plate attached to the top of the ARES and was aligned with the ring of the partitioned plate by three alignement stages.

With the use of the CPP, edge fracture is delayed since only the center of the sample is measured and it will take some time before the edge fracture will progress towards the center of the sample. The main advantage of using the CPP is that higher shear rates can be achieved compared to a standard cone and plate geometry since non-linear melt-instabilities such as edge fracture and wall slip can be delayed. Therefore, even at high rates, exceeding the inverse Rouse time, the complete start-up shear curves can be measured reliably and a steady-shear viscosity can be achieved. The other method which can be used to extend the range of rates is time-temperature superposition (Auhl et al., 2008), but this is tricky when a cone is used.



Figure 2.19: a) CPP attached to ARES rheometer, b) 6 mm parallel plate aligned with outer ring and c) the home-made ceramic oven which fits around the experimental setup.

2.9 Experimental Challenges and Solutions

As a short summary of Chapter 2, Table 2.6 focuses on the solutions to the three major experimental problems, some of which we address in this thesis: 1) low sample quantities produced by anionic polymerization, 2) difficulty of characterization of branching and 3) the challenge of producing homogeneous non-linear flows.

Experimental Challenges	Approach	
Recent developments in anionic synthesis and low sample quantity.	- Development of fixtures to adapt to smaller sample size such as the use of smaller diameter parallel plates.	
	- Development of tools such as SER and CPP which allow for easy and quick measurements with very low sample quantity.	
Characterization of branching structure	- Development and use of Temperature Gradient Interaction Chromatography (TGIC) which allows detection of even small amounts of side products otherwise undetectable in SEC.	
Obtention of reliable non-linear data	- Combination of non-linear rheology with optical methods such as particle image velocimetry.	
	- Checking different geometries	
	- Cone-partitioned plate attached to conventional rheometers to delay melt fracture in non-linear shear.	
	- Filament stretching rheometer which delays sample failure by incorporation of an on-line control of diameter during stretch.	

Table 2.6 Major experimental challenges and solutions

Chapter 3

Understanding the Physical Origin of Chain Stretch

In this chapter, we investigate the uniaxial extensional rheology of simple linear monodisperse polymers, subsequently more complex H polymers and finally comb polymers. Our goal is to understand how the molecular architecture effects chain stretch and the uniaxial extensional response. For linear monodisperse polymers, chain stretch is well understood and the onset of extensional hardening can be predicted from the value of the Weissenberg number, the ratio of rate of stretch and the Rouse rate. For H polymers, the pom-pom model offers a fairly complete picture of the role of the molecular features on the extensional response. However, for comb polymers, the pom-pom model is not adequate and hence, we present a modified version of the pom-pom model taking into account the unique structural characteristics of the comb.

3.1 Introduction

The parameter free modeling of nonlinear rheology of branched polymers, including both shear and extensional flows still poses challenges. However there are important recent developments, at different levels of coarse graining, such as the pom-pom model (McLeish and Larson, 1997) and the molecular-stress function approach (Wagner and Rolon-Garrido, 2008; Rolon-Garrido et al., 2009). Interestingly, these models are highly successful in predicting data with ill-defined commercial polyethylenes. However, the main open problem is the direct analogy of molecular characteristics and nonlinear response, as done in the linear case. To this end, not much progress has been reported (van Ruymbeke et al., 2010a; Nielsen et al., 2006; Rasmussen et al., 2009). This is a direct consequence of very limited experimental data on well-defined polymers, which is due to both the difficulty of obtaining appropriate macromolecules and performing experiments with tiny amounts of samples synthesized anionically. The effects of number and size of branches are of prime importance to explore. Note that, experimentally the filament stretch rheometer and the rotating drums fixture constitute an established combination of instrumentation for obtaining reliable data at a wide range of extensional rates (Hassager et al., 2010; Sentmanat et al., 2005).

In entangled polymers undergoing fast flows the concept of chain stretch becomes important (Marrucci and Grizzuti, 1988; Marrucci and Ianniruberto, 1999). It is due to friction of the chain retracting within its tube and occurs at high deformation rates exceeding the reciprocal Rouse time of the chains, i.e. when the chain segments remain oriented and stretched in quiescent state. The macroscopic consequence of chain stretch in uniaxial extension is strain hardening, i.e. the upturn in the tensile stress growth coefficient above its viscoelastic value. The uniaxial extensional rheology of monodisperse linear polymers (Bach et al., 2003) has been investigated systematically and seems to be reasonably well understood. In particular, the $\frac{1}{2}$ power-law scaling of the steady state tensile stress growth coefficient in relation to the extensional rate was rationalized by invoking the interchain pressure term (thermal pressure exerted on the tube wall) which is balanced by tube contraction due to the applied deformation and consequently, a reduction in tube diameter (Marrucci and Ianniruberto, 2004). The tube pressure concept although it has been to shown to be useful to predict the extensional response of long-chain branched polymers and some wellcharacterized branched architectures (Rolon-Garrido et al., 2009; van Ruymbeke et al., 2010a), has many shortcomings, for example, when it comes to its applicability to entangled solutions (Marrucci and Ianniruberto, 2005), which are currently being considered (Ianniruberto et al., 2012). Also, the same authors have reviewed this concept and have determined that the discrepancy in the slope is not due to the tube pressure concept but rather can be explained by a stretch/orientation dependent friction (Ianniruberto et al., 2011; Yaoita et al., 2012).

Chain stretch becomes especially important for polymers with chain segments contained between two branch points. For these types of polymers such as the H polymer (Mcleish et al., 1999), pom-pom (Nielsen et al., 2006) and Caylee trees (van Ruymbeke et al., 2010a), strain hardening will occur even at very low deformation rates. The increased amount of chain stretch can be attributed to the fact that the segment between two branch points is not free to relax its stress until the branches have fully retracted (McLeish and Larson, 1998).

Eventually, branch point withdrawal occurs since it becomes more entropically favorable to withdraw the branches than to continue to stretch the backbone (McLeish and Larson, 1998).

From the above it is evident that a systematic investigation of the effects of branching on the extensional rheological behavior of well-characterized branched polymers is much needed. This is exactly the goal of this work. We investigated the underlying molecular origin of chain stretch for architectures of increasing complexity: linear, H and comb polymers. The linear polymers serve as our reference sample.

3.2 Uniaxial extensional response of linear polymers

The uniaxial extensional rheology is directly influenced by the magnitude of the rate of stretch as shown in Figure 3.1 for a linear monodisperse polymer. When a deformation is applied, the test chain and the surrounding chains are oriented and/or stretched depending on the value of the Weissenberg number, the ratio between the experimental deformation rate and the Rouse relaxation rate. The consequence is a displacement of surrounding chain entanglements and as a result, a deformation of the test tube. Due to entropic elasticity, the test chain can retract and relieve the imposed tension and return to its equilibrium length, the same primitive path length as before the imposed deformation.

At low rates, in Region I (Figure 3.1), below $1/\tau_d$, the chains are at an equilibrium state (flow) where the tensile stress growth coefficient is equivalent to $3\eta_0$ according to the Trouton Ratio. In Region II, in between $1/\tau_d$ and $1/\tau_R$, the entropic chain tension (due to constraining tube) is equivalent to 3kT/a (Doi and Edwards, 1986) where kT is equivalent to the thermal energy and a is the tube diameter (as explained in Chapter 1). Also, the chains are oriented in the direction of the flow and will relax faster than they are deformed and keep their equilibrium conformation, hence the contour path occupied by the retracted chain equals the equilibrium length. The stress saturates with tube orientation to a constant value and therefore, the tensile stress growth coefficient decreases with a slope of -1. Experimentally, this is seen as a slope of -1/2. In Region III, at rates larger than $1/\tau_R$, there is a transition from orientation to stretching of chains, retraction occurs in a Rouse-like motion of the test chain along the deformed tube, and the contour path occupied by the retracted chain is larger than the equilibrium length. In Region IV, the chains are fully stretched and the tensile stress growth coefficient reaches a plateau value.



Figure 3.1 Schematic of tensile stress growth coefficient versus time where all four regions are shown (Marrucci and Ianniruberto, 2004; Malkin and Petrie, 1997).

Small Amplitude Oscillatory Shear (SAOS) was performed on a linear PS of M_w =262k, PDI=1.1 in order to obtain a linear viscoelastic mastercurve (Figure 3.2 a). Also, uniaxial extensional rheology was performed using the Sentmanat Extensional Rheometer (SER) at a rate of 1 s⁻¹ at temperatures ranging from 130°C to 180°C. The tensile stress growth coefficient obtained at each of the temperatures was then shifted to 170°C by time-temperature superposition using the same shift factors as obtained in linear rheology (Figure 3.2 b). We show that in Figure 3.2 b), time-temperature superposition can be successfully applied also in uniaxial extensional rheology. This is in congruence with previous studies, where time-temperature superposition has been shown to be applicable in start-up shear (Kapnistos et al., 2009) and extension (Auhl et al., 2008) studies.



Figure 3.2 a) symbols: linear viscoelastic response of linear PS 262k at 170°C and lines: comparison with fit of (Likhtman and McLeish model 2002) and its respective entanglement rate $(1/\tau_e)$, Rouse rate $(1/\tau_R)$ and relaxation (crossover) $(1/\tau_d)$ rate indicated by the dashed lines b) master curve of the extensional response of the same sample at 170°C after performing time-temperature superposition plotted together with the linear viscoelastic envelope. The arrow indicates the predicted onset of strain hardening determined from the definition of the Rouse rate.

As seen in Figure 3.2 b), the transient tensile stress growth coefficient for the lowest rates follow the linear viscoelastic prediction. As mentioned in the introduction of this chapter, the chains will begin to stretch and display extensional hardening at rates higher than the reciprocal Rouse time due to chain-induced friction. In order to be able to predict the onset rate of strain hardening, the first step is to calculate the Rouse time which is not obvious since there is more than one definition which currently exists in the literature (Doi and Edwards, 1986; Menezes and Graessley, 1982; Roland et al., 1982). We use the classical definition (Doi and Edwards, 1986) to calculate the Rouse time which is derived from an expression that is independent of the tube model.

$$\tau_R = \frac{\zeta N^2 b^2}{3\pi^2 k_R T} = \tau_e Z^2 \tag{3.1}$$

where ζ is the monomeric friction constant, k_B is the Boltzmann's constant, N is equal to the number of monomers, b is the statistical segment length and Z is the number of entanglements. Using the parameters: $M_e=15500\pm1500$ g/mol and $\tau_e=7.5E-4\pm2.5E-4$ s, a value of Rouse rate of $5.6\pm 2.8 \text{ s}^{-1}$ is obtained which corresponds roughly to the rate at which we start to observe strain hardening experimentally, between 3 and 13 s⁻¹. Despite the simplicity of this approach, it works quite well to approximate the onset of strain hardening for linear polymers. Linear polymers can also display significant strain hardening if the rate of stretch is significantly higher than the Rouse rate (Region III and IV in Figure 3.1) as seen for PS 262k at a very high rate of 640 s⁻¹. The amount of stretch will increase with the rate until molecular finite chain extensibility is reached which acts to limit this maximum value. Marrucci and Ianniruberto were the first to suggest that linear polymers may behave like branched polymers in the steady state of fast elongational flows (Ianniruberto and Marrucci, 2013). They successfully compared their theoretical predictions to a limited data set of pompom and asymmetric star melts. Therefore, it is worth examining with more experimental evidence whether architecture has a significant influence at these high rates where the chains are aligned and the maximum amount of chain stretch has been reached.

3.3 Uniaxial extensional rheology of H polymers

Although the onset of chain stretch of linear polymers is rather easy to predict and is influenced solely by the friction of the chain retracting within its tube, the extensional
behavior of branched polymers is more complex. As explained previously, in a small amplitude oscillatory shear measurement the branches act to delay the final reptation time. In extensional deformation, the branches allow the melt to support a higher force per unit area and avoid early failure. More specifically, the presence of branches allows for stronger strain hardening and a smaller onset rate.

In order to determine the influence of the molecular structure on the extensional behavior of more complex branched polymers, we start first with the simplest branched polymer, the H polymer. We use two PS H polymers characterized as having the same molar mass of backbone and arms and a high volume fraction of arms, whose molecular characteristics are explained in Chapter 3.1. The linear viscoelastic properties of the H polymers, also characterized in the past (Roovers, 1984) and remeasured again are shown in Figure 3.3. The quality of the samples and measurement, is confirmed by the agreement between our data and the data of Roovers. Due to the large number of entanglements in the H polymer arms, the backbone is heavily diluted by the arms ($\phi_b=0.19$), rendering it virtually If $\varphi_b M_b \le M_c$, the backbone chains are not mutually entangled and the unentangled. intermediate terminal relaxation has the characteristic G'~G''~ $\omega^{1/2}$ which is clearly seen by the $\frac{1}{2}$ slope just before the terminal relaxation. Due to the short arms and equally short backbone (less than 3 entanglements), there is no clear separation between the relaxation time of the arms and backbone in the case of the lower M_w H2A1 polymer. For the higher M_w sample H3A1 which consists of a well-entangled backbone and arms, the timescale separation is much more well-defined.



Figure 3.3: symbols: linear viscoelastic data at 130°C of (a) H2A1 and (b) H3A1, lines: TMA modelled data and the respective arm and backbone curves.

We calculate the Rouse time for both H polymers using the expression of (Ianniruberto and Marrucci, 2013):

$$\tau_R = \tau_{R,b} \left(\frac{\lambda}{q} + 4\lambda \frac{M_a}{M_b} + 4\frac{M_a^2}{M_b^2}\right)$$
 3.2

where $\tau_{R,b}$ is the Rouse time of the backbone, q is the number of arms, λ is the backbone stretch ratio and λ =q for a Gaussian backbone.

We utilize the Time Marching Algorithm (TMA) (van Ruymbeke et al., 2006) in order to isolate the linear rheology curve of the H polymer arms and backbone and define a respective relaxation time of arms and backbone (Figure 3.3). The model uses the same molecular-based tube model but differs in the implementation of the relaxation mechanisms. The same relaxation mechanisms are used ie. CLF, DTD, reptation and CR, however the coordinate system used differs. The relaxation mechanisms occur simultaneously and there is no clear separation between the relaxation processes. Due to this difference, there is no need to have a p^2 parameter although the familiar $\alpha = 1$ dilution exponent is used. Also, an extra consideration is taken in the treatment of dynamic tube dilation, where the Struglinksy-Graessley criterion is taken into account. The TMA approach was successfully applied to linear, star polymers and other more complicated branched (comb, pom-pom) and blend structures (van Ruymbeke et al., 2006, 2007, 2010, 2011, 2012; Ahmadi et al., 2011). The relaxation times of arms, backbone and crossover relaxation times determined from TMA are listed in Table 3.1.

Code	φ _a	$\tau_{d}(s)$	$\tau_{a}(s)$	$\tau_{b}(s)$	$ au_{\mathrm{R}}(\mathbf{s})$
H2A1	0.81	77	50	200	71
H3A1	0.81	1E6	1E4	1.6E6	577

Table 3.1: H2A1 and H3A1 arm volume fraction (φ_a) and characteristic relaxation times

For the H2A1 polymer sample, the state-of the art filament stretching rheometer was used to measure the uniaxial extensional response. As explained in Chapter 2, the filament stretching rheometer equipped with a feedback-controlled loop enables an extended stretch time (from 4 to 6 Hencky strain units) and the obtention of a steady-state tensile stress growth function for all rates (Figure 3.5a). The steady state viscosity is achieved for the H polymer at a Hencky strain between 3 and 4 as shown in Figure 3.5a. Moreover, at all rates (Figure 3.4a), extensional hardening is observed, even at rates lower than the inverse Rouse time and the inverse crossover relaxation time, indicating the effect of the presence of a segment contained between two branch points. As demonstrated also in other works (van Ruymbeke et al., 2010; Bach et al. 2003a), the steady state state tensile stress growth coefficient plotted versus stretch rate results in a slope of -1/2 (Figure 3.4 b).



Figure 3.4: a) H2A1 transient tensile stress growth coefficient obtained at $T_{ref} = 130^{\circ}C$ at different Hencky strain rates (from 0.001 s⁻¹ up to 0.3 s⁻¹) and b) steady-state tensile stress growth coefficient versus rate.

In order to examine more closely the strain hardening behavior and its dependence on the molecular structure of the H polymer, we calculate the strain hardening factor (SHF) for the

quantification of the amount of stretch. The SHF is defined as the ratio of the experimental steady state tensile stress growth coefficient and three times the shear viscosity (LVE envelope). In Figure 3.5, b) the SHF is plotted vs Hencky strain. The SHF varies between a minimum value of 2 at a rate of $3E-4s^{-1}$ and a maximum value of 5 at a rate of $0.3 s^{-1}$, indicating the effect of the rate on the amount of chain stretch. We make the analogy of SHF with the pom-pom value q (number of branches) where the maximum stretch occurs before branch point withdrawal. The pom-pom model will be explained in more detail below. The value of SHF is on average higher than the number of branches. (Kempf et al., 2013) demonstrated that the SHF increases with the number of branches for a series of monodisperse comb polymers.



Figure 3.5 (a) Shear stress growth function and (b) strain hardening factor (SHF) versus Hencky strain at rates from $3E-4 \text{ s}^{-1}$ to 0.3 s^{-1}

The multi-mode pom-pom constitutive equations (Bishko et al., 1997; McLeish and Larson, 1998), were utilized in order to study the extensional rheology of H polymers. The model is based on the molecular structure of a model "pom-pom" molecule which consists of a long flexible backbone with multiple arms attached to each of the two chain ends. The original purpose of the model was to provide for a molecular framework for the understanding of the non-linear rheological response of industrially branched polymers. One of the goals of the thesis is to verify its applicability for model H and comb polymers. In other studies, semi-quantitative agreement has been demonstrated in simultaneous fitting of both start-up shear and extension of model H polymers (McLeish and Larson, 1998; McLeish et al., 1999). We believe that the H2A1 experimental data would be an ideal test for the pompom model since the data covers a large range of Hencky strain rates and captures both the startup and steady uniaxial extensional data.

The model incorporates some basic mechanisms such as reptation, hierarchical relaxation, dynamic dilution and chain stretch, however, it misses mechanisms such as constraint release. Moreover, a failure of the pom-pom model is the excessive shear thinning in fast shear flows, a known constitutive instability, the same deficiency in the Doi-Edwards model (Doi and Edwards, 1986). This issue can be resolved by the use of a multi-mode pom pom model. The solutions of the multi-mode pom pom equations (Inkson et al., 1999) are able to describe both the shear thinning behaviour in shear and strain hardening in extension. The dynamic equations of the original pom-pom model consist of a separate integral orientation and differential backbone stretch evolution equation.

At low rates, the deformation separates the two branch points, only the backbone can sustain stretch due to the entropic penalty of branch point withdrawal. At intermediate rates, the stretch of the backbone increases with increasing deformation. At high rates, above the inverse Rouse time, it becomes entropically more favorable to withdraw the arms into the tube. Arms are withdrawn into the backbone tube when the sum of all arm tensions balances the tension of the backbone (Figure 3.6 b). In Figure 3.7, we plot the pom-pom model fit against the experimental data at rates lower than the Rouse rate. We find that the fit is quite satisfactory however a q value of 4 is needed in order to capture the magnitude of the strain hardening. This might indicate that perhaps a larger value of q>number of branches is needed in order to capture the extent of the strain hardening for pom-pom structures.



Figure 3.6: a) The H polymer b) the fully aligned conformation of the H polymer, the arms are withdrawn and the tube contour length is larger than its equilibrium length.



Figure 3.7: Comparison of multimode pom-pom predictions (black lines) with H2A1 (blue squares) a) tensile stress growth coefficient data and b) tensile stress growth function data versus Hencky strain.

G _i (Pa)	$\tau_{b}(s)$	Q	τ_b/τ_s
26400	891	4	2
139300	44	1	1

Table 3.2: Two mode pom-pom parameters of H2A1 fit

In order to determine the influence of an increase in M_a and M_b in model H polymers, we compare the H2A1 with the H3A1 experimental data. The H3A1 has about three times larger number of entanglements of arms and backbone as compared to the H2A1. However, it should be noted that the H3A1 data was measured with the SER (explained in detail in Chapter 2) and hence only the start-up and not the steady part of the curve is captured. As shown in Figure 3.8, the increase of the molar mass of the branches and backbone act to enhance the strain hardening and the magnitude of the tensile stress growth coefficient.



Figure 3.8: Transient stress growth coefficients at 130°C of black: H3A1 curve and blue: H2A1 curve. The extensional rates shown for the H2A1 sample (from left to right) $0.3s^{-1}$, $0.1s^{-1}$, $0.03 s^{-1}$, $0.01 s^{-1}$, $3E-3 s^{-1}$, $1E-3 s^{-1}$, $3E-4 s^{-1}$ and for the H3A1 sample (from left to right) $0.1 s^{-1}$, $0.01 s^{-1}$, $6E-3 s^{-1}$, $2E-3 s^{-1}$, $2E-4 s^{-1}$ and $6E-5s^{-1}$

3.4 Uniaxial extensional rheology of comb polymers

From Chapter 3.3, we already see the large effect of having only two branch points, mainly an earlier onset rate of strain hardening (below the Rouse rate) and a higher overall amount of strain hardening (except at the very high rates). It is worth also looking at a more technologically relevant example of a comb polymer, a structure with multiple branch points. We use a series of model, anionically synthesized, nearly monodisperse PS and PI comb polymer series as explained in Chapter 2.1. This choice is based on the fact that this model branched polymer is one of the simplest that possess multiple branch points, a key feature of industrially relaevant long-chain branched polymers. In addition, its linear viscoelasticity has been studied in great detail (Roovers and Graessley, 1981). Moreover, these sets of combs have been experimentally studied by others under different flow conditions. (Kapnistos et al., 2009) developed an analytical model for the PS combs based on oscillatory shear data. He further modified this model to include the non-linear response after a large step strain (Kapnistos et al., 2009). Moreover, (Kirkwood et al., 2009) modified the analytical model of Kapnistos, to describe the oscillatory shear and non-linear step strain data for a subset of the PI combs. Here we characterize the combs carefully and explore systematically their extensional rheology with special attention on the role of the molecular parameters, i.e. the molar mass of branches or arms (M_a), molar mass of backbone (M_b), molar mass of segments between branches (M_{seg}) and number of branches (q). We rationalize our findings by accounting for the stretch relaxation time of the backbone after the branches have relaxed. We present the TGIC characterization, the results and the discussion. A rationalization of the results by invoking simple scaling arguments based on the characteristic times of the combs is offered in part IV. Finally the main conclusions are summarized in part V.

3.4.1 Experimental results and discussion

3.4.1.1 Temperature-gradient interaction chromatography

Figure 3.9 depicts the results of the analysis of the larger- M_b PS combs from Table 3.3, where the GPC and TGIC results are compared. All polymers showed sharp unimodal peaks in both GPC and TGIC. To a first approach, this is in contrast to the work of (Chambon et al., 2008) who reported TGIC results on combs exhibiting multiple peaks, representing the distribution of numbers of branches on the molecules. Whereas this is in principle expected

from the synthesis, which attaches branches randomly to the backbone, the present combs should have small dispersity in the number of branches per molecule. Moreover, the combination of large number and, more importantly, low molar mass of branches in our combs, makes it difficult to resolve small differences in the number of branches, even by TGIC.

The absolute molar mass and PDI were obtained from the GPC/LS detection. In addition, the relative molar mass was measured by using a polystyrene standard set (1090, 336, 135, 30.9, 11.5, 3.6, 1.1 kg/mol). The results are summarized in Table 3.3. It should be noted that the analysis of sample C742 may involve some error because the retention volume was out of range of the PS standard set. Nevertheless, we believe that we can draw two interesting conclusions: (i) the new GPC analysis of these polymers reveals very similar results to the original ones obtained about 30 years ago. This is consistent with the nearly identical linear viscoelastic data shown briefly here and discussed in detail by (Kapnistos et al., 2005). More importantly, it confirms the fact that the samples have not suffered any degradation while stored for 30 years. (ii) The TGIC analysis indicates that the quality of the combs is very high, i.e. nearly all synthesized product has the targeted architecture (one well-defined and reasonably narrow peak).

From this analysis we are confident that we can proceed with the extensional rheology investigation without the need for sample fractionation.

Property /code	C712	C722	C732	C742
M _w (absolute molar mass kg/mol)	976	1117	1447	2155
PDI (absolute)	1.007	1.007	1.006	1.005
M _w (relative molar mass kg/mol)	752	882	1072	1369
PDI (relative)	1.12	1.11	1.12	1.12

Table 3.3: Results from the GPC/TGIC analysis of the high-M_b PS combs



Figure 3.9: Analysis of PS comb polymers from Table 1. GPC (a) and TGIC (b) analysis.

3.4.1.2 Linear viscoelasticity

This serves two purposes in this study, namely the characterization of the materials used (complementary to the GPC/TGIC analysis) and the determination of characteristic times of the combs, as discussed below. In particular for the PS combs, the linear response has been studied in detail by (Kapnistos et al. 2005). Here we present the summary of the data in the form of master curves of the loss angle $\tan\delta=G''/G'$ versus shifted frequency $a_T\omega$. Figure 3.10 depicts the results for the PS (a) and PI (b) combs.



Figure 3.10: (a) Linear rheology data of the PS combs(Δ) C622, (\blacktriangleright) C642, (\bullet) C712, (X) C722, (\circ) C732, (right triangle) C742 at a reference temperature T_{ref}=170°C. The tangent of the phase angle is plotted against the shifted angular frequency $a_T\omega$. (b) Respective data of the PI combs (hexagon) PI211k, (\circ) PI254k, (+) PI472k at T_{ref}=0°C.

For both chemistries the same remarks apply. The high-frequency data virtually collapse for all molar masses, as expected for segmental relaxation. The nearly identical glass transition temperature for different PS combs conforms to this result (Kapnistos et al., 2005). As the frequency is decreased the different features of hierarchical relaxation are revealed. The arms relax first (intermediate-frequency peak) and later the (diluted) backbone. Note that in some combs the two peaks are well separated (when the arms are sufficiently entangled and the backbones long enough so that they remain entangled after dynamic dilution), whereas in others the two modes essentially merge into one broad peak (Ahmadi et al., 2011; Kapnistos et al., 2010; Kirkwood et al., 2009).

We now focus on the experimental results obtained with the two comb chemistries and discuss them in the context of the classification of section II.1 in terms of the role of different molecular parameters.

3.4.1.3 General results of polystyrene C6 and C7 series

Figure 3.11 depicts the measured time-dependent tensile stress growth coefficient for the PS combs of two different M_b (a-d and e-f) and different M_a . The first qualitative observation is the occurrence of strain hardening in all combs for different ranges of extensional rates. It is evident that the larger the branch molar mass, the stronger the strain hardening and the smaller the onset rate for its appearance. For a linear entangled polymer having a molar mass $M=M_b$ of the comb backbone, the onset rate of strain hardening is expected to occur at the inverse of the effective Rouse time, $\tau_{R,lin}$, which can be obtained from the formula (Dealy and Larson, 2006):

$$\tau_{R,lin} = \tau_e Z^2 \tag{3.3}$$

where $Z = M/M_e$ is the number of entanglements in the linear chain and τ_e is the entanglement time. For a comb, considered as a linear backbone chain with grafted branches, the Rouse time may be estimated by accounting for the increased monomeric friction of the branches, giving:

$$\tau_{R,comb} = \tau_e Z_b \left(Z_b + q Z_a \right) \tag{3.4}$$

where Z_b and Z_a are the number of entanglements in the backbone and branches (arms) respectively. We estimated τ_e from the linear data as the time where the *G*' Rouse line with slope 1/2 through the high-frequency data intersects the plateau modulus (Kapnistos et al., 2005), yielding 5×10^{-4} s. Using this value and $M_e=17$ kg/mol, we can estimate the Rouse time of the C712 comb to be around 1.6s, which is not very different from the Rouse time of a linear chain with the same molecular weight as the backbone. This would suggest an onset rate for strain hardening of approximately 0.6 s⁻¹, which is very consistent with the experimental value (though we note that the Hencky strain rates used were separated by a factor of 3, so there is an error involved in this estimation).

For the C712 comb, the short branches are unentangled having a molar mass M_a=6.5 kg/mol (C712) well below the entanglement value of PS. As a result, the Rouse time provides a good estimate of the onset rate for strain hardening. In general, the inverse of the onset rate for strain hardening is referred to as the effective stretch relaxation time τ_s (Auhl et al., 2009). When Ma=11.7kg/mol (C722 or C622), slightly below Me, the onset rate for hardening shifts to a lower value of 0.1 s⁻¹ (see also Table 3.4 below, for τ_s). This is already suggestive of the role of branch points (see also discussion on the role of Mseg below) on extension hardening and the fact that combs with short branches are different from linear chains (also in linear viscoelastic response (van Ruymbeke et al., 2007). This aspect was not investigated further due to the lack of appropriate samples in sufficient amounts. For constant M_b, the larger the M_a of the comb, the larger the downshift of the onset rate for strain hardening from the inverse of $\tau_{R,comb}$. This is attributed to the branching structure of the comb polymer: in general, we expect $\tau_s \ge \tau_{R,comb}$, since the Rouse time only includes the effects of monomeric friction, whilst for longer side branches one should account for increased friction due to entanglements. The segments between branches cannot relax their stress until the outer segments with free dangling ends (branches) have retracted. Therefore, the larger the branch length, the larger the friction of the diluted backbone and the longer the effective stretch relaxation time. In the most extreme case studied, i.e., for M_a=47kg/mol which is about three times their Me, the enhancement of the effective stretch relaxation time in comparison to the Rouse time of the comb is roughly a factor of 100 for the C7 series (C742)

and 60 for the C6 series (C642). The stronger effect of the former is attributed to the fact that is average molar mass between segments is $M_{seg}>M_e$, as discussed further below.

The above points to the important role of M_a in controlling and tailoring the stretch relaxation time of highly entangled combs. When changing the total number of entanglements Z of a linear monodisperse polymer, the enhancement of effective stretch relaxation time is expected to follow the Rouse time (Auhl et al., 2009). which we can estimate from equation (2). Using this as a guide, if we compare the two extreme combs studied here, sample C742 with highly entangled branches (M_a =47 kg/mol) and sample C712 with unentangled branches (M_a =6.5 kg/mol), this simple relation for τ_s is clearly violated since the ratio of the total comb molar mass is 2.4, whereas the τ_s ratio is about 330. Therefore, not surprisingly the presence of long entangled branches appears to act as the more significant factor for the enhancement of stretch relaxation time.

By comparing combs with the same M_a and different M_b as C742 vs C642 (Fig.3.11 a,e) and C722 vs C622 (Fig.3.11 c,f), those with larger average M_{seg} (about 29 kg/mol vs 9 kg/mol), i.e. the C742 and C712 in this example, strain harden at smaller rates. Another qualitative observation is the significant increase in the magnitude of the extensional viscosity when increasing the molar mass of the backbone segments between branches (the number of branches q being constant). This difference can already be predicted from the linear rheology curves, since the relaxation time of the C6 series is significantly shorter (smaller τ_d in Table 3.4 below) and the zero-shear viscosity is significantly lower.



Figure 3.11: Transient tensile stress growth coefficients obtained at T_{ref} =170°C for comb PS samples of different molecular characteristics at different Hencky strain rates (from 0.003 s⁻¹ up to 10 s⁻¹). The samples from (a) to (d) have the same backbone molar mass M_b =860kg/mol and varying branch (arm) molar mass a) C742 with M_a =47 kg/mol, (b) C732 with M_a =25.7 kg/mol, (c) C722 with M_a =11.7 kg/mol and (d) C712 with M_a =6.5 kg/mol. Samples (e) and (f) have the same M_b =275 kg/mol but varying M_a : (e) 47 kg/mol and (f) 11.7 kg/mol. Samples (e) and (f) have the same M_b =275 kg/mol but varying M_a : (e) C642 with 47 kg/mol and (f) C622 with 11.7 kg/mol. The rates from right to left are: 0.003s⁻¹, 0.01s⁻¹, 0.03 s⁻¹, 0.05 s⁻¹, 0.07 s⁻¹, 0.1 s⁻¹, 0.3 s⁻¹, 1 s⁻¹, 3 s⁻¹, and 10 s⁻¹. Also, plotted as a solid line are the linear viscoelastic data.

3.4.1.4 General results of polyisoprene series

The same observations hold for the PI combs data which are depicted in Figure 3.12. Here, interestingly, for the three samples studied, the average molar mass between branches is about the same $M_{seg} \approx 18 \text{ kg/mol}$. Therefore, inspection of the data of PI211 and PI472 suggests that increasing the number of branches while keeping the same M_a results in stronger strain hardening and smaller onset rate (compare Fig. 3.12a and 3.12c). On the other hand, inspection of the PI211 and PI254 data shows that, for the same q and M_b, increasing M_a results again in stronger strain hardening starting at smaller rates (compare Fig.3.12b and 3.12c), as also observed with the PS combs (Figure 3.11). The comparison of PI472 and PI254 reveals the dominant role of M_a (over q and M_b) in affecting the onset rate for extension hardening: despite having smaller q (by a factor of 2.5) and smaller M_b (by a factor of 3, albeit still well above M_e), the increase of M_a by a factor of 3 results in a smaller onset rate by a factor of 30 (compare Fig.3.12a and 3.12b).



Figure 3.12 Start-up transient tensile stress growth coefficients obtained at $T_{ref}=0^{\circ}C$ of comb PI samples of different molecular characteristics: (a) PI472k, (b) PI254k, and (c) PI211k at different Hencky strain rates (from 0.003 s⁻¹ up to 10 s⁻¹). The rates from right to left are: 0.003 s⁻¹, 0.01 s⁻¹, 0.03 s⁻¹, 0.1 s⁻¹, 0.3 s⁻¹, 1 s⁻¹, 3 s⁻¹, and 10 s⁻¹. Also, plotted as a solid line is the linear viscoelastic envelope from the linear viscoelastic data.

3.4.1.5 The effect of Hencky strain rate in extension hardening

Figure 3.13 depicts the transient tensile stress growth functions for two different combs, PI472 and PS C732 at different Hencky strain rates, at the same distance from T_g . The purpose of these plots is to elucidate the effects of the rate. In both cases, its increase by two orders of magnitude leads to a nearly equivalent increase in tensile stress at large values of the Hencky strain. Clearly, the imposed Hencky strain rate can induce strain hardening.

Moreover, the polystyrene C732 sample ruptures quicker (strain at break less than 3) at the lower rates (0.01 s^{-1} and 0.03 s^{-1}) in comparison to the higher rates (0.1 s^{-1} up to 10 s^{-1}). This can be a problem since the stresses at these lowest elongational rates have probably not reached steady state. Moreover, it remains unclear also whether at the highest rates a clear steady state has been reached, since the stress reaches a maximum and then decreases quickly. This trend becomes even more apparent when plotting the engineering stress versus the rate and is due to the Considère criterion (McKinley and Hassager, 1999).



Figure 3.13: Start-up transient tensile stress growth functions plotted against Hencky strain ε obtained at (a) T_{ref}=0°C for PI472 k and (b) T_{ref}=170°C for PS C732, and different Hencky strain rates (shown in the plots).

3.4.1.6 Further analysis of extension hardening: The roles of M_a and M_{seg}

The above qualitative, albeit unambiguous observations can be made more transparent with some further phenomenological analysis. In Figure 3.14, we plot the transient tensile stress growth function against the Hencky strain ε for different PS comb samples of the C7 series having the same M_b but different M_a (samples C712, C722, C732 and C742). We choose 3 different values of the Hencky strain rate. For a large value of 10 s^{-1} , there is virtually no difference among samples. Therefore, for large Hencky strain rates the molar mass of the branches has little influence on the magnitude of the tensile stress growth coefficient and the strain hardening. Here the backbone chains are fully stretched and the tensile stress reaches a maximum of 46 MPa (Figure 3.14a) at full extension (exceeding the plateau modulus G_N^0 by two orders of magnitude). Still the behavior of these combs differs drastically from a linear elastic solid as seen by comparing against the neo-Hookean prediction in Figure 3.14a. On the other hand, at lower Hencky strain rates of 0.3 and 0.01 s⁻¹ the effects of M_a become apparent and whereas the overall functional dependence of σ_{E}^{+} on t is not clear, the strong increase of $\sigma_{\rm E}^+$ with M_a is undisputable (Figures 3.14b,c). At these intermediate rates, lower than the inverse of the effective stretch time of the comb backbone (as discussed in section IV below), the magnitude of the tensile stress growth function is dependent on the molar mass of the branches. At a rate of 0.3 s⁻¹, the comb with the smallest $M_a=6.5$ kg/mol has arms which are unentangled and hence the backbone chains are free to relax their stress. The decrease in stress at full extension (by a factor of 20 across the comb series) is depicted in Figure 3.14b. At the lowest stretch rate of 0.03 s^{-1} , only the comb sample with the longest branches exhibits strain hardening and has not fully relaxed its stress. The other comb samples have relaxed their stress to a value close to the plateau modulus $G_N^0 \approx 0.2$ MPa and behave like a viscous liquid. Moreover, in this case, for all combs the chain segments should be oriented in the direction of flow since the value of this low Hencky strain rate is above the inverse of their longest relaxation time (τ_d).



Figure 3.14: (a) Tensile stress growth functions σ_E^+ plotted against Hencky strain ϵ obtained at T_{ref} =170°C for PS comb C7 series samples of equal backbone $M_b = 860$ kg/mol and varying branch (arm) molar mass M_a =47kg/mol (filled hexagon), M_a =25.7kg/mol (open diamond), M_a =11.7kg/mol (filled square), and M_a =6.5kg/mol (filled star), at high Hencky strain rate of 10 s⁻¹; (b) respective data at intermediate Hencky strain rate of 0.3 s⁻¹; (c) respective data at low Hencky strain rate of 0.01 s⁻¹. Also plotted in (a) as a dotted line is the Neo-Hookean prediction. (d) Tensile stress growth functions σ_E^+ plotted against Hencky strain ϵ obtained at T_{ref} = 0°C for samples PI211k (open star), PI254k (filled circle) and PI472 (open hexagon) at high Hencky strain rate of 3 s⁻¹; (e) same as (d) but at intermediate Hencky strain rate of 0.3 s⁻¹.

The PI comb data conform to the picture emerging from the analysis of the PS comb data. This suggests a universal extensional behavior for model branched polymers. In particular, in addition to the established result that combs do indeed strain harden even at low rates, it is clear that here with M_{seg} virtually constant, M_a , M_b and q are important for hardening (Figure 3.14d). Focusing at the lower Hencky strain rates, we can appreciate that even with small $M_a \approx M_e$, large q and large M_b result in clearly larger σ_E^+ for PI472 (Figure 3.14e,f). Moreover, PI254 with about the same $Z_a \approx 3$ with PS C742, shows a similar continuous increase of σ_E^+ with Hencky strain (Figure 3.14c,f). The role of M_b appears to be

less significant in extensional deformation at high Hencky strains, as judged by the comparison of PI211 and PI254 in Figure 3.14e,f.

In Figure 3.15, we compare σ_E^+ of two PS combs of the same M_a (the largest) and different M_b and M_{seg} . In this case the main difference between C642 and C742 is that the average M_{seg} is about 9 kg/mol and 29 kg/mol, respectively. Whereas the stronger strain hardening of the latter was already discussed in the context of Figure 3.11, here it can be appreciated more by direct comparison of the more sensitive σ_E^+ vs. ϵ plot and at three Hencky strain rates. As the rate is decreased by two orders of magnitude from 3 to 0.3 to 0.03 s⁻¹ (Fig. 3.15 a,b, and c, respectively), the difference of σ_E^+ between C642 and C742 becomes more pronounced and extends all the way to the lowest values of Hencky strain reached.



Figure 3.15: Transient tensile stress growth functions plotted against Hencky strain obtained at T_{ref} =170°C for comb PS samples of equal M_a = 47 kg/mol but of different backbone molar mass: C742 with M_b =860kg/mol (filled circle) and C642 with M_b =275 kg/mol (open

pentagon). Data are shown at (a) high Hencky strain rate of 3 s⁻¹, (b) intermediate Hencky strain rate of 0.3 s⁻¹ and (c) low Hencky strain rate of 0.03 s⁻¹.

3.4.1.7 Rationalizing the Experimental Data

In an effort to obtain deeper understanding of the experimental data, we look for trends with molecular parameters. Inspired by the pom-pom model, we have attempted at predicting the entire time-dependent tensile stress growth function (McLeish and Larson; 1998), however our first results were hard to interpret as good fits required use of different modes with a range of q values that varied in an incomprehensible way. This is the subject of our current investigations aimed at modeling the whole tensile stress growth functions for different rates, and will be presented in the final section of this Chapter. On the other hand, to further elucidate the role of comb parameters on their response in uniaxial extension and provide a rational explanation of the experimental results and the trend of the data, we focused on the onset rate for strain hardening.

We based our simple analysis on two different characteristic stretch time scales which we define as follows:

(i) The "bare Rouse time" $\tau_{R,comb}$ of the comb, as given in equation (2), which is the longest time one would get by ignoring entanglements and simply solving the dynamics of a bead-spring model for the polymer with local monomeric friction. Here there is an analogy with the classic Rouse time of a linear chain.

(ii) The effective "stretch time" τ_s of the comb is the timescale for stretch relaxation along the tube when accounting for the large friction that comes from the branches (i.e., if the arms are entangled, then the hopping of the branch point gives large friction). We would expect to see the onset of extension hardening at rates greater than $1/\tau_s$. Hence, the experimental stretch relaxation time $\tau_s e_{xp}$ is obtained from the transient stress growth coefficient curve and is defined as the inverse of the rate at which the first sign of strain hardening (deviation from linear viscoelastic curve) is observed.

To get a theoretical estimate of the stretch time, let us consider the linear viscoelastic curves (e.g., Figure 3.10 or Figure 9 below). At low frequencies all the branches are relaxed (hierarchical relaxation) and the comb can be thought of as an effective linear polymer with

dilated tube (rescaled entanglement modulus) and larger friction (slowed-down terminal time τ_d), both due to the branches. The diluted number of entanglements Z_{dil} of this rescaled linear polymer is defined as:

$$Z_{dil} = Z_b \frac{Z_b}{Z_b + qZ_a}$$

$$3.5$$

It represents the effective number of backbone entanglements after the side-arms have relaxed, assuming a dilution exponent of 1. Note that the branch and backbone relaxation times of the combs are estimated in a consistent manner from the linear viscoelastic data (Figure 3.10 or 3.16 below) and in particular the minima or inflection points in tan δ at high and low frequencies, respectively, based on the good agreement with model predictions (Kapnistos et al., 2005; Kirkwood et al., 2009).

We now make the hypothesis that the ratio of the terminal time to the stretch time for the comb is the same as the ratio of terminal time to the Rouse time for an equivalent linear polymer with the same number of effective entanglements along its tube (Z_{dil}). This is illustrated in Figure 3.16 where the entangled linear chain relaxes in a well-defined manner as in (a), while on the other hand after relaxation of the arms, the (dilated) comb backbone becomes an effective linear chain with the same number of entanglements as the linear chain, i.e. same tube diameter and characteristic times as in (b). This equivalence can be expressed as: $\tau_d / \tau_R |_{linear} = \tau_d / \tau_s |_{comb}$. We can now estimate all times as follows: We obtain the terminal time, τ_d for the comb from the linear viscoelastic data. For the equivalent linear polymer, the ratio $\tau_d / \tau_R |_{linear}$ is obtained from (Likhtman and McLeish, 2002), where the Rouse time for a linear polymer is as given in equation (1) and the terminal time by:

$$\frac{\tau_d}{3Z_{dil}^{3}\tau_e} = (1 - \frac{3.38}{Z_{dil}^{1/2}}) + \frac{4.17}{Z_{dil}} - \frac{1.55}{Z_{dil}^{3/2}}$$
3.6

The value of Z_{dil} for this estimation is obtained from equation (3.5), i.e. accounting for their diluted number of entanglements of the backbone due to the relaxed arms. The estimated and experimental times are listed in Table 3.4. Each time was taken as the inverse of the Hencky strain rate where an unambiguous deviation from the linear viscoelastic stress growth curve was first seen. We defined this deviation in terms of the strain hardening factor (Barroso et al., 2010), the ratio between the extensional viscosity data and the respective data from the Trouton ratio (linear response). A strain hardening factor greater than 3 at a Hencky strain of 2.5 was considered as a criterion for the stretch time.

Given the obvious simplicity of this approach we believe that the agreement between estimated and experimental stretch times is very satisfactory. We note, in particular, that this approach seems to work for both entangled and unentangled side arms. This result is encouraging and indicates a success of the hierarchical concept of stress relaxation: at long timescales, the combs can indeed be considered as renormalized linear polymers. It also suggests the importance of this considering the effect of entangled branches of the combs in controlling their extensional rheology. This can form the basis for a more rigorous modeling development in the future.



Figure 3.16: Top: Indicative master curves of frequency-dependent G' and G'' for entangled linear (a) and (b) polymers whose diluted backbone has the same number of entanglements Z as the linear chains. Bottom: Cartoon representation of the tube of the linear chain (left) and the comb (b). In the latter case, once the branches have escaped their tubes, the backbone tube diameter increases (and becomes equal to that of the linear chain for the present considerations) and bears extra friction due to the branches.

Sample code	\mathbf{Z}_{dil}	τ _{d exp} (s)	$ au_{ m d}/ au_{ m eexp} \ (x10^{-5})$	τ _{R,comb} (s)	τ _{s predicted} (s)	τ _{s exp} (s)
PI472k	48.3	1440	144	0.49	16.6	10
PI254k	9.5	304	30.4	0.08	36.7	100
PI211k	19.5	41.2	4.1	0.09	1.65	0.3
C622-PS	7.1	10.3	0.2	0.30	2.05	3
C642-PS	2.7	63.1	1.3	0.78	56.1	100
C712-PS	41.2	274	5.5	1.57	3.9	1
C722-PS	36.6	838	16.8	1.77	13.9	10
C732-PS	28.5	2510	50.2	2.27	58.5	33.3
C742-PS	19.6	7940	159	3.31	313.8	333.3

Table 3.4: Experimental and predicted times scales for assessing the onset of extension hardening. For PI we used $T_{ref}=0^{\circ}C$ and for PS $T_{ref}=170^{\circ}C$.

3.4.1.8 Conclusions

In this study, we have investigated systematically the transient uniaxial extensional rheology of a series of well-characterized, anionically synthesized comb polystyrenes and polyisoprenes. The main results can be summarized as follows:

i. At very high Hencky stretch rates, about the inverse Rouse time, all polymers will strain harden. Monodisperse linear entangled polymers will not do so at lower rates.

At such high rates, there is virtually no effect of molecular parameters of the combs (molar mass of backbone or branches or backbone segment between branches).

- ii. Combs will also strain harden at lower rates, because of the branches. In general, as the rate is increased, strain hardening becomes more pronounced and appears earlier.
- iii. For such lower rates, increasing the average number of entanglements of the backbone segments between branch points and/or the branches results in stronger strain hardening and its faster onset. In particular the number of entanglements per branch appears to be the key parameter for controlling the extensional rheology and strain hardening.

The onset of strain hardening can be rationalized by accounting for the effective stretch relaxation time of the comb, which is the timescale for stretch relaxation along the dilated backbone tube when accounting for the large friction that comes from the branches. It can be estimated from the molecular characteristics of the combs by assuming that the ratio of this time to the terminal time of the comb is equal to that of Rouse to terminal time of a linear polymer with the same number of entanglements as the diluted backbone. The onset of extension hardening occurs at a rate equal to the inverse stretch time. Given the simplicity of this analysis, the predicted and experimental onset rates (times) are in good agreement, suggesting that the important physics is captured. This result is promising and opens the route for further analysis toward the fundamental understanding of the uniaxial extensional rheology of branched polymers.

3.4.2 Modelling uniaxial extensional rheology of combs

3.4.2.1 Modelling linear rheology of combs

The linear rheology of the PS dataset of combs was modelled previously by (Kapnistos et al., 2005; Ahmadi et al., 2011). The shared common challenge of both of these tube-based molecular models in modelling this series of combs is related to the unentangled or barely entangled arms grafted on the linear backbone. The lack of clear separation of the arm and backbone relaxation time scales is the underlying deficiency. This is a known limitation of tube models due to the inherent limitations of the DTD theory. (Kirkwood et al., 2009) accounted for this in other combs with similarly short branches. There added ad-hoc more

effective friction by artificially increasing the M_a using ideas from Zhou and Larson (asymmetric stars).

As a first step, we use BOB to fit the linear rheology of the PS and PI combs with a consistent set of parameters. This is not an easy task for a few reasons. Firstly, due to difficulty of obtaining monodisperse combs and their subsequent characterization (as explained in Chapter 2). Hence, the chemical parameters obtained from the characterization such as M_w and PDI may not be fully accurate. A more accurate molecular weight distribution can be determined using Temperature Gradient Interaction Chromatography (TGIC), since this technique can detect even very low level of contaminants. However, for the samples used in this study, although TGIC was used, the final M_w and PDI were not extracted from this technique. Since SEC was used for the characterization, it may be that there is up to 10% variation in the M_w and the PDI.

Second, the difficulty with obtaining a consistent set of parameters is due to the limitations inherent in tube models. Due to the limitations inherent in the synthetic procedure (Roovers et al., 1979; 1981), the branchpoints are randomly distributed along the backbone. The assumption made in all the current models for reason of simplicity is uniform distribution of branches. Moreover, the theory of dynamic tube dilution is not as rigorous as is required for more quantitative analysis of combs. Although DTD is both simple and has been shown in some specific cases to be remarkably accurate (especially for star polymers), it has considerable limitations. The requirement of DTD is that the relaxation times of the arms and backbone are well-separated and independent. Another limitation in tube model analysis is the parameter inconsistency. The values of α and p^2 remain a controversial topic despite a considerable amount of research efforts (Graessley, 2008; Rubinstein and Colby, 1990; Park and Larson, 2003; van Ruymbeke et al., 2012). Moreover, even the method of determination of the molecular parameters such as M_e and τ_e remain unclear. The M_e can be extracted from the definition of the experimental plateau modulus by using the pre-factor of 4/5 or 1. From data, the equilibrium modulus (defined by rubber-elasticity theory) is extracted. In the Doi-Edwards framework 1986, the plateau modulus $G_N=4/5$ this value. The other uncertainty is related to the values of plateau modulus which can vary either due to small experimental inconsistencies (sample overfilled or under-filled) or in the case of polyisoprene, small differences in microstructure. Otherwise, M_e or τ_e can be obtained from published literature

values. Good agreement with the experimental moduli is achieved when using the following BOB parameters to model our PS and PI combs respectively, α =1, M_e (PS)=12.9 kg/mol, τ_e (PS)=1E-4 s at a temperature of 170°C and M_e (PI)=4.09 kg/mol, τ_e =5E-4 s and p²=1/40 at a temperature of 0°C. As demonstrated in Figure 3.17, the BOB fit matches very well to the PI254k comb moduli.



Figure 3.17: Linear rheology data of PI254k comb and BOB fit. Symbols: experimental data at 0°C and lines: fits to the BOB model

3.4.2.2 Combs fitted with pom-pom model

We use the multimode pom-pom equations to fit the uniaxial extensional rheology of the combs as seen in Figure 3.18. In all cases, the pom-pom model provides a satisfactory fitting except at the fast rates larger than the inverse Rouse time. However the connection between the rather large number of free parameters and the molecular architecture remains unclear. The procedure used to fit the pom-pom multimode equations involves the following: first, a Maxwell model is used to fit the linear rheology curve. From this fit, we extract, moduli and relaxation times for each mode (two first columns in Table 3.5 and 3.6). Next, we use the extensional rheology data to fit two additional parameters, q and ratio of backbone orientation/stretch time (two last columns in Table 3.5 and 3.6). The solutions of the pompom model are limited to rates below the inverse of the Rouse time of the backbone for two main reasons:

- Since only one stretch parameter λ is used for the entire backbone, the assumption is that local differences in stretch will equilibrate rapidly on timescales on the order of the Rouse time of the backbone.
- 2) At high rates, it is not possible for branch point-withdrawal to occur and therefore the backbone is stretched more than the amount that the maximum stretch condition implies. In the case of an H polymer, where the inner segment is separated by two arms, the maximum tension that the backbone can sustain is equivalent to two. Therefore, if the tension in the backbone exceeds this, branch-point withdrawal occurs so the molecule redistributes the tension at timescales of $\tau_{R,backbone}$. If the rate is much larger than the inverse of this timescale, then this process is not captured and the backbone will continue to stretch.



Figure 3.18: (a) C742-PS and (b) C642-PS tensile stress growth coefficient experimental data at 170°C in black and comparison with pom-pom fits in red.

Table 3.5: Pom-pom fitting comb parameters of C742-PS at rates which vary from $0.001s^{-1}$ to $0.1s^{-1}$.

Mode	G _i (Pa)	$\tau_{b}(s)$	q	$\tau_{\rm b}/\tau_{\rm S}$
1	2.71E+06	4.83E-06	1	1
2	6.05E+05	4.32E-05	1	1
3	1.89E+05	3.87E-04	1	1
4	3.34E+04	3.46E-03	1	1
5	6.07E+04	3.09E-02	1	1
6	7.04E+04	2.77E-01	1	1
7	2.11E+04	2.48E+00	1	1
8	2.43E+03	2.21E+01	1	1
9	7.62E+03	1.98E+02	6	4
10	1.15E+04	1.77E+03	6	4
11	7.80E+03	1.59E+04	6	4
12	2.06E+02	1.42E+05	7	3.6

Table 3.6: Pom-pom fitting comb parameters of C642-PS at rates which vary from $0.03s^{-1}$ to $0.3s^{-1}$

Mode	G _i (Pa)	$\tau_{o}(s)$	q	τ_b / τ_S
1	1.17E+07	2.99E-06	1	1
2	1.03E+06	2.10E-05	1	1
3	2.75E+05	1.47E-04	1	1
4	1.17E+05	1.03E-03	1	1
5	5.74E+04	7.23E-03	1	1
6	8.66E+04	5.07E-02	1	1
7	5.91E+04	3.55E-01	1	1
8	1.13E+04	2.49E+00	1	1
9	3.67E+03	1.74E+01	1	1
10	2.96E+03	1.22E+02	10	1.5
11	7.40E-01	8.57E+02	12	1.5
12	6.97E-02	6.01E+03	12	1.5

3.4.2.3 Comb-adopted modified pom-pom model

I. Generalized pom-pom stretch equations for comb polymers

Given the above limitations, our next goal is to modify the original pom-pom model of (McLeish and Larson, 1998) in order to tailor it specifically for comb architectures and to test this model with our uniaxial extensional rheology data. We consider a comb polymer with a linear backbone of Z_b entanglements and assume that n_a side-arms of length Z_a are grafted uniformly along this backbone. The assumption of uniform grafting does not fit reality but has been successfully used in molecular tube models for a variety of comb structures (Kapnistos et al., 2005; Ahmadi et al., 2011). Moreover, for reasons of simplicity, we assume that n_a is odd and that the number of backbone segments n_s between branch-points and between branch points and the free end backbone segments corresponds to $n_s = n_a + 1$.

Fig. 3.19 shows the numbering scheme of the comb branch-points and the contour lengths of the backbone segments. We assume that both halves of the backbone about the central branch-point behave the same way, therefore only one half of the comb is considered. All backbone segments have the same tube contour lengths l_{eq} . The contour length is equivalent to the mean square end to end distance of a free polymer chain $l_{eq}a = R^2 = Nb^2$ where the tube diameter a is related to the Kuhn segment length b by the following relation: $a^2=N_eb^2$.



Figure 3.19: (a) Schematic of a seven arm comb polymer where only half of the comb is considered. Branch-points are labelled from the center of the molecule (i=0) and progressively towards the free ends. In flow, the contour length of the backbone segment between the branch-points i and i - 1 is l_i . (b) The dynamics of the branch-point i is determined by the balance of the viscous force and the elastic recovery force at i. The drag force is related to the friction of the side arm retraction. The elastic recovery force is due to the different contour lengths l_i and l_{i+1} from their relaxed contour lengths l_{eq} .

Similarly to all the current tube model theories (Doi and Edwards, 1978), we consider only the average dynamics for reasons of simplicity. As in H and pom-pom molecules, the backbone of the comb will stretch at timescales between $1/\tau_d$ and $1/\tau_a$ due to the hierarchical relaxation that prevents a fast retraction process. The stretch of the comb backbone segments will not occur uniformly on these timescales and rather the sretch of every individual segment is dependent on its position along the backbone. Therefore, we do not assume an average stretch factor λ as is done in the original pom-pom but rather a distribution of stretch factors λ_i along the comb segments. Considering the center of the backbone as the origin and maximum stretch point, a force balance constraint is imposed on each branch point, which requires that the stretch stretch λ_i in segment i is always less than or equal to $\lambda_{i+1}+1$ (Inkson et al., 1999; Blackwell et al., 2000; Marrucci et al., 2008) in any given segment cannot exceed the stretch in the adjacent segment plus one. The segment which has the highest stretch ratio (λ_{max} corresponding to $n_s/2$) is the backbone segment just to the left and right of the middle and the one with the lowest stretch ratio is the outermost backbone segments (the free ends) which do not contribute to the stretch at all. (Marrucci et al., 2008) used a similar reasoning in order to determine the expected position of the second maximum in shear-flow start-up for a complex comb-like structure. However, the rates they consider are of much higher order and not in the range of $1/\tau_d < \dot{\epsilon} < 1/\tau_a$. Moreover, they assume that the maximum in shear stress is reached when the whole comb is contained within the backbone.

The original differential version of the pom-pom model (McLeish and Larson, 1998), consists of both a stretch dynamic term and an orientation dynamic term as well as respective relaxation times for each. We modify the stretch dynamic equations but keep the orientation dynamic equations exactly the same. We assume that there is one single average orientation distribution of the comb backbone segments and one single backbone orientation time τ_0 . The backbone reptation time or orientation relaxation time τ_0 is the average time needed for the branch points to diffuse along the backbone tube, out of a tube of unstretched length. This approximation is not exactly accurate because similarly to the stretch, the orientation should also be dependent on position, where the free end segments are barely oriented compared to the middle segments. However, we assume that the tube is fully aligned in the direction of flow and at the experimental flow rates of interest, that an average orientation distribution is sufficient to describe the orientation dynamics.

As with the original differential version of the pompom equations we determine the orientation tensor S by working with an auxiliary tensor A satisfying the upper convective Maxwell model:

$$\frac{\partial}{\partial t}\underline{\underline{A}} = \underline{\underline{K}} \cdot \underline{\underline{A}} + \underline{\underline{A}} \cdot \underline{\underline{K}}^{T} - \frac{1}{\tau_{o}} \ (\underline{\underline{A}} - \underline{\underline{I}})$$
3.7

Where K is the deformation rate tensor and I is the identity tensor. The expression for the average orientation tensor is the following:

$$\underline{\underline{S}}(t) = \frac{\underline{\underline{A}}(t)}{\text{trace}[\underline{\underline{A}}(t)]}$$
3.8

At time-scales longer than the side-arm retraction time τ_a , the branch-points act like localized drag points. The additional friction is originating from the relaxed arms. The curvilinear diffusion constant is D=p²a²/2 τ_a . From an Einstein argument, the friction coefficient ζ describing the branch-point diffusion along the tube diameter a(t) is given by (Das et al., 2006a).

$$\zeta(t) = \frac{2k_B T \tau_a}{p^2 a(\tau_a)^2} \left(\frac{a(t)}{a(\tau_a)}\right)^2$$
3.9

The parameter p corresponds to the average hop size of length p*a in units of the tube diameter $a(\tau_a)$ at the time scale τ_a . The value of p is not well-defined in the litterature, it will be described in more depth in Chapter 4.

At rates higher than the inverse reptation time $1/\tau_d$ of the dynamically diluted backbone, the backbone segments are oriented in the direction of flow. At rates between $1/\tau_d$ and $1/\tau_a$, only the backbone segments between branch-points are stretched. The dynamic stretch equation is essentially Rouse-like and describes motion of the entangled backbone chains along the tube. The dynamics of the stretch of the backbone segments is determined from a force balance at each branch-point during tube motion. The imposed flow causes a drag force and the relaxation from the imposed stretch results in an elastic recovery force. More specifically, the drag force is due to the velocity of separation of the branch-point (branch point hopping) with respect to the tube velocity, and the elastic recovery force from the neighboring backbone segments. Considering branch-point i (Fig. 3.19b), we define its curvilinear velocity along the tube axis, relative to the central branchpoint, to be v_i . The difference between v_i and the velocity of the surrounding tube matrix at the branch-point gives rise to a viscous force.

$$f_{v} = -\zeta \left[v_{i} - \left(\underline{\underline{K}} : \underline{\underline{S}}\right) \sum_{j=1}^{i} l_{j} \right]$$
3.10

Here, K is the applied deformation rate tensor, S is the average tube orientation tensor, and the contraction K:S is the average increase of length per length of tube. The relative curvilinear velocity is K:SL. The Gaussian segments l_{i+1} and l_i contribute to an elastic recovery force.

$$f_e = k(l_{i+1} - l_{eq}) - k(l_i - l_{eq})$$
3.11

with k being the spring constant describing the Hookean elastic recovery response of the backbone segments. Setting $f_v + f_e = 0$, we find the branch-point velocity.

$$\zeta v_i = k(l_{i+1} - l_i) + \zeta \left(\underline{\underline{K}} : \underline{\underline{S}}\right) \sum_{j=1}^{l} l_j$$
3.12

The difference of velocity between the branch-points i and i - 1 gives the rate of change of the contour length of the segment between the two branch-points as

$$\zeta \frac{dl_i}{dt} = \zeta (v_i - v_{i-1}) = k(l_{i+1} - 2l_i + l_{i-1}) + \zeta \left(\underline{\underline{K}} : \underline{\underline{S}}\right) l_i \qquad 3.13$$

Dividing by the equilibrium segment lengths l_{eq} and defining the dimensionless stretch $\lambda_i = l_i/l_{eq}$ we arrive at

$$\frac{d\lambda_i}{dt} = \frac{1}{\tau_{seg,0}} (l_{i+1} - 2l_i + l_{i-1}) + \left(\underline{\underline{K}} : \underline{\underline{S}}\right) l_i \qquad 3.14$$

Here, we define the time $\tau_{seg,0} = \zeta/k$ that determines stretch relaxation between backbone segments separated by branch-points. Hence, the expression for τ_{seg} is the relaxation time of a spring (k) working against the drag force (ζ).

In addition to acting like effective drag points after their relaxation, the arms will act as a dynamic solvent for the unrelaxed backbone and increase the effective diameter. Therefore, the expression for tube diameter becomes:

$$a^{2} = N_{e}b^{2} = \frac{N_{e,o}b^{2}}{\phi_{b}^{\alpha}} = \frac{a_{0}^{2}}{\phi_{b}^{\alpha}}$$
 3.15

From rubber-elasticity theory the spring constant $k = 3k_BT/Z_sa^2$, the drag coefficient ζ is given from expression 3.9 and taking into account the effective enlarged tube with Z_s being the number of entanglements of the backbone segments, the following expression for τ_{seg} results.

$$\tau_{seg,0} = \frac{\zeta}{k} = \frac{2k_B T \tau_a \phi_b^{\alpha}}{p^2 a_0^2} \frac{N_{seg} b^2}{3k_B T} = \frac{2\tau_a \phi_b^{\alpha} N_{seg}}{3p^2 N_{e0}}$$
$$\tau_{seg,0} = \frac{2\tau_a \phi_b^{\alpha}}{3p^2} Z_{seg} = \frac{2\tau_a \tilde{Z}_{seg}}{3p^2}$$
3.16

where the weight fraction of backbone material $\varphi_b = (Z_b - 2Z_a)/(Z_b + n_aZ_a)$ and α is the dilution exponent that we set as 1. We estimate Z_s as $Z_s = Z_b/(n_a + 1)$. Therefore, the backbone segmental relaxation time is proportional to both the retraction time of the arms and the diluted number of entanglements per backbone segment and inversely proportional to the friction parameter p^2 . The τ_{seg} time is the main input parameter which determines the onset rate of strain hardening. The larger the value of τ_{seg} , the lower the onset rate of strain hardening.

The relaxation of the arms results in a drag force on the branch point which is exponentially dependent on the entanglements of the arm. There is experimental evidence that suggests that this drag is not constant and that the drag force should be coupled to the branchpoint dynamics (McLeish et al., 1999). The branch point dynamics depends only on stretch and is therefore negligeable at low rates of deformation. We can approximately include the effect of local (\leq tube diameter a) displacement of branch-point which results from tension difference between the two sides of a branch-point (from relaxed and unrelaxed segments), leading to so-called "drag-strain coupling" (Blackwell et al., 2000). Drag-strain coupling was first introduced in order to explain the discrepancies which existed between the

pom-pom model predictions and the experimental data at high rates, when maximum stretch was reached. Modified pom-pom models have included this correction in numerical simulations in order to explain unexpected processing phenomena such as transient "stress fangs" in the processing of polyethylene (Lee et al., 2001). For small displacements, considering the probability distribution of displacement to be Gaussian, the position of the branch-point can be considered as a Brownian walk in a quadratic potential (Doi and Edwards, 1986). Balancing the force from this localizing potential to the elastic force at branch-point i, the effective contour length of the side-arm at i. that participates in relaxation by retraction, is reduced by a factor proportional to $|\lambda_i - \lambda_{i+1}|$. Exponential dependence of the retraction time-scale on the side-arm length leads to an effectively shorter segmental stretch relaxation time from this drag-strain coupling as

$$\tau_{seg}(i) = \tau_{seg,0} \exp(-2\left|\lambda_i - \lambda_{i+1}\right|)$$
 3.17

Incorporating this drag-strain coupling, the equations for the stretch dynamics become:

$$\frac{d\lambda_i}{dt} = \frac{1}{\tau_{seg,0}} \left[e^{2|\lambda_i - \lambda_{i+1}|} (\lambda_{i+1} - \lambda_i) - e^{2|\lambda_{i-1} - \lambda_i|} (\lambda_i - \lambda_{i-1}) \right] + \left(\underline{\underline{K}} : \underline{\underline{S}} \right) \lambda_i$$
 3.18

For large deformations, it is possible that our imposed stretch constraint is not valid, the difference in stretch between adjacent backbone segments may differ by more than one, i.e. $|\lambda_i - \lambda_{i+1}| > 1$. An entropic force balance argument, comparing the tension in the side arm and two backbone segments, indicates that such a situation is unsustainable, and "branchpoint withdrawal" occurs, in which the side arm is pulled into, and oriented along, the backbone tube. The branch-point encounters a constant force in such large deformation and hence an equivalent linear confining potential. This is analogous to the pom-pom model where $\lambda_{max}=q$ the number of arms on each branch point when it becomes entropically more favorable to withdraw the arms than to continue stretching. In the case of the H and pom-poms, however, branch point withdrawal of all the arms occurs at the same time. Alternatively, in this modified model, branchpoint withdrawal occurs first from the outer segments, moving inwards through the molecule. The maximum stretch condition is reached when the $\lambda_{max}=n_s/2$, ie half of the number of backbone segments. The branch point withdrawal process is depicted in Figure 3.20.


Figure 3.20: Sketch of the dynamics of branch point withdrawal for combs. At deformation rates between $1/\tau_d$ and $1/\tau_a$, branch point withdrawal occurs from the outer segments (λ =1) and progresses inwards to the center. The maximum stretch occurs in the center backbone segment when λ_{max} is equal to half the number of backbone segments.

The total stress for the stretching backbone segments of the comb in a non-linear flow is a function of the modulus G, the separate contributions of average orientation S(t) and the quadratic distribution of stretch factor $\lambda_i(t)$.

$$\underline{\underline{\sigma}}(t) = 3 \frac{G}{n_s - 1} \sum_{i=1}^{n_s - 1} \lambda_i^2(t) \underline{\underline{S}}(t)$$
3.19

This is the same stress expression as the original pom-pom model except for the inclusion of the distributions of stretch factors. Using the same methodology as the multimode version of the original pom-pom model, the SAOS data of the combs is characterized by a set of n_M Maxwell modes. We assign Maxwell modes for each mode a with characteristic modulus G_a and relaxation time $\tau_{o,a}$ to both slower modes coming from the dynamically dilated backbone and to faster modes, coming from the contribution of the arms and outermost backbone segments. The criteria used to assign the stretching and non-stretching modes is the following: we treat the Maxwell modes with relaxation times faster than the arm retraction time as non-stretching ($\lambda_i = 1$ for all i). All slower modes are treated as stretching modes. We also tested other criteria for assigning the modes. For example, one can assign Maxwell

modes to the backbone relaxation as the sum of the slowest relaxation modes which sum up to the estimated modulus of the diluted backbone $G_{b,dil} = G_e \phi_b^{\alpha+1}$. The remaining modes are assigned as non-stretching modes. Both methods work equally well and choosing one or the other, affects minimally the fit of the final transient extensional rheology data.

The uniaxial extensional response of the fast modes, considered to be the non-stretching molecules such as the arms and the outermost backbone segments is modeled using the non-stretching version of the pom-pom model, ie without a stretch factor λ .

$$\underline{\sigma_f} = 3 \sum_{i=1}^{k} G_a \underline{S_a(t)}$$

$$3.20$$

We consider a separate expression for the stretching modes where equal weight is given to the modulus from each of the internal segments of the backbone with $\lambda_{i,a}$ being the stretch on the i'th backbone segment that contributes to the α 'th Maxwell mode. Assuming there are k non-stretching modes, and n_{M-k} comb modes, the total stress is obtained from:

$$\stackrel{\circ}{\underline{\sigma}} = 3\sum_{i=1}^{k} G_a \underbrace{\underline{S}_a}_{\underline{i}}(t) + \frac{3}{n_s - 1} \sum_{a=k+1}^{n_M} \sum_{i=1}^{n_s - 1} G_a \lambda_{i,a}^2(t) \underbrace{\underline{S}_a}_{\underline{i}}(t)$$
 3.21

Here, $\underline{S}_a(t)$ is the average tube orientation experienced by the fraction that contributes to the a'th Maxwell mode evaluated from Eqns. 3.7 and 3.8.

II. Comparison with Experimental Data

As mentioned previously, the extensional rheology measurements were performed at 170°C for the polystyrene combs and at 0°C for the polyisoprene combs using an SER fixture (Sentmanat, 2004) mounted on an ARES 2KFRTN1 strain-controlled rheometer. Due to the limitations inherent in SER, experiments are limited to a maximum Hencky strain of 4, and a steady-state tensile growth coefficient was not achieved. Therefore, the modeled data can only be compared to the experimental data in a limited Hencky strain range. On the other hand, a wide range of extensional rates (especially in the high limit) is available.

In applying our model, we start by fitting the linear viscoelastic moduli measured from small angle oscillatory shear (SAOS) with approximately three Maxwell modes per decade in frequency range of the experimental data. Both a least-square fit and a regularization term (Press et al., 1992) were applied to ensure that all G_M are smooth.

For combs with long side-arms, the phase angle (δ) shows a distinct peak in the SAOS data. When the side-arms are barely entangled, there is a change of slope in the phase angle. For each of the combs, we select τ_a from either the peak or the transition point in the phase angle. There are other methods of obtaining arm relaxation times which will be mentioned more in depth in Chapter 4. All methods of obtaining arm relaxation times are in relative agreement and the values of τ_a do not vary much between all the methods. The time-scales of the Maxwell modes define the orientation relaxation times of the modes. We keep the segmental stretch relaxation time $\tau_{seg,0}$ as a global constant fitting parameter. More specifically, we assign a value for $\tau_{seg,0}$ which best fits the onset rate of strain hardening. Also, we calculate separately $\tau_{seg,0}$ from expression 3.16. In most instances, the fitted and calculated $\tau_{seg,0}$ are in close agreement. These values can be found in Table 3.7. We use the analytically known solution for A in uniaxial extension and numerically solve the coupled stretch equations (Eqn. 3.16) by using a fifth order Cash-Karp Runge-Kutta method with adaptive step-size (Press et al., 1992).

Fig. 3.21a shows the phase angle for the PI combs with a distinct peak for PI254 at 1.5 1/s giving $\tau_a = 0.67$ s. For both PI211 and PI472, there is a change of slope at 320 1/s giving $\tau_a = 0.003$ s. In Fig 3.21b-d, we show the experimental data (symbols) and model predictions (lines) for the start-up stress growth coefficients (transient viscosity η^+) in uniaxial extension for the PI combs at a number of extension rates. The underestimation of stress at the highest flow rate for PI254 is most likely due to the flow rate exceeding the bare Rouse relaxation rate which is estimated as 13 s⁻¹. As explained in Chapter 3.4.1, for a comb, considered as a linear backbone chain with grafted branches, the Rouse time may be estimated by accounting for the increased monomeric friction of the branches. The Rouse dynamics are not included both in the original pom-pom model and this present modified version. At such high rates there is not sufficient time for the arms to withdrawal. Similar results for the PS combs are shown in Figs. 3.22 and 3.23.



Figure 3.21(a) Phase angle $\delta = \tan^{-1} (G''/G')$ for the PI combs. The arrows indicate peak (PI254) or change of slope (PI211, PI472) in $\delta(\omega)$ signifying side-arm retraction times τ_a (b-d) Experimental data (symbols) and model predictions for the start-up stress growth coefficients in extensional flow at the indicated rates.



Figure 3.22 (a) Phase angle δ for PS622, PS642, and PS712 with arrows indicating peaks/change in slope selected to find τ_a . Experimental data (symbols) and model predictions (lines) for η + at the indicated rates for (b) PS622, (c) PS642, and (d) PS712



Figure 3.23: a) Phase angle δ for PS722, PS732, and PS742 with arrows indicating peaks/change in slope selected to find τ_a . Experimental data (symbols) and model predictions (lines) for η^+ at the indicated rates for (b) PS722, (c) PS732, and (d) PS742.

In Table 3.7, values of $\tau_{seg,0}$ used in the fitting procedure and estimated from Eq. 3.16 assuming $\alpha = 1$, M_e (PI) =4.1 kg/mol, M_e (PS) = 12.9 kg/mol, and p² = 1/40 are depicted. These values correspond to the best fit parameters of the linear rheology data of the PS and PI combs using the BOB computational algorithm as explained peviously. Note that the definition of M_e used here includes a (4/5) prefactor (Fetters et al., 1994).

Our estimates for τ_a from visual inspection of the phase angle could give an error of a factor 2. We use a single segment length Z_s ; though the synthesis procedure should create a wide distribution of Z_s . The value of p^2 can be different by a factor of 2 from the value used here and may depend on the architecture (Bačova et al., 2014). Considering these uncertainties, the agreements between the fit values and the estimates from Eq. 3.16 are

satisfying. This is even more remarkable (and perhaps surprising) because some of the PS combs have barely entangled side-arms and backbone segments between branch points that are shorter than the entanglement molecular weight. Overall, the agreement between model predictions and experiment, and the self-consistency of the model parameters, are encouraging.

Code	$\tau_a(s)$	$\tau_{\mathrm{seg},0}^{1}(s)$	$\tau_{\mathrm{seg},0}^{2}(s)$
PI472k	0.003	0.45	0.29
PI254k	0.67	20	21.13
PI211k	0.003	0.25	0.22
C622-PS	0.013	0.04	0.09
C642-PS	1.25	1.0	2.60
C712-PS	0.0016	0.025	0.07
C722-PS	0.0029	0.12	0.12
C732-PS	0.07	0.9	2.4
C742-PS	1.0	20.0	20.4

Table 3.7: The PI and PS combs characteristic relaxation times τ_a , $\tau_{seg,0}^{-1}$ (best fit parameter), $\tau_{seg,0}^{-2}$ (s) (estimated from Equation 3.16)

Moreover, since the model successfully captures the comb data series, we can further study the internal dynamics of the stretch of the backbone segments based on their respective positions during start up flow. We investigated the stretch dynamics for C732-PS, a 27 arm comb, with barely entangled arms and long backbone with characteristic relaxation times $\tau_a = 0.07$ s, τ_{seg} , 0 = 0.6 s and $\tau_0 = 10^3$ s. Fig. 3.24 shows the steady state stretch in different positions of the backbone for a range of extension rates. During start up extensional flow, the stretch increases with time until it reaches the steady state value. Experimentally, this steady-state value corresponds to the steady-state tensile stress growth coefficient and is usually observed between a Hencky strain of 3 and 4 and can only be measured using the FSR (as explained in depth in Chapter 3). The curves in Figure 3.25 are quite similar to the flow-rate dependent priority designation for backbone segments (Read et al., 2011) since the maximum

stretch varies with flow rate. Towards the outside of the molecule it is clear that the maximum stretch is set by the branchpoint withdrawal limit; at higher rates the outermost segment has a stretch of 1, the adjacent one has a stretch of 2, the next one has stretch of 3, such that there is a linear envelope to the maximum stretch. The stretch varies with the position such that $d\lambda_n/dn = -1$.

However, once the outermost branchpoints are withdrawn, they no longer contribute friction to the remaining stretch dynamics in Eqns. 3.14 and 3.18. Thus, the effective friction is confined to the remaining central part of the molecule, comprising segments with nonwithdrawn branchpoints; this section has a progressively faster relaxation time as more of the outer branchpoints are withdrawn. As a result, at intermediate flow rates, a steady state is reached in which stretching due to the flow is balanced by relaxation of this central section of the backbone. In the absence of drag-strain coupling (Fig. 3.24a), this region of intermediate flow rates is quite narrow. Increasing the rate from 0.01 1/s to 0.03 1/s results in a transition from nearly unstretched to almost fully stretched conformation. With typical experimental measurements at rates separated by a factor of 3, it predicts a sharp critical value of strain rate above which nearly unstretched molecules reach their maximum stretch (except for the very center of the molecule). Drag-strain coupling (Fig. 3.25) smoothens this transition significantly.

Fig 3.25 depicts the steady-state stretch in the central segment as a function of the extension rate. With drag-strain coupling there is about a decade of extensional rates in which a concept of flow-rate dependent priority (Read et al., 2011) is valid for the central segment.



Figure 3.24: Steady state stretch in different backbone segments in extensional flow at the indicated rates for a 27 arm comb with $\tau_a = 0.07$ s, $\tau_{seg,0} = 0.6$ s, and $\tau_o = 103$ s. The stretch factor increases from the central segments towards outside of the comb molecule. The plot on the left is predictions without drag-strain coupling (Eqn. 3.14) and the plot on the right is including drag-strain coupling (Eqn. 3.18) in the stretch evolution equations.



Figure 3.25: Steady state stretch in the central segment for the comb molecule considered in Fig. 3.24 as a function of extension rate. Without drag-strain coupling (circles), there is a very short range of rates in which the segment reaches its maximum stretch from essentially unstretched conformation. Drag-strain coupling (squares) smoothen out this transition to some extent.

III. Discussion

We have presented a simple self-consistent model, based on an extension of the pom-pom model, that captures the coupled stretch dynamics in a comb polymer under uniaxial extensional flow. We use this model to successfully fit uniaxial extensional data for a series of polystyrene and polyisoprene combs with a rather large range of molecular characteristics. Our strategy is to separate the linear rheology data into Maxwell modes associated with the inner backbone stretching modes $t>\tau_a$ and the arms and outer backbone non-stretching modes at $t<\tau_a$. Matching the extensional data requires a single fit parameter $\tau_{seg,0}$ for stretch relaxation in each of the backbone segments. We also demonstrate that our fitted values are physically reasonable (in the context of branchpoint hopping dynamics) across all combs considered.

We include a short summary of the equations of the modified pom-pom model for combs:

Stress Expression :	$\underline{\sigma} = 3\sum_{i=1}^{k} G_{a} S_{a}(t) + \frac{3}{n_{s} - 1} \sum_{a=k+1}^{n_{M}} \sum_{i=1}^{n_{s} - 1} G_{a} \lambda_{t,a}^{2}(t) S_{a}(t)$
Orientation Dynamics :	$\mathbf{S}(t) = \frac{\mathbf{A}(t)}{\text{trace}\left[\underline{\mathbf{A}}(t)\right]}$
	$\frac{\partial}{\partial a} \underbrace{A = K \cdot A + A \cdot K^{T}}_{a = a = a = a = a = a = a = a = a = a =$
Stretch Dynamics :	$\frac{d\lambda_{i}}{dt} = \frac{1}{\tau_{\text{sg},0}} \left[e^{2 \lambda_{i}-\lambda_{i} } (\lambda_{i+1} - \lambda_{i}) - e^{2 \lambda_{i}-\lambda_{i} } (\lambda_{i} - \lambda_{i-1}) \right] + \left(\underline{K}: \underbrace{S}_{=} \right) \lambda_{i}$

Summary of input parameters needed for modified pom-pom model for combs:

Topology dependent parameters: number of comb arms n_a , number of backbone segments n_s , vol. fraction of backbone φ_b , number of entanglements per backbone segment Z_s

Chemistry dependent parameters: entanglement molecular weight M_e , entanglement plateau G_e

Tube model parameters: dilution exponent $\alpha=1$ and branch point hopping fraction $p^2=1/40$

Parameters extracted from linear rheology: retraction time of comb arms τ_a , moduli G_a associated with stretching and non-stretching modes

Non-linear relaxation time constants: segmental relaxation time τ_{seg}

Chapter 4

Influence of the Environment on the Entanglement Dynamics

In this chapter, we investigate the influence of the environment (varying length of linear chains) on the entanglement dynamics of a probe model polymer (H and comb architecture). Very short linear chains with few or no entanglements act simply as a solvent and dilute the entanglements of the probe chains. When the number of entanglement of linear chains increases, the overlap between the reptation time of the linear chains and the retraction time of the arms (by CLF) becomes more significant as well as the interdependence between these relaxation processes. Our goal is to quantify the dependence of CLF and reptation on the environment (length of linear chains). We use tube based models such as TMA and BOB in order to determine the respective relaxation times associated with each of the relaxation processes as well as to model our blend linear rheology data.

4.1 Introduction

There is considerable scientific and technological importance in the study of model polymer blends. All industrial polymers are blends, either of different architectures (involving structures such as linear, stars, H, combs, pom-pom, Caylee trees, etc. and their combinations), chain lengths (bimodal, trimodal, etc.), monomer chemistry (copolymers) or inorganic/organic (fillers) composites. As explained in the Introduction, in order to target a final product application, the link between macromolecular structure, polymer rheology and final product properties has to be well understood. Refinement in experiment and modeling of the dynamics of model polymer blends allows one to bridge the design gap.

All the early studies of linear viscoelasticity of linear monodisperse polymer blends have focused on phenomenological blending laws (Ferry et al., 1954; Graessley, 1971; Prest 1970). These blending laws provided for a simple method of calculating long-term properties such as zero shear viscosity, zero shear compliance and final relaxation times. There are a couple of key parameters to consider in the linear viscoelasticity of simple blends such as the ratio between the relaxation times (is there an overlap or are the linear viscoelastic curves well separated) and the volume fraction of each of the components (concentrated or diluted). One example of a blend is a dilute amount of a fast relaxing component trapped in a permanent (cross-linked) or temporary entanglement network. Another example is a 50% volume fraction of two blend components with similar relaxation times. In the dilute case, the chains do not overlap and the linear viscoelastic curves can be added together. In the concentrated case, the interactions between the entanglements of the chains become important and simple blending laws are no longer sufficient.



Figure 4.1: Example of monodisperse blends include (a) one dilute component trapped in a temporary network analogous to pure reptation (Colby and Rubinstein, 1990) or (b) two components whose relaxation times overlap and there are mutual interactions between the chains, hence there are entanglements created by the short-long chains and entanglements between the short chains and long chains (Watanabe et al., 2004).

The linear rheology of monodisperse entangled linear polymers is well understood and can be predicted with tube-based molecular models (Likhtman and McLeish, 2002). However, the current tube model theories are not yet at the level of refinement where they can in all cases predict the linear rheology of blends of two or more monodisperse polymers. The problem remains that there is no truly quantitative and universal self-consistent tube model mean field theory for polydisperse polymers due to the uncertainty around the interpretation of Constraint Release (CR). Examples of models which interpret CR include "double reptation" (Tsenoglou, 1987; des Cloizeaux, 1988), "Constraint Release Rouse" (Graessley, 1982; Watanabe, 1999) and "dynamic tube dilation" (Marrucci, 1985; Ball and McLeish,

1989). Although they have shown to be successful in limited cases, these models are not universal for all types of blends i.e. for a wide range of volume fractions and relaxation times of the respective monodisperse components. Most of the literature has focused on bidisperse linear blends (Watanabe and Kotaka, 1984; Struglinsky and Graessley, 1985; van Ruymbeke et al., 2010; Read et al., 2012; Watanabe et al., 1985; 2004; 2013; Park and Larson; 2004; 2006) and blends of linear and star polymers (Blottiere et al., 1987; Struglinsky et al., 1988; Watanabe et al., 1988; Milner et al., 1998; Lee and Archer, 2002; van Ruymbeke el al., 2010) since they are the most straight-forward blend cases and tube model theories are most successful at predicting their linear viscoelasticity. However, other than experimental studies involving star and linear mixtures, there are few other studies of binary mixtures of model branched polymers. One notable study involved the mixture of ring polymers with a dilute amount of linear polymers which lead to the penetration of rings by linear chains and an opening of the double-folded ring structure (Kapnistos et al., 2008).

As stated previously, one of the deficiencies of the expanded tube model theory for blends is a lack of thorough understanding of the relaxation mechanism of constraint release (CR). The influence of CR on macromolecular motion has not reached the level of understanding of other mechanisms such as reptation and CLF. For instance, most tube model theories on polydisperse systems include a full dynamic tube dilation theory, DTD (Marrucci, 1985; Ball and McLeish, 1989; Milner and McLeish, 1997) where the relaxed segments are immediately taken as a solvent. However, as was recently demonstrated by (Watanabe et al., 2004; 2008; 2013), it may be that only partial DTD is needed in order to provide a universal molecular picture for polydisperse polymers. The concept they present is that of a chain which reptates along a partially dilated tube that wriggles in the fully dilated tube (Matsumiya et al., 2013). Watanabe demonstrated that full DTD is only applicable in the blend case of two monodisperse linear polymers where the components have widely separated relaxation times. The failure of full DTD has also been observed by others (Archer et al., 2001). They demonstrated experimentally that in the case of a blend of bidisperse linear polymers, the ratio between their M_w values should be much larger than 1 in order for full DTD to be applicable. Moreover, they determined that the terminal relaxation properties are dependent on a critical value of M_w of short chains. Below this value, the terminal properties depend only on the volume fraction of the long chains, similarly to entangled

polymer solutions. However, above this M_w , the terminal properties are only affected by the M_w of the short chains.

In addition to DTD, i.e., the constraint release where the relaxing segments act as a solvent and enlarge the tube, there is a second type of constraint release acting at shorter time scales and linked to the motion and renewal of the tube, known as thermal Constraint Release (Graessley, 1982; Watanabe, 1999). This type of constraint release occurs when relaxing segments act to release topological constraints and enable lateral motions of the tube, modeled by the Rouse model (as explained in the Introduction), and becomes very significant in the study of polydisperse polymers. As first explained by (Struglinsky and Graessley, 1985), there is a crossover point where CR dominates over all other mechanisms of relaxation of the chain in the tube, primarily reptation and CLF. Struglinsky and Graessley were the first to approximate this transition for bidisperse linear polymers, in the form of the "Struglinsky-Graessley" criterion (SG), equivalent to the ratio of the reptation of the long chains in an undilated tube τ_{dL} and the Constraint Release Rouse time τ_{RCR} .

$$r_{SG} = \frac{\tau_{dL}}{\tau_{RCR}} = \frac{3Z_L^3 \tau_e}{3Z_L^3 Z_s^3 \tau_e} = \frac{M_L M_e^2}{M_s^3}$$
 4.1

where M_L and M_s are the molecular weights of the long and short polymer chains respectively. When the value of this parameter is small, then reptation of the long chains occurs along the thin tube, otherwise, the long chains relax in a dilated tube mediated by Constraint Release Rouse. More specifically, in a mixture of long entangled chains dispersed in a short unentangled chain matrix, the final reptation of the long chains by CRR mechanism will occur only under the condition that the long chain CR time is significantly faster than the reptation time. Otherwise, the final reptation of the long chains will occur in a skinny tube. Hence, the CR mechanism can be properly analyzed only if there is a distinct separation of time scales, and this is not often the case. A numerical value of 1 (Struglinsky and Graessley, 1985) and 0.064 (Park and Larson, 2004) has been proposed for this criterion but this is still under question. The value of 0.1 was determined from diffusivity measurements (Green et al., 1984) and shown to be applicable in linear viscoelastic data (Park and Larson, 2004). More specifically, tracer diffusion data for the long chains diffused in a matrix of short chains demonstrated that reptation is the dominant diffusion mechanism at large values of M_c

(critical M_w) of short chains, whereas at smaller values, the diffusion coefficient associated with CR dominates.

The influence of the constraint release (CR) on the terminal relaxation of each of the components of the blend is also not fully understood. Moreover, it becomes important to distinguish between each of the CR events. Taking the example of earlier works (Doi et al., 1987; Viovy et al., 1991), (Read et al., 2002) have simplified the CR picture by assigning only two constraint release events (although there are many), one representing entanglements of long chains with all other chains and a second representing entanglements with long chains only. The simplified tube-based picture (Figure 4.2) is that of two tubes, one 'thin' tube (representative of all entanglements) contained with one 'fat' (dilated) tube (representative of entanglements). The long chains will reptate in the dilated ($\oint_{\alpha}^{\alpha/2}$ larger than the thin tube) tube only if they have enough time to explore all the conformations in this tube, otherwise their reptation will occur in a skinny tube. The associated time needed for a chain to move from its skinny tube to its dilated tube is not instantaneous and corresponds to its Rouse time.



Figure 4.2: Test chain in a thin tube (entanglements of long chains with short chains) trapped in a dilated tube (entanglements of long chains). There are two possibilities of long chain reptation: either in the thin tube with tube diameter a_0 or in the dilated tube with tube diameter $a_0^* \phi_L^{\alpha/2}$.

Note that this molecular picture is similar to the one of Watanabe, again invoking the idea of two tubes, a thin tube trapped within a dilated tube. Using this simplified depiction of CR, these authors have successfully modeled both linear and elongation rheology of bidisperse linear blends (Auhl et al., 2009). (Read et al., 2012) have adapted the (Viovy et al.,

1991) diagram (Figure 4.3) in order to provide an illustrative picture of the four regimes associated with the relaxation dynamics of bidisperse linear polymers. The terminal relaxation properties of the bidisperse blends are dependent on the Struglinsky criterion r_{SG} (y axis) and the number of entanglements of the long chains (x axis). The solid lines represent the transition between the regimes. If the values of both r_{SG} and ϕ_L are large, reptation of the long chains will occur in a dilated tube, mediated by CR in the thin tube. However, if the value of ϕ_L is large but the value of r_{SG} is small, reptation of the long chains will occur in a thin tube. Alternatively, if the ϕ_L is small and the value of r_{SG} is large, then the relaxation occurs by Constraint Release Rouse. The last option is that both the values of r_{SG} and ϕ_L are small and therefore, reptation occurs in a thin tube mediated by CR along the thin tube.





Others such as (Liu et al., 2006) have explored the consequences of CR on chain dynamics. To this end, they have attempted to switch-off CR events by properly choosing blends with specific ratios of characteristic times of the components, say a short one and a much longer representing an effective 'sea' of fixed constraints. This type of study allows quantifying the "amount" of CR and is known as probe dynamics. When a dilute amount of short but entangled polymer chains are added to a melt of concentrated overlapping long

chains, the constraint release associated with the short chain entanglements can be effectively switched-off. This is analogous to a mixture of dilute polymer chains fixed in a cross-linked network (Kan et al., 1980). (Liu et al., 2006) and others (Glomann et al., 2011; Watanabe et al., 2013) have shown that there is a retardation (slowing down) of the terminal relaxation time of the short polymer chains in the environment of long polymer chains because the tube motion of the short chains is essentially frozen (no CR of short chains to speed-up the process). They have made a convincing argument by proving that the terminal relaxation time versus the molecular weight conforms to the well-known power law reptation scaling of 3.1 in the nearly permanent matrix environment (associated with the combination of reptation and CLF) and 3.4 in the monodisperse case (CR also included) (as shown in Figure 4.4). (Liu et al., 2006) have also shown that this retardation factor is a function of the length of the short polymer chains. More specifically, the shorter the chains or the larger the difference between the M_w of the short and long chains (hence, on the relaxation times), the more significant the retardation factor becomes. (Watanabe et al., 2013) have also shown that the CR mechanisms accelerate dielectric and viscoelastic relaxation of linear PI and the suppression of CR on blending with a much longer polymer, retards the relaxation in the blend. (Glomann et al., 2011) have shown that the dielectric relaxation spectra for linear PI are independent of CR contribution and hence the combination of viscoelastic and dielectric characterization provides a full description of chain dynamics. (Watanabe et al., 2013) have also recently developed a "blend model" for bidisperse linear blends which works for a wide range of M_s and M₁ values. They consider self-consistently all types of possible entanglements (shortlong, short-short, long-long) and take into account a relatively new concept of CR-activated tension equilibration (Ruymbeke et al., 2012).



Figure 4.4: Plot of the crossover relaxation time vs M_w (Liu et al., 2006) which conforms to a 3.1 power law scaling (suppression of CR) and 3.4 power law scaling (with CR tube motions)

From the above, it becomes evident that it is interesting now to try to understand CR events in the context of more complex blends of polymers, since CR will interfere not only with reptation but also with fluctuation mechanisms. We investigate the relaxation dynamics of a binary mixture of a dilute amount of H polymer (our probe) and a concentrated linear polymer (matrix). The well-defined monodisperse H polymer, that has recently been characterized by Temperature Gradient Interaction Chromatography (TGIC), whose linear viscoelastic properties have been well characterized in the past (Roovers, 1984) was blended with monodisperse linear chains of varying length.

In order to study the effect of the size of the linear matrix on the relaxation time of the arms and backbone of the H polymer, we chose seven different linear PS matrix M_w 's, 5k, 22k, 51k, 129k, 185k, 483k and 1M. Since we are interested in performing probe rheology, more specifically probing the dynamics of a dilute H polymer in a concentrated mesh of linear chains, we chose to have very low concentrations of H polymer in the blend, specifically concentrations considerably below the overlap concentration (1.5%, 3% and 10%).

The H polymer melt will undergo hierarchical relaxation where the outer arms will retract by fluctuations and act as a solvent for the backbone which will only relax by reptation (center of mass diffusion of chains out of their tube) after the arms have fully retracted (McLeish et al., 1999). In addition, there are continuously constraint release events occurring when relaxed segments (first arms and then outer backbone) release topological constraints on un-relaxed segments thus speeding up the process of reptation. When we dilute the H3A1 polymer in a long linear matrix, we attempt to turn off constraint release events associated with the H polymer chains and consequently this will lead to a slowing down of the relaxation. However, when we dilute the H3A1 polymer in a short linear matrix, we expect a speeding up of the relaxation of the H polymer due to constraint release events. Quantifying these effects is the real challenge.

Moreover, in addition to the H polymer, we study a well-defined PI comb PI254k (Kirkwood et al., 2009) as our probe model branched polymer and examine the effect of the environment (length of linear chains) on the entanglement relaxation dynamics of the comb polymer. We vary the length of the monodisperse linear chains (22k, 96k and 1.5M) in our mixture and keep a constant volume fraction of 10% of comb probe. Our main reasoning for the choice of comb as our probe is due to the well separated relaxation time of the respective arms and backbone. Although the H3A1 polymer (Roovers,1984) is a good candidate as a probe model polymer since both the arms and the backbone are well entangled, the inherent limitation is the difficulty of extracting very accurate relaxation times for the arms and the backbone due to the overlap of their linear viscoelastic curves.

Specifically, two questions that we would like to answer during this study are:

How can we quantitatively determine the relaxation time of the arms in the bulk H polymer and, more importantly, in the blends?

How much do we expect the arm relaxation time and the backbone relaxation time to speed-up (in the case of short chains) or slow-down (in the case of long chains)?

4.2 Characterization of linear polymers and blends

4.2.1 Dynamic light scattering study (DLS)

A hydrodynamic radius for the H3A1 polymer of 20 nm in good solvent THF was calculated from the diffusion coefficient (Figure 4.5) obtained following a systematic dynamic light scattering study (details of the method found in Chapter 2). The overlap concentration c* of the H3A1 polymer in THF was estimated to be 0.03g/mL. The overlap concentration divided by the density of THF, multiplied by 100 results in 3% weight fraction

of H3A1 in THF. Moreover, according to the Flory theory, there is a universal power law dependence of polymer size R on the degree of polymerization (Colby and Rubinstein, 2003):

$$R \sim N^{\nu}$$
 4.2

The scaling exponent v is equivalent to 0.5 in a theta solvent (such as the PS linear chains) and 0.588 in a good solvent (THF solvent). Therefore, the radius of the H3A1 polymer in the PS mixture is equivalent approximately to 9.5 nm and the overlap concentration is equivalent to 0.3g of H3A1/mL PS mixture. Now, dividing this value by the density of PS results in a weight fraction or volume fraction of 29%. Moreover, in order to ensure that the H polymer chains are in fact truly diluted (no interpenetration of the chains) we chose to have a concentration of H3A1 polymer of 1.5%, 3% and 10% in the blend.



Figure 4.5: The linear fit of the diffusion constant of the H3A1 polymer in a good solvent THF (dilute concentration of 0.0126 wt%) at all values of q^2 results in a diffusion constant value of 2.2E-7 cm²/s.

4.2.2 Differential scanning calorimetry and temperature ramp test

All the details related to Differential Scanning Calorimetry (DSC) are explained in Chapter 2. DSC was performed in order to determine the glass transition temperature of the linear samples and blends of linear PS and H polymer H3A1. Below, Table 4.1 depicts the measured glass transition temperatures (T_g). The difference in glass transition temperature between the lowest M_w PS linear and the highest M_w PS sample corresponds to a horizontal shift in the frequency axis (due to a difference in respective entanglement times). In order to

compare all the linear and blend viscoelastic curves with respect to one another, it was necessary to horizontally shift the PS22k, the PS51k and the PS1M curves in order to have the same temperature difference between the reference of the linear viscoelastic curve and their respective glass transition temperatures. The higher M_w PS samples have a constant measured T_g value of 106±1°C. As expected, the barely entangled linear PS22k has a lower T_g of 103±1°C and a shift factor of 0.47 and PS51k has a T_g of 104±1°C and a shift factor of 0.6. In contrast, PS1M has a higher T_g value of 107±1°C and a shift factor of 1.3. The method used to obtain the shift factors was to shift the linear viscoelastic data in order to compare at the same (T_m - T_g) difference, taking the average value of 106°C as the reference $T_{g,a}$. For example, for PS22k, the T_g - $T_{g,a}$ difference corresponds to -3°C. Since our reference measuring temperature T_m is 130°C (ie the ref T of the TTS mastercurve), therefore, the PS22k data is shifted to 127°C.

Linear and blend PS	T _g (°C)
PS 22k	103±1
PS 51k	104±1
PS 129k10% H3A1	106±1
PS 185k	106±1
PS 185k10% H3A1	106±1
PS 1M	107±1

Table 4.1: Glass transition temperatures as obtained by DSC



Figure 4.6: DSC curves for linear samples PS22k, PS182k and PS1M and for blend samples PS182k10% H and 129k10% H

In addition to DSC, another method which was used to obtain the glass transition temperature is a dynamic temperature ramp test. This test is analogous to the commonly used Dynamic Mechanical Analysis (DMA) method. We performed a temperature ramp from 100°C to 70°C at a rate of 1°C/min. We assign the T_g of 82°C as the temperature at which we begin to have a decrease of G' and G'' due to the mobility of the chains. For this sample, the T-T_{g,a} is very large, -24°C and hence, the SAOS data of the PS5k has to be shifted to 106°C. The horizontal shift factor for this sample is very significant and corresponds to 6E-3.



Figure 4.7: Dynamic temperature ramp test for PS5k. Indicated by an arrow is the glass transition temperature T_g at 82°C.

4.2.3 Size exclusion chromatography

All the details concerning the Size Exclusion Chromatography (SEC) measurements are explained in Chapter 2. In Table 4.2, the weight average molecular weight values measured by SEC equipped with a refractive index (RI) detector for a select number of linear and blend samples are depicted. In a few cases, these M_w values are quite different than those which are provided by the manufacturing companies or synthetic chemists (Table 2.5). The last column in Table 4.2 indicates the % difference between the M_w values as given by the synthetic chemists and those determined independently by SEC analysis. The discrepancy between the M_w values could be due to the error and variability (different procedures employed in different locations) associated with SEC measurements. For all the PS samples listed in table 4.2, the PDI is still relatively low and the samples can still be considered to be monodisperse. The M_w value and PDI are input parameters in the tube model theories that we are currently using (TMA and BOB) and therefore, it is important to ensure the values are accurate as possible. TMA and BOB will be explained in more details in Chapter 4.3.

Linear PS	M _w (kg/mol)	PDI	% M _w difference
PS 22k	24.3	1.07	9%
PS 22k 10%	H3A1H: 550.4	1.105	
пзатп	PS 22k: 24.5	1.118	
PS 51k	63.3	1.08	22%
PS129k	121	1.15	6%
PS 185k	153	1.08	17%

Table 4.2: Weight average molecular weight values obtained with SEC equipped with RI detector

4.3 Description of computational tube-based models

The first computational model for predicting the linear rheology of blends of branched polymers was the "hierarchical model" (Larson, 2001). The original model was based on the Milner and McLeish model (Milner and McLeish, 1997) and it has been more recently updated to include refinements in tube model theory (Park et al., 2005) and can predict a larger variety of complex blend structures. More recently, (Das et al., 2006), developed a similar computational model nicknamed BOB (Branch-on-Branch) that predicts the linear rheology of branched structures. Both BOB and the hierarchical model are based on the tube model hierarchical framework and hence take into account all relaxation mechanisms such as arm retraction, CLF, DTD, reptation and CR-Rouse motion. There are quite a few discrepancies between the computational hierarchical model and BOB (Wang et al., 2010). One of the most important differences is observed in the treatment of the arm retraction mechanism. Contrary to BOB, the hierarchical model includes a heuristic treatment of branch collapse (Park et al., 2005).

4.3.1 BOB tube-based computational algorithm

In Table 4.3, we describe the main characteristic features associated with the BOB hierarchical computational algorithm. To summarize briefly, following a small step strain, a branched polymer will undergo a series of relaxation processes at different time scales. At

rates larger than τ_e , the free ends will retract towards the branch points by fluctuations (taking into account Milner and McLeish, 1997). After the branch point hopping process, additional frictional drag will be added to the local friction of the remaining unrelaxed segments attached to these free ends, thus resulting in a compound arm.

In addition, these free ends will also dilute the entanglements of the unrelaxed segments, with dilution exponent α =1 (Marrucci, 1985) except in the case of Constraint Release Rouse (Viovy et al., 1991; Milner et al., 1998). The DTD evolves with time, the resulting compound arm will further dilute the fixed segments (immobile segments trapped between branch points) closest to it and further form additional compound arms. When only 2 compound arms remain, they form an effective linear chain, reptation will occur in a thin tube (no DTD associated with reptation) mediated by slow thermal CR events on a timescale which is well separated from the retraction time.

Relaxation pathways	 Stress relaxation G(t) = G_{fast}(t)+G_{slow}(t) G_{fast}(t) at times faster than τ_e: Fast Rouse motion along the tube Redistribution of chain segments along the tube via longitudinal Rouse motion. G_{slow}(t): Escape of chain segments from the deformed tube. Timescale depends exponentially on the distance from the free ends of the chain. Relaxation of the tube itself via constraint release.
Arm retraction	 Entropic spring behavior for the curvilinear retraction, same as for star polymers (Milner and McLeish 1997) Hierachical relaxation, following arm retraction, dynamic tube dilution Z=Zφ^{-α}, φ is almost always equal to the unrelaxed fraction except in the case of CR-Rouse motion
Compound arm fluctuation	 Compound arm is one containing one or more localized drag points due to collapsed side arms. Compound arm retracts in the same way as a simple arm except with a different effective friction and potential. Modeled as a series of springs connected at the branch points.

Table 4.3: Characteristic features related to the treatment of the relaxation mechanisms in the BOB computational algorithm.

$\begin{array}{c} \text{Arm retraction} \\ \text{potential } U_{\text{eff}} \\ \text{and } \tau_{\text{late}} \end{array}$	- Numerical evaluation of Taylor expansion at each step	
Branch point friction	 Branch point takes hops of size pa at timescale τ_a where p² = 1/40 Tube diameter scaled at the timescale of arm retraction. 	
Dilution exponent α	- $\alpha = 1$, according to tube dilution theory the plateau modulus becomes $G_{dil} \sim G_0 \Phi^{1+\alpha}$	
Determination of M _e	- the entanglement molecular weight is determined by the following definition: $M_{e} = \frac{4\rho RT}{5G_{N}^{0}}$	
Reptation	 When only 2 arms remain unrelaxed, the chain becomes effectively linear. Friction from backbone proportional to its length and added to friction of collapsed arms. Reptation occurs in thin tube (no DTD since in most cases, no clear separation of time scales of blend components). Struglinsky-Graessley criterion and partial DTD not included in the model. Clear timescale separation of retraction time and reptation time. 	
CR-Rouse regime	- During supertube relaxation, the effective tube constraint of reptation and retraction is that of a thin tube.	

We consistently use the same BOB parameters ($M_e=14k$, $\tau_e=0.5s$, $G_N^0=192k$, $\alpha=1$, $p^2=1/40$) for all of our PS H, linear and blend samples at a temperature of 130°C. These values are consistent with other works (Kapnistos et al., 2005) when taking into account the horizontal and vertical shift factors associated with temperature differences.

4.3.2 Time marching algorithm model for H polymer analysis

Similarly to BOB, the TMA model is based on the tube concept and uses the same relaxation mechanisms as any tube-based model. However, a different molecular coordinate system is defined (van Ruymbeke et al., 2006; 2007). In particular, the relaxation of a polymer segment is followed hierarchically on a discretized time axis (τ_{xi} , where x_i corresponds to a normalized molecular segment) and can thus handle all relaxation processes in a simultaneous fashion. We consider for example an H polymer with two branches

attached to each end of a linear backbone with a defined molecular coordinate system depicted in Figure 4.8. The main difference from other tube models is that here, whereas the center of the molecule is of course the same (at $x_b=1$), one follows the relaxation continuously from $x_b=0$ to $x_b=1$, i.e., past $x_b=x_{brpt}$. Instead, the other tube models follow the relaxation of the branch from $x_{br}=1$ to x_{brpt} and then that of the backbone from $x_b=x_{brpt}$ to $x_b=1$. In doing so, the backbone relaxation encompasses the friction coming from the branch already and there is no need for adjusting the value of p^2 (which is set to 1) (van Ruymbeke et al., 2006; 2007; 2011).



Figure 4.8: H polymer molecular coordinate system. Two reference paths, the first from the end of the branches to the branch point and the second from the end of the branches to the middle of the backbone.

The faster relaxation modes (common to all linear and branched polymer systems) are the high-frequency Rouse modes which occur at time scales shorter than the entanglement time, before the chains have time to experience the tube. Additionally, longitudinal relaxation modes (Likhtman and McLeish, 2002) also occur at these early time scales and correspond to a redistribution of monomer reorientation along the tube, corresponding to 1/5 of the total early stress relaxation. At timescales larger than τ_e , the H polymer relaxation proceeds hierarchically and begins with the relaxation of the branches (arms). The ends of the branches, corresponding to $x_b=0$ relax first by end-point diffusion and at later times, the inner segments of the branches will proceed with an activated retraction which is exponentially suppressed towards the branch point ($x_b=x_{br,pt}=1$). This is analogous to the star polymer relaxation and involves an exponentially broad spectrum of CR-mediated relaxation times. After arm retraction, the backbone segments are free to move and will proceed to relax by two different fluctuations modes (van Ruymbeke et al., 2006). The first, involves equilibrium length fluctuations of the outer parts of the backbone (similar to star arms) that begin at the branch free ends ($x_b=0$) and end at the branch point ($x_b=x_{brpt}$) with the associated friction which originates from the monomeric friction of the chain itself. The second, also involves fluctuations which begin at the branch free ends ($x_b=0$) (even though the arms have relaxed they still have a non-zero equilibrium length) and terminate at the center of the backbone ($x_b=1$) and are associated with the enhanced friction (drag) produced by the relaxing arm segments.

The branch points are considered to be effective friction blobs following arm relaxation. Also, a delay time associated with the backbone relaxation due to the arm relaxation needs to be added to the Rouse segmental relaxation. Moreover, after the equilibrium length fluctuations of the outer and inner parts of the backbone, the extended backbone (similar to a 2 arm star) will undergo an activated retraction towards the center of the backbone. The reptation of the backbone will eventually take over as fluctuations will become exponentially slow. It will either occur in a skinny tube or in a fat tube depending on the extent of dilution. If the relaxation of the arms and backbone are well separated in time, the relaxed branches will act as a solvent and swell the backbone and full DTD (Watanabe, 2004; 2008; 2013) is applicable. In order to apply DTD, it becomes necessary to rescale the tube model parameters, ie the molecular weight between entanglements M_e , the equilibrium length L_{eq} and the tube diameter a as a function of the dynamic tube dilution of the unrelaxed fraction ϕ_{unr} :

$$M_e(t) = \frac{M_e(0)}{\phi_{uur}^{\alpha}}$$

$$4.3$$

$$L_{eq}(t) = L_{eq}(t)\phi_{unr}^{\alpha/2}$$

$$4.4$$

$$a(t) = \frac{a(0)}{\phi_{unr}^{\alpha/2}}$$
 4.5

Alternatively, the backbone can relax by a Rouse relaxation process (if the volume fraction of the arms is large enough as to completely dilute the backbone) taking into account only monomeric friction under the condition that the backbone is completely diluted by the arms.

Moreover, there are additional constraint release events to take into account when considering a mixture of the H polymer in a linear matrix. When the constraint release events associated with the linear chains are slow, the fastest motion available is that of a skinny tube subject to monomeric friction or alternatively, if the constraint release events are fast, the motion can occur along the fat tube, mediated by constraint-release events from the relaxed entangled segments.

The relaxation modulus G(t), based on Milner and McLeish theory (1997) can be considered as a sum of the survival probability p of every molecular segment, taking into account all relaxation processes (ie reptation, fluctuations and CR) and the renormalized values of the tube model parameters (due to DTD).

$$\frac{G(t)}{G_0^N} = \sum_i v_i \int_0^1 (p_{rept}(x_i, t), p_{fluct}(x_i, t), p_{CR}(x_i, t))$$
4.6

We consistently use the same TMA parameters ($M_e=14.8k$, $G_N^0=230k$, $\tau_e=0.5s$ and $\alpha=1$) for all of our PS linear and blend samples at a temperature of 130°C. Similary to the BOB parameters, these values are consistent with other works (Kapnistos et al., 2005) when taking into account the horizontal and vertical shift factors associated with temperature differences.

We use both the BOB and the TMA computational algorithm as a tool to model the linear rheology of the H, the linear and the blends of these in order to try to understand the effects of the environment (length of linear chains) on the entanglement dynamics of the model polymer. The use of different models provides the opportunity to show that the basic premises of tube models is right. The use of different models with the unique data sets offers the opportunity to test the assumptions and details that mark their differences.

Meanwhile, we discover the inherent limitations of the models. Moreover, we also compare the model predictions associated with both tube-based hierarchical models. Both models are excellent predictors of linear and star polymer linear viscoelasticity. The inherent problems arise when predicting the rheological response of more complex structures such as H, combs and the deficiencies become more pronounced with predictions of blends of these. The problem lies in the lack of understanding of CR (as explained in the Introduction) even for basic blends such as linear bidisperse blends or also in the context of complex hierarchical structures such as the H and comb polymer. In order to determine the relaxation times of the H polymer arms and backbone in our blend samples, we use the TMA model since there is an option to deconvolute the linear viscoelastic curve of the arms and backbone.

4.3.3 Value of tube model parameters: α and p^2

All molecular parameters for both TMA and BOB are determined self-consistently from the chemical characterization and from analysis of the linear rheology. The two exceptions are the dilation exponent α and the p² parameter related to the branch point friction. There is yet to be a clear agreement on the value of the dilation exponent α and the p² parameter. Recently, there has been significant research progress towards the determination of these parameters self-consistently (van Ruymbeke et al., 2012; Bacova et al., 2014)

The dilution exponent of the plateau modulus associated with static dilution ie the dilution associated with a polymer dissolved in a theta solvent (no excluded volume interactions) is α =4/3. (Colby and Rubinstein, 1990; Colby et al., 1992) determined this scaling by considering that the entanglement constraints in polymer solutions are composed of a fixed number of intermolecular binary contacts. The density of binary contacts in a theta solvent scales as c² and the distance between binary contacts scales as c^{-2/3}. Moreover, the tube diameter a scales as c^{-2/3}. The corresponding volume is a sphere a³ filled with blobs of diameter ξ . The number of blobs are calculated by assuming a random walk of blobs. The length scale of the blob scales as c^{-3/4}. Finally, the plateau modulus can be defined by the following expression as G $\approx kT/a^2\xi$ which finally implies that G~c^{7/3} and α =4/3.

Many experimental works using tube-based models have shown better viscoelastic data prediction agreement using a dilution parameter α =1 rather than α =4/3 (Park and Larson, 2003; Ruymbeke et al., 2006). In all our model fittings, we therefore consistently use a dilution parameter of α =1 although it could be that this is an oversimplification. However, the advantage of consistently using the same value, which is independent of architecture, monomer chemistry and polydispersity of the polymer sample is that we are not creating a bias. Some evidence suggests that the value of the dilution exponent could be model dependent. For example, in the hierarchical model of Larson and colleagues (Park and Larson, 2005), α =4/3 is considered to be the best fit parameter, whereas in the BOB (Das et al., 2006) and TMA (Ruymbeke et al. 2006) computational algorithm, a value of α =1 is

recommended. Moreover, the analysis of linear viscoelastic data also reveals the uncertainty related to the dilution exponent as well as the difficulty of extracting the dilution parameter from rheological data. In the case of well separated relaxation times of entangled branched segments, it is possible to calculate with linear viscoelastic data, the experimental value of the dilution exponent. Utilizing the data for well-defined monodisperse combs, (Kapnistos et al., 2006) plotted the ratio of the second rubber plateau modulus (representing the dynamically diluted backbone) and the global plateau modulus versus the volume fraction of the backbone and found that the data scattered between $\alpha=1$ and $\alpha=4/3$ (Kapnistos et al., 2006). This may suggest that the dilution exponent should be chosen on a case by case basis. Following their study of the dielectric spectroscopy and the linear viscoelasticity of bidisperse linear blends, (van Ruymbeke et al., 2012) determined that both dilution exponents should be used at different time scales. More specifically, at short times, a dilution exponent of $\alpha=1$ is most appropriate whereas at long times a recommended dilution exponent of $\alpha = 4/3$ is required. The authors suggest that the exponent $\alpha = 4/3$ is achieved only after tension equilibration (an additional relaxation process) and conformational adjustment of the long chains activated by the short chains. Additionally, there is a transition zone, where the effective dilution exponent corresponds to a value between 1 and 4/3.

Moreover, there is also uncertainty related to the value of p^2 , the dimensionless parameter related to the hopping distance of a branch point relative to the tube diameter. Similarly to the dilution exponent, p^2 also appears to be model dependent since in the Hierarchical model (Park et al., 2005), the recommended value is $p^2=1/12$ (Das et al., 2006), in BOB, it is 1/40 and in the TMA model (van Ruymbeke et al., 2006) $p^2=1$. There are many unresolved issues related to branch point hopping, first, the length scale associated with hops. By definition, the hopping distance is p times the tube diameter. However, one fundamental question is whether to assume hopping occurs in a thin or in a fat tube. (McLeish et al., 1999) assumed that hopping occurred in a dilated tube and determined that a value of $1/p^2=12$ provided the best fit for rheological data on H polymers. Another fundamental question is related to the direction of the hopping motion, more specifically, should the branch points be considered to occur along the thin tube contour or fat tube contour. Different versions of hierarchical tube based-models have incorporated different assumptions about branch point hopping length and direction (Frischknecht et al., 2002; Daniels et al., 2001; Inkson et al., 2006; Kapnistos et al., 2005; Kirkwood et al., 2009; McLeish et al., 1999; Park et al., 2006) and consequently, a broad range of p^2 values has been reported in the literature. Recently, (Bacova et al., 2014), systematically investigated very different macromolecular architectures and determined that the most consistent description of p^2 can only be achieved by considering both the backbone friction and hopping in the dilated tube.

There is evidence that suggests that perhaps the value of p^2 is dependent on the polymer architecture and the length of the branches for complex branched structures. For example, (Frischknecht et al., 2002) varied the value of p^2 from ¹/₄ to 1/60 in order to quantitatively fit the linear viscoelastic data of asymmetric three arms stars and determined that its value was dependent on the length of the arms and their associated frictional drag. The value of p^2 used for intermediate-short arms were shown to be similar to those needed for H polymers, whereas the small values of p^2 for the short arms (even for unentangled arms) indicate a larger than predicted amount of drag.

It is possible to calculate p^2 for complex branched systems taking into account some already developed theoretical equations. At the timescale of branch relaxation, the branch points perform diffusive steps (hops) along the tube contour with a diffusivity which is proportional to the p^2 parameter and the tube diameter a^2 (either original or dilated). Moreover, the friction for branched polymer systems can also be assumed to be dominated by the arms.

$$D = \frac{p^2 a^2}{2\tau_a q} \tag{4.6}$$

For a linear chain, the entanglement time is calculated by equation 4.7. Note for more complex architectures and blends, the entanglement time will also need to be rescaled due to DTD. For these cases, an effective entanglement segment relaxation time $\tau_{e,dil}$ is calculated.

$$\tau_{e} = \frac{\zeta N_{e}^{2} b^{2}}{3 \pi^{2} k_{B} T}$$
4.7

Where N_e is the number of monomers per entanglement segment, ζ is the monomeric friction constant and b is the Kuhn segment length. Also, the diffusivity (due to only to monomeric

friction) can be calculated by expression 4.8. However, for more complex architectures and blends, the diffusivity may also need to be adjusted to take into account CR events.

$$D = \frac{k_B T}{(\zeta Z N_e)}$$

$$4.8$$

Moreover, since the chains are Gaussian, the following expression for tube diameter applies:

$$a_0^2 = N_e b^2 \tag{4.9}$$

By combining equations 4.7 to 4.9 and by considering the effect of dilution on both the entanglement segment and the number of entanglements, the expression for the diffusivity results in the following expression:

$$D = \frac{a^2}{3\pi^2 \tau_{e,dil} Z_{dil}}$$

$$4.10$$

Now, by combining equations 4.6 and 4.10, it becomes possible to calculate p^2 simply by taking into account the arm relaxation time, the entanglement spacing and equilibration time.

$$p^{2} = \frac{2\tau_{a}q}{3\pi^{2}\tau_{e,dil}Z_{dil}}$$
 4.11

All the parameters in equation 4.11 can be calculated from the linear rheology curve. The determination of arm relaxation time can be tricky. In an effort to identify the arm relaxation time for complex branched polymers, three different indirect methods can be used:

1. Analysis of the tube survival probabilities provided by the BoB computational algorithm.

2. Analysis of the intermediate peak in the frequency dependence of the experimental loss tangent $\tan \delta = G''(\omega)/G'(\omega)$

3. Defining the time at which $G(t) = G_N^0 \phi_{unr}^2$, where G(t) and G_e are the experimental stress relaxation function and entanglement modulus, respectively. The quantity ϕ_{unr} is the fraction of unrelaxed material at the timescale of the arm relaxation time.

Moreover, the relaxation time of the arms for complex branched systems can be also directly determined from hierarchical models such as TMA where the deconvolution of the arm and backbone linear viscoelastic curves is achievable. We apply all direct and indirect methods when applicable for the determination of relaxation times associated with the H, combs and blends of these.

4.4 Linear rheology results of H3A1 polymer

In Figure 4.9, the linear viscolastic data of the H3A1 polymer measured recently are compared with the linear viscoelastic data of (Roovers, 1981). The agreement between the two curves in addition to the TGIC characterization, demonstrates that the H polymer is still of good quality and monodisperse despite the long period of storage. Moreover, in Figure 4.10, the linear rheology experimental data of the H3A1 polymer are compared to fitted predictions using the software program BOB (Branch on Branch rheology) and the TMA (Time Marching Algorithm).



Figure 4.9: Comparison of H3A1 G' and G'' experimental data recently obtained and the data obtained by (Roovers, 1981)

The main relaxation features of the H3A1 polymer are directly observed in the rheological data (indicated by arrows in Figure 4.9). The hierarchical relaxation of the H3A1 polymer is clearly observable in the loss modulus G'' data. The broad G'' shoulder is representative of the exponentially slow arm time retraction and the peak in G'' is representative of the backbone late-time relaxation. Due to the large number of entanglements

in the arms, the backbone is heavily diluted by the arms, the backbone chains are not mutually entangled and the characteristic Rouse relaxation G'~G''~ $\omega^{1/2}$ is clearly seen by the $\frac{1}{2}$ slope (Figure 4.11 (a)) just before the terminal relaxation. The volume fraction of the backbone is 19% and the number of entanglements of the backbone is 8±1 (M_e=14-18). Therefore if we consider the theory of DTD (although this is an approximation due to coupled arm and backbone relaxation time) and hence, the number of entanglements of the dynamically diluted backbone is equivalent to $Z_{bdil} = Z_b \phi_b^{\alpha}$. The backbone would then have one effective entanglement after the arms full relax.

Both fits based on tube model theories capture reasonably well the linear viscoelastic behavior of the well entangled H polymer (Figure 4.10 and 4.11) in both the low (Figure 4.11(a)) and high frequency (Figure 4.11(b)) region. However, there are clear discrepancies between the fits and the experimental data for both models. More specifically, the TMA model captures the data quite well in the high frequency region although not perfectly (Figure 4.11(b)), however, the $\frac{1}{2}$ Rouse slope is extended and consequently, the crossover relaxation time predicted is slower (Figure 4.11(a)). The TMA model predicts a slower relaxation time of the inner H polymer backbone since the transition from retraction of the arms to the relaxation of the backbone by the Rouse process is not well defined. In effect, this a limitation in all tube-based molecular models. Contrarily, BOB predicts accurately the crossover relaxation time τ_d , however, the plateau modulus is under-predicted and the $\frac{1}{2}$ intermediate slope is not captured. The under-prediction of the plateau modulus is an inherent limitation of the Milner-McLeish theory (1997) which has been incorporated in the BOB algorithm.



Figure 4.10: Comparison of H3A1 G' and G'' experimental data with BOB and TMA model fits.



Figure 4.11: The H3A1 G' and G'' experimental data, the BOB and TMA model fits in (a) the low frequency region where the ½ Rouse slope is clearly visible and (b) high frequency region

One of the goals of our study is to clearly identify the arm relaxation of the H polymer alone and in the blends. As depicted in the linear rheology data of Figure 4.10, distinguishing one single relaxation time is not clear since the arm relaxation time is very broad and coupled to the backbone relaxation. In effect, the arm relaxation time for an H polymer is even broader than for a star polymer with the same number of arms since the arm retraction is delayed further by the presence of the backbone (which acts similarly to a permanent network). Moreover, we discover that the relaxation behavior of the H3A1 polymer can be compared to a blend of a long linear polymer of 2.5M ($v_1=0.19$) and a 4 arm star polymer $(v_2=0.81)$ with volume fractions associated with respective H3A1 polymer backbone and arms. This is quite evident by the positive agreement of the BOB fit of the H3A1 polymer moduli compared with the BOB fit of the linear and star mixture and the H3A1 experimental data. In the case of a monodisperse star, the arm relaxation time is exponentially dependent on Za, the number of entanglements of each arm. However, for an H polymer, both Za (number of entanglements of each arm) and φ_a (volume fraction of arms) are included in the exponent of the longest relaxation time of the arm retractions (McLeish et al. 1999) (equation 4.12).
$$\tau_{a} \approx \exp\left[\frac{15Z_{a}}{4} \frac{1 - (1 - \phi_{a})^{\alpha+1}(1 + (1 + \alpha)\phi_{a})}{(1 + \alpha)(2 + \alpha)\phi_{a}^{2}}\right]$$
4.12
$$\left(\frac{0}{9} \frac{10^{4}}{9} \frac{10^{4}}{10^{4}} \frac{10^{2}}{(1 + \alpha)(2 + \alpha)\phi_{a}^{2}} \right)$$

$$\left(\frac{0}{9} \frac{10^{4}}{10^{4}} \frac{10^{2}}{10^{4}} \frac{10^{2}}{10^{6}} \frac{10^{4}}{10^{6}} \frac{10^{2}}{10^{6}} \frac{10^{6}}{10^{4}} \frac{10^{2}}{10^{6}} \frac{10^{6}}{10^{6}} \frac{10^{4}}{10^{6}} \frac{10^{2}}{10^{6}} \frac{10^{6}}{10^{6}} \frac{10^{4}}{10^{2}} \frac{10^{2}}{10^{6}} \frac{10^{6}}{10^{6}} \frac{10^{6}}{1$$

Figure 4.12: Comparison of the H3A1 G'(ω) and G''(ω) experimental data with the respective BOB fit of the H3A1 polymer and a blend of linear 2.5M (19 vol% same backbone fraction as H3A1) and a 4 arm star polymer (81 vol% same arm fraction as H3A1).

4.5 Determination of arm and backbone relaxation time of H

The most reliable and straight-forward method to obtain respective arm and backbone relaxation times is with the use of a molecular model such as TMA where the arm and backbone linear viscoelastic curves are deconvoluted. As already presented in Chapter 3 and shown again in Figure 4.13, the TMA model fit of the H3A1 storage $G'(\omega)$ and loss modulus $G''(\omega)$ data was decomposed into two curves, one which is representative of the arm time retraction process and the other, the dynamically diluted backbone relaxation.



Figure 4.13: symbols: \bigcirc G'(ω) storage and \bullet G''(ω) loss modulus experimental data of H3A1 at 130°C, solid black lines: G' TMA modelled data and dashed lines: G' TMA modelled data and the respective arm and backbone curves (grey lines). The crossover time of the arms τ_a and crossover time of the backbone τ_b corresponds to the inverse of the crossover frequency indicated by the dashed arrows.

In addition to the low ω crossover time τ_d , the longest relaxation time τ_0 (Graessley, 2008) was determined. This was deemed necessary since there is one or more additional relaxation mode which occur after the crossover time associated with complex branched polymers and blends of these. This is most evident with further examination of the H3A1 SAOS data, where the backbone relaxation τ_b is clearly slower than the crossover relaxation time τ_d . Moreover, there is a clear discrepancy between the crossover times and the longest relaxation times for each respective component (ie arm, backbone or global H) (Table 4.4).

The values of the longest relaxation time τ_0 are determined by the following expression:

$$\tau_{0} = \eta_{0} J_{0} = \eta_{0} \frac{1}{\eta_{0}^{2}} \lim_{\omega \to 0} \frac{G'}{\omega^{2}} = \frac{\lim_{\omega \to 0} (G'/\omega^{2})}{\lim_{\omega \to 0} (G''/\omega)}$$
4.13

The longest relaxation times τ_o , the arm relaxation times τ_a and crossover relaxation times τ_d associated with both the experimental data and the corresponding TMA model fit are presented in Table 4.4.

Relaxation times	H3A1 data ¹	H3A1 TMA model ²
$\tau_d(s)$	2E5	1E6
$\tau_0(s)$	1.8E6	4.9E6
τ _d arms (s)		1E4
$\tau_0 \operatorname{arms}(s)$		3.2E4
τ_d backbone (s)		1.6E6
τ_d backbone (s)		5.8E6

Table 4.4: Comparison of arm relaxation times τ_a , longest relaxation times τ_0 and crossover relaxation times τ_d of the experimental data¹ and TMA model²

Moreover, in an effort to try to identify the respective arm and backbone relaxation times of the H3A1 polymer by utilizing only the linear rheological data, several other indirect methods are evaluated. The first method involves an identification of a range of arm relaxation times representative of the exponentially broad arm relaxation times. We model a star polymer with the same molecular parameters as the H polymer, namely 4 arms, M_a =132k and PDI=1.1 with the use of BOB computational algorithm (Figure 4.14). The initial relaxation time of the H polymer arms is determined as the terminal relaxation of the star (inverse of crossover frequency), a value of 1E4s. Moreover, the terminal relaxation time of the arms corresponds to the inverse crossover frequency of the H polymer, a value of 2E5s. Also, the backbone relaxation time can be approximated as the inverse frequency at the G" peak, a value of 1.3E6s.

The experimental stress relaxation modulus G(t), can also serve as an important tool to extract characteristic relaxation times. In Figure 4.14, the modulus of the H3A1H polymer is compared with the modulus of an equivalent linear polymer (half the M_w of the H) and a 4 arm star with the same molecular characteristics as the arms of the H polymer. At short time scales, the G(t) response is associated with Rouse and longitudinal modes, at intermediate times, the shoulder is representative of the arm relaxation and the sharp drop in modulus is due to backbone relaxation. To determine the final arm retraction time, first, we calculate the remaining volume fraction after the arms have relaxed, which is approximately equal to the volume fraction of backbone φ_b . At this time, the relaxation modulus G(t) should equal, approximately, $G_N \varphi_b^2$ assuming full DTD (ie that the arms should be taken as a solvent) and a dilution exponent of α =1. Note that this is just an approximation since full DTD is not applicable due to the coupled arm and backbone relaxation times. For the PS H polymer,

 G_N =2E5 Pa and φ_b is equivalent to 0.19. Therefore at a relaxation time G(t) corresponding to 7200 Pa, we determine an approximate relaxation time for the arms of 3E5s.



Figure 4.14: Stress relaxation modulus G(t) of H3A1 polymer, BOB fit of G(t) of star with same M_a and G(t) of a linear polymer with M_w equivalent to half of the H polymer M_w

Additionally, another method of estimation of arm retraction time of complex branched polymers is the analysis of the tube survival probabilities $\Phi(t)$ provided by the BOB computational algorithm. We estimate that the arm relaxation time τ_a as the time at which $\Phi(\tau_a) = \Phi_{unr}$, with $\varphi_{unr} = \varphi_b = 1 - \varphi_a$ In Figure 4.15, the un-relaxed fraction of H3A1 polymer is plotted versus time. We identify the arm relaxation time after the full relaxation of the arms at $\varphi_b=0.19$ as 3.4E5s.



Figure 4.15: Plot of BOB prediction of unrelaxed fraction of H31A polymer versus time. The arm relaxation time at a $\varphi_b=0.19$ is indicated by the dotted line.

An additional method which is used in order to better resolve the relaxation times associated with both the H polymer arms and backbone is to transform the dynamic moduli $G'(\omega)$ and $G''(\omega)$ into a continuous relaxation time spectrum H(t). Two software programs, Orchestrator and NLREG (non-linear-regularization) were used to perform this conversion. When the relaxation spectrum H(t) is multiplied by time and plotted versus time, two relaxation peaks appear which correspond to the respective arm and backbone distribution of relaxation times (Figure 4.16). Although the area under the peak is not the same for the plots generated by using NLREG in comparison to Orchestrator, the time at which the peaks appear is exactly the same. We determine that the small early peak corresponds to an average arm relaxation time of 6E4 s and another much larger peak associated with the backbone relaxation time at 1E6 s. This method also allows an extraction of a range of arm relaxation times which correspond to the peak (1E4-1.5E5s).



Figure 4.16: Plot of relaxation spectrum H(t) multiplied by time versus time . The two characteristic peaks which appear, the first corresponding to the average arm relaxation time and the second, to the backbone relaxation time.

In Table 4.5, a summary is depicted of the different graphical methods used to obtain the characteristic relaxation times associated with the H3A1 polymer hierarchical relaxation. Since the arm relaxation is exponentially broad, there is a time scale (~1 decade long) associated with its terminal relaxation, more specifically from approximately 1E4s to 3E5s. The backbone relaxation time is approximately 1E6s and a good convergence is found with all methods used.

Table 4.5: Comparison of different graphical methods used in order to obtain characteristic H3A1H polymer arm and backbone relaxation times.

Methods	$\tau_{a}(s)$	$\tau_{b}(s)$
Comparison of star relax time (range defined)	1E4 – 2E5	
Survival probability (BOB)	3.4E5	
Defining the time at which $G(t) = G_N^0 \phi_{unr}^2$	3E5	
Transformation to H spectrum (range defined)	1E4-1.5E5	1E6
Peak in G''		1.3E6
Eta'' plot		1E6

4.6 Determination of arm retraction time of comb polymer

Contrary to the H polymer, the terminal relaxation times of the arm and backbone of the PI254 comb differ by several orders of magnitude and hence it becomes more straightforward to separate the two relaxation processes using only linear rheology. Again, as a first estimation, we utilize the tube survival probability, an output of the BOB computational algorithm. In this case, the expression for the φ_{unr} at the timescale of the arm retraction is equal to the following, taking into account the contribution of arms (Kapnistos et al., 2005):

$$\phi_{unr} = 1 - (\phi_a + \phi_c) = 1 - \frac{qM_a + 2M_b / (q+1)}{qM_a + M_b}$$

$$4.14$$

where φ_a and φ_c are the volume fraction of the arms and dangling backbone ends, respectively. The values of M_a and M_b correspond to the arm and backbone molar mass respectively. In addition, we determine a lower bound τ_a at which the fraction of unrelaxed material is given by $\varphi_{unr}=1-\varphi_a$. Both arm time estimations are indicated by arrows in the Figure below. Also, for comparison, the experimental tanð plot versus frequency is included in the same graph. The analysis of the intermediate peak in the tanð frequency domain is another method which can be utilized to estimate the arm retraction time. A Gaussian function can be fit to the loss angle tanð versus frequency curve and the inverse frequency of the fitted peak is taken as the corresponding τ_a . Moreover, the inverse frequency at which the zero value of the derivative of the same curve is also computed to obtain the arm retraction time. An arrow indicating the retraction time corresponding to the tanð peak is also shown in the figure below. From the

combination of these methods, a range of arm retraction times between 0.06s and 0.6s is obtained.



Figure 4.17: Unrelaxed volume fraction $\Phi(t)$ (solid line) obtained from BOB computational algorithm and experimental tan δ (dashed line) as a function of time. The arrows indicate the lower bound $\Phi(\tau_{al})=1-\varphi_a$ and the higher bound $\Phi(\tau_{ah})=1-(\varphi_a+\varphi_C)$

4.7 Linear PS SAOS

The main rationale for the measurement of linear viscoelastic data for the linear PS and PI series is for use as a reference for comparison with the blends. Moreover, the timescale separation between the linear and probe arm and backbone relaxation is critically important in the assessment of constraint release. As was demonstrated by experimental studies on bidisperse linear blends (Struglinsky and Graessley, 1985; Watanabe et al., 2013), CR leads to an acceleration of probe relaxation time when the probe time is slower than the matrix relaxation time (since the matrix acts to dilute the effective number of entanglements) or when the reverse is true, a suppression of probe relaxation time occurs (since the matrix acts as a type of temporary network and tube probe motion is frozen). Figure 4.18 depicts the linear viscoelastic mastercurves of the linear monodisperse PS matrix (5k, 22k, 51k, 129k, 182k, 483k and 1M). The main relaxation features of the linear polymers are directly observed in the rheological data. The G'(ω) and G''(ω) moduli for the PS linear 5k and 22k, whose M_w is below the critical M_c of PS, follow a characteristic Rouse relaxation. The other well-entangled PS linear samples have a characteristic plateau modulus (which increases with increasing M_w) and a characteristic G'=G'' crossover relaxation time at $\tau_d=1/\omega_c$ (since the

linear samples are monodisperse). In addition, the characteristic terminal slopes of 2 (G' $\sim \omega^2$) and 1 (G' $\sim \omega$) are observed. The superposition of the plateau modulus and the G' and G'' moduli in the high frequency region demonstrates that the microstructure is consistent in all the PS samples. Moreover, as mentioned previously, the linear rheology curves of the two unentangled PS samples (PS22k and PS51k), were shifted horizontally based on respective differences in glass transition temperatures. According to our earlier assessment of H3A1 arm relaxation times, it is evident that the terminal relaxation of all the linear samples except for the PS1M occurs earlier than the H arm time retraction. Moreover, PS483k has a crossover relaxation time τ_d which is slightly faster than the H3A1 arm relaxation time whereas PS1M has a crossover relaxation time which is similar to the crossover relaxation of the H3A1 polymer. In Figure 4.19, we present a schematic relaxation time scale.



Figure 4.18: linear viscoelastic mastercurves of the linear monodisperse PS (5k, 22k, 51k, 129k, 182k, 483k and 1M) samples. The moduli of the vertically shifted H3A1 polymer (10x) is also shown for comparison.



Figure 4.19: Relaxation time scale which follows the order of relaxation of the blend components. The unentangled linear chains have the fastest relaxation by a Rouse process. All the PS monodisperse linear samples in our study relax by CLF/reptation at an earlier time than the H polymer arms except for the PS1M. The H3A1 polymer backbone has the slowest relaxation.

We use three different molecular models, BOB (Das et al., 2006), TMA (Ruymbeke et al., 2006) and (Likhtman and McLeish, 2002) to fit the PS linear rheology data (Figure 4.20). In all models, the dilution parameter $\alpha=1$ is used and the relaxation time of each entanglement spacing is kept constant at $\tau_e=0.5$ s. In addition, the M_e values are quite similar for all three models taking into account the definition of Me with 4/5 pre-factor (Me=14kg/mol in BOB and M_e=14.8kg/mol in TMA) and without pre-factor (M_e=17kg/mol in Likhtman and McLeish). All the models are based on the tube-model concept. In addition, the theory of Likhtman and McLeish is incorporated into the BOB computational algorithm. The difference between the two models is the p^2 hopping parameter which is absent in the Likhtman and McLeish model and instead, the former includes constraint release parameter c_y linked to the number of chains needed to create an entanglement. Moreover, incorporated in the BOB algorithm, there is an option to include the polydispersity index associated with each of the linear samples. The fits are satisfactory in most cases except for the linear PS51k, where all three models fail to fit the data. This is related to the inherent problem of all tubebased models to predict the rheology of chain lengths which are approximately 2-4 Me. The problem is linked to an overlap between Rouse and reptation dynamics for short chains. The BOB fits all show a lower G" minimum in comparison to the experimental data and to the

other model fits. A higher PDI value incorporated in BOB would reduce this G'' value and provide for a better fit. The lower G'' minimum in comparison to the experimental data is also observed in the other two models. This could also be linked to the problems of the linear PS samples that have a higher PDI than what is reported by the manufacturers. The PS1M fits are also not perfect due most likely to the rheological limitations associated with its measurement and a higher PDI compared to the other samples. The PS1M G'' slope (located between the minimum of G'' and the crossover frequency) is approximately ¹/₂ for the fits and closer to ¹/₄ for the experimental data, indicating a higher polydispersity.



Figure 4.20: The PS linear data is modelled with a) Likhtman and McLeish 2002 b) TMA (Ruymbeke et al., 2006) and c) BOB (Das et al., 2006). The circles correspond to experimental data and the lines to model fits. The linear samples relax in order of chain length, PS5k (dark

grey), PS22k (brown), PS51k (red), PS129k (light grey), PS185k (green), PS483k (blue) and PS1M (orange)

4.8 Linear PI oscillatory rheology results

Figure 4.21 depicts the linear viscoelastic mastercurves of the linear monodisperse PI (22k, 96k and 1.5M) and the vertically shifted PI254k comb. Due to the well separated comb arm and backbone relaxation of the PI254k comb, there are two visible G' moduli, the first, corresponding to the global plateau modulus and the second, to the dynamically diluted plateau modulus. In addition, a peak in G'' representative of the terminal relaxation time of the comb arms is easily distinguishable. The relaxation of the PI22k by CLF/reptation occurs before the arm retraction of the comb arms whereas the relaxation of the PI96k occurs between the comb arm and backbone relaxation. The PI 1.5M has a slow relaxation due to the higher number of entanglements and relaxes after the comb backbone. A graphical representation of hierarchical relaxation time scale of each of the monodisperse components is depicted in Figure 4.22.



Figure 4.21: Linear viscoelastic mastercurves of the linear monodisperse PI (22k, 96k and 1.5M) samples. The moduli of the vertically shifted PI254k comb is also shown for comparison.



Figure 4.22: Relaxation time scale which follows the order of relaxation of the PI blend components.

A consistent set of parameters are used to fit the PI linear rheology data (Figure 4.23) by both BOB (Das et al., 2006) and (Likhtman and McLeish, 2002) model. The parameters determined using BOB and Likhtman and McLeish model are τ_e =1.3E-5s and M_e=4k and τ_e =1.5E-5s and M_e=4.8k respectively. The fits although not perfect are quite reasonable in all cases.



Figure 4.23: The monodisperse linear PI storage G'(ω) and loss modulus G''(ω) data is compared with two model fits, BOB (Das et al., 2006) (above) and (Likhtman and McLeish, 2002) (below). The circles correspond to experimental data and the lines to the model fits. The linear samples relax in order of chain length, PI22k (red), PI96k (black) and PI1.5M (blue).

4.9 Linear and dilute H PS mixtures oscillatory results

Figure 4.24 depicts the linear viscoelastic mastercurves of the 10% by volume fraction of the H3A1 and 90% by volume fraction of a set of linear monodisperse samples. Due to the small amount of H polymer in the blend, its characteristic rheological features are overshadowed by the relaxation of the linear polymer. The linear samples which have the highest ratio of their crossover relaxation time versus the crossover relaxation time of the

H3A1 polymer, demonstrate the strongest effect of the H polymer response on their G' and/or their G'' data. As depicted in Figure 4.24, the PS 22k and PS 51k mixtures have a noticeably different G'(ω) and G''(ω) moduli compared to the linear monodisperse matrix. The H polymer relaxation feature in the PS 51k, PS129k and PS182k mixtures is seen as a small transition region in the storage G' moduli at low frequencies (Figure 4.24). The lower G'' slope (in the region between the minimum and crossover G'') of the mixtures of H3A1 with the higher M_w samples (PS483k and PS1M) is also due to H polymer response. The BOB fits are plotted in Figure 4.25. For the mixtures with the high M_w linear chains, the BOB fits match quite well except for the lower estimated plateau modulus. In the case of the PS182k mixture, the fit is satisfactory except for the overprediction of the second, diluted plateau modulus. The BOB model seems to underpredict the dilution effect from the linear chains. The overall BOB fit for the mixture with the barely entangled chains, the PS51k is poor, but this is a limitation which is consistent amongst all tube models since they consider that the chains are composed of at least a few entanglements.



Figure 4.24: linear viscoelastic mastercurves of 10% vol.fr. H3A1 blended with linear PS of varying M_w (5k, 22k, 51k, 129k, 182k, 483k and 1M) samples. The storage modulus data are represented by open circles and the loss modulus data by closed circles.



Figure 4.25: BOB fits (solid lines) of the 10% H3A1 and 90% linear PS mixtures (circles) of varying M_w (51k, 182k, 483k and 1M).

4.10 Linear and dilute comb polymer blend oscillatory results

Figure 4.26 displays the linear viscoelastic mastercurves of the 10% by volume fraction of the PI254k comb and 90% by volume fraction of the linear monodisperse samples. Due to the small amount of comb polymer in the blend, its characteristic rheological features are overshadowed by the relaxation of the linear polymer. The comb polymer response is most evident in the PI22k blend G' curve where an extra relaxation process occurring after the relaxation of the linear PI22k is clearly visible (shown in the Figure below with an arrow). A small transition region is also visible in the G' of the PI96k blend, however, it is less obvious. Moreover, the PI1.5M blend has a G'' minimum which extends one decade. This is contrary to the monodisperse linear PI1.5M which has a much more sharp G" minimum. This difference can be attributed to the additional comb arm retraction process which occurs at the same frequency as the G" minimum. The experimental data is plotted alongside the theoretical predictions of BOB. Interestingly, the fit associated with the PI1.5M is satisfactory, while the other two fits are not as successful at capturing the data. The BOB fit for the PI96k blend matches well until reaching a low frequency value of 0.1 rad/s. The poor fit at the low frequency region indicates that the BOB model overpredicts the response associated with the comb backbone relaxation, indicating perhaps the extent of the dilution of the backbone is not taken into account. In the case of the PI22k blend, BOB does not match the experimental SAOS data well at both high and low frequency time scales. The relaxation predicted is at least two decades slower than the experimental data.



Figure 4.26: linear viscoelastic mastercurves (circles) of the 10% by vol.fraction of PI254k comb blended with linear PS of varying M_w (22k, 96k and 1.5M) samples. Plotted alongside the experimental data are the BOB fits (solid lines).

4.11 Discussion: dilution of H in short linear chains

We first investigate the relaxation dynamics of binary mixtures consisting of a dilute amount of H polymer (probe) in a 'sea' of short linear chains (matrix), more specifically PS linear 5k (unentangled) and PS linear 22k (barely entangled, ~1 entanglement).

When short linear chains are added to a dilute amount of H polymer, three global hierarchical relaxation processes occur at different time scales. The short linear chains are the first to fully relax at short time scales by Rouse relaxation, the H polymer arms will retract by fluctuations at short and intermediate time scales mediated by CR events and finally the unentangled backbone will relax immediately after the arms by Rouse relaxation with a strong solvent effect (due to static dilution and dynamic tube dilation). A schematic illustration is depicted in Figure 4.27. These three global relaxation processes do not occur in isolation, there is a mutual interdependence between all three of these relaxation processes. This mutual interdependence becomes more pronounced, the greater the overlap of these

relaxation processes. In the case of our H polymer blends, these three relaxation processes are not well-separated in time and hence their relaxation times are interrelated. As mentioned previously, the H polymer arm entanglements will dilute the backbone entanglements by DTD. The added influence of the short linear chains on the other two relaxation processes is a further static dilution of both the arm and backbone entanglements. In both static dilution and dynamic tube dilation, there is a dilution of the modulus and an apparent $M_e \sim \phi_{\mu r}^{\alpha}$. Moreover, DTD is a time-dependent CR process associated with an increase of tube diameter (reduction of effective entanglements) at short and intermediate time scales which slows down the overall relaxation, whereas static dilution occurs on short time scales and speeds up the overall relaxation. The H3A1 backbone is therefore diluted twice, first by the static dilution associated with the short linear chains and second by DTD associated with the H polymer arms. Hence the number of entanglements of the backbone after linear and H polymer relaxation is equivalent to $Z_{b,dil} = Z_b \phi_H^{\alpha} \phi_b^{\alpha}$ and therefore fewer than 0.1 entanglements remain (assuming vol. fraction of H between 1.5 and 10%) and the backbone can be considered to be unentangled and its terminal relaxation is defined by a Rouse process mediated by CR events.



Figure 4.27: Schematic depiction of the hierarchical relaxation process associated with the short linear chains PS5k or PS22k blended with the H3A1 polymer. The short chains will relax by a fast Rouse relaxation. They will then act as solvent for the early time τ_{early} H polymer arm fluctuations. The solvent and arms will then dilute the backbone, which willremain unentangled, and will relax quickly with a strong solvent effect.

The expression for G(t) is a combination of these two dilution processes which occur at different time scales. The G(t) is a function of the fraction of unrelaxed polymer after occurrence of these relaxation processes and can be defined by the following expression:

$$G(t) = G_0^N \varphi_{Rouse}^{\alpha} \varphi_{DTD}^{\alpha} = G_0^N \varphi_H^{\alpha} \varphi_b^{\alpha}$$

$$4.14$$

The storage modulus G' and loss modulus G'' of linear PS5k and that of a 10% volume fraction of H3A1 and 90% volume fraction of PS5k is displayed in Figure 4.28. We use the TMA model and consider that the short linear chains act as a solvent for both the early time and activated fluctuations of the branches. For very early times, the entropic barrier to retraction is less than k_BT , therefore, $U_{eff} < k_BT$. The effective potential has no significance and the free arm ends diffuse freely by Rouse tube motion. The mean square displacement of any monomer on a Rouse chain in a tube, scales as $x^2 \sim t^{1/2}$. The expression for τ_{early} , taking into account static dilution by the short chains is the following where τ_R is the Rouse relaxation time of the arms.

$$\tau_{early}(x) = \frac{9\pi^3}{16} \left(\frac{M_a}{M_{e,0}\phi_{unr}^{-\alpha}}\right)^2 \tau_{R,chain} x^4$$
 4.15

The effect of the solvent dilution is also extended to the late time arm retraction. Normally, this late arm time retraction process is defined as being entropically unfavorable and exponentially slow when the arms are long and well entangled. However, due to static dilution by the short chains $Z_{a,dil}=Z_a\varphi_{unr}$ where φ_{unr} is equal to φ_H , therefore there is approximately only one arm entanglement remaining (assuming a vol. fraction of 10% H) after full dilution due to the short chains and the H probe arm retraction, the static dilution is considered to fully applicable. Hence, there is no longer a strong exponential dependence of the arm retraction time on the number of arm entanglements (equation 4.16). However, in the case where the linear chains of are well-entangled, when they no longer act as a simple theta solvent, the arm retraction process has a more significant exponential dependence on the number of entanglements of the arms. Moreover, in this case, the fluctuations are assumed to occur in a skinny tube. Therefore, the original expression for arm retraction time (equation 4.16) also needs to be adjusted for DTD. In addition to the dilution associated with the short

chains, there is also a DTD process (if the arms remain entangled after the first static dilution) associated with an exponential separation of arm relaxation times (Ball and McLeish, 1988).

$$\tau = \tau_1 \exp\left(\frac{v M_a}{M_{e,0} \phi_{unr}^{-\alpha}}\right)$$
4.16

As depicted in Figure 4.28, the TMA model does fit the linear PS5k moduli data quite well in the low frequency region. However, in the high frequency region, the fit is not in agreement with the data. Moreover, the TMA model fit of the 5k blend data moduli is again satisfactory for the low frequency region, however, the predicted storage G' and loss moduli G'' are lower than the experimental data. An explanation for this could be due to the CR process mediated by the relaxation of the short chains does not have sufficient time to take place in order to speed up the relaxation of the H polymer. The consequence is that the value of the second rubber plateau modulus is closer to $G_N^0 * \varphi_H^0$ rather than $G_N^0 * \varphi_H^2$ where φ_H is the volume fraction of the H polymer chains. This issue could be corrected by adding the condition that the CR process cannot take place faster than the intrinsic Rouse time of the H.



Figure 4.28: Linear rheology data of PS5k linear (above) and a mixture of v_H =0.10 blend of H3A1 with the PS5k linear matrix v_I =0.9 (below). The experimental data is plotted with the TMA model fits.

The storage modulus G'(ω) and loss modulus G''(ω) of linear PS22k and the moduli of the three blend mixtures (1.5, 3 and 10%) are displayed in Figure 4.29. The moduli data of the blends is shifted vertically upwards for better clarity. The tan delta values (G''/G') values are also shown below the moduli data. Both a low and high frequency tan delta minimum is observed for all three different concentrations of H polymer. The high frequency value of ω is associated with the global plateau modulus whereas the low frequency value of ω is associated with the diluted H polymer modulus, following the relaxation of the linear chains. The frequency value at the second tan δ minimum associated with the diluted H polymer relaxation is the same for all three blends. This indicates that there is little effect of the concentration of the H polymer on its relaxation time in the mixture, proving that we are indeed below the overlap concentration. Hence, the H polymer chains are not mutually entangled.



Figure 4.29: Linear rheology data (above) of PS 22k (\circ) and blends with 1.5% H3A1 polymer PS (shifted vertically upwards by 100) (Δ), 3% H3A1 polymer (shifted vertically upwards by 1E4) (\Box) and 10% H3A1 polymer (shifted vertically by 1E6) (\bigcirc) and respective tan delta (G''/G').

Again, we use the TMA model to fit the PS22k10% blend linear rheology curves as depicted in Figure 4.30. We also plot the de-convoluted H polymer arm and backbone curves. Again, it is evident that the predicted storage $G'(\omega)$ and loss modulus $G''(\omega)$ are lower than those associated with the experimental data which could be due to the H polymer which relaxes by its intrinsic Rouse relaxation faster than the CR process mediated by the relaxation of the short chains. From Figure 4.30, it is clear that the terminal relaxation time

of the mixture is similar to the terminal relaxation time of the branches (in green) due to the fact, that the inner backbone is heavily diluted by the branches. The total volume fraction of the backbone in the mixture is only 1.9% and considered marginal, hence the terminal relaxation is dominated by the arm relaxation. In the TMA model, this is taken account by ignoring the friction associated with the small branches in the fluctuation processes of the inner backbone. Therefore, the inner backbone fluctuates immediately after the fluctuations of the long branches but with a stronger solvent effect rather than a strong friction effect.



Figure 4.30: Linear rheology data (circles) of 90% PS22k and 10% probe H3A1 mixture. The experimental data is plotted alongside the TMA fit (lines) as well as the deconvoluted arm and backbone relaxation curves.

4.12 Dilution of H in well-entangled linear chains

As the length of linear chains is increased above a critical molecular weight then they no longer act as simply as a theta solvent for the H polymer arms and backbone. More specifically, this means that the fast chains (linear chains) will only act effectively as a solvent for the slow chains (the H polymer) if the latter have had enough time to explore all the conformations of their dilated tube. For bidisperse blends, as explained in the Introduction, this is defined as the Struglinsky-Graessley parameter (Struglinsky and Graessley, 1985). For mixtures of linear polymers with more complex structures such as H and comb, this transition region has not been properly defined. The condition is that there is a large timescale separation between the relaxation of each the components. In the case of the H3A1 polymer, the arms are well entangled (8±1 entanglements) and coupled with the backbone relaxation and hence the full arm retraction process occurs over a large range of time scale (2 decades long, the equivalent of the frequency range of the G'' shoulder). Therefore, the ratio between the relaxation of the short chains and the arm retraction process would need to be large enough to satisfy the condition of static dilution. This condition is only reached for the very short length of chains, specifically for the PS5k and the PS22k.

For larger M_w PS, the interactions between the linear chains and the H polymer chains become important and the short chains can no longer be considered as a simple theta solvent. We consider that the early fluctuations processes of the branches are not influenced by the CR of the well-entangled linear chains and hence, are considered to happen in a skinny tube. Again in this case, the relaxation mechanisms follow a hierarchical relaxation (depicted in a schematic in Fig. 4.31), the linear chains are the first to relax by CLF/reptation, the H polymer arm retraction will then follow, first by early-time fluctuations followed by exponentially slow fluctuations (influenced by CR events) and finally, the backbone, which is completely un-entangled by dilution, will relax immediately after the arms.

The expression for G(t) is a combination of these two relaxation processes which occur at different time scales. The G(t) is a function of the fraction of unrelaxed polymer $1-\varphi_1-\varphi_a$ after entangled linear and H polymer arm relaxation and can be defined by the following expression:

$$G(t) = G_0^N \varphi_{reptation}^{\alpha} \varphi_{DID}^{\alpha} = G_0^N \varphi_H^{\alpha} \varphi_b^{\alpha}$$

$$4.18$$



Figure 4.31: Schematic depiction of the hierarchical relaxation process associated with the linear PS51k, PS129k, or PS 182k blended with the H3A1 polymer. The short chains will relax by CLF/reptation. The early arm time fluctuations will occur in a skinny tube. Finally, the heavily diluted backbone will relax immediately after the arms with a strong solvent effect.

The storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ of linear PS51k and the moduli of the three blend mixtures (1.5, 3 and 10%) are displayed in Figure 4.32. The moduli data of the blends is shifted vertically upwards for better clarity. The tan delta values (G''/G') values are also shown below the moduli data. Moreover, the TMA model fits as well as the deconvoluted curves for the linear, H polymer arms and backbone are displayed in Figure 4.33. The model fits are in agreement with the experimental data, although the plateau modulus is under-predicted. However, in order to fit the linear rheology data, the M_w needed to be adjusted in comparison to the value given by the manufacturer of 51k to 64k, the value determined by independent SEC measurement. By using the TMA model deconvoluted curves, we define relaxation times associated with the linear, the H arms and backbone relaxation at each of the three H polymer concentrations, ie 1.5%, 3% and 10%. The relaxation times of each of the respective blend components are depicted in Table 4.6. It is evident that for the linear, H arms and H backbone, all three relaxation times (corresponding to each respective concentration) are almost identical. Thus demonstrating that the concentration of H polymer in the mixture clearly has no effect on the relaxation times of each of the blend components



Figure 4.32: Linear rheology data (above) of PS 51k (\circ) and blends with 1.5% H3A1H (shifted vertically upwards by x10) (Δ), 3% H3A1H polymer (shifted vertically upwards x100 (\Box) and 10% H3A1H polymer (shifted vertically upwards by 1000) (\bigcirc) and respective tan delta (G''/G') (below).



Figure 4.33: Storage $G'(\omega)$ and loss $G''(\omega)$ modulus data of PS51k and a) 1.5%, b) 3% and c) 10% mixture of H3A1. The experimental data are plotted alongside the TMA fit as well as the deconvoluted linear, arm and backbone relaxation curves

Component	Relaxation	PS51k 1.5%	PS51k 3%	PS51k 10%
Linear	$\tau_d(s)$	13	14	14
	$\tau_0(s)$	20	20	20
H arms	$\tau_d(s)$	130	130	130
	$\tau_0(s)$	750	800	800
Н	$\tau_d(s)$	640	640	700
backbone	$\tau_0(s)$	8.2E3	8.3E3	9.4E3

Table 4.6: Relaxation times associated with each of the blend components, ie linear, H arms and backbone of the PS51k mixtures.

The SAOS data of linear PS129k and the two blend mixtures (3% and 10% vol. fr.) are displayed in Figure 4.34. The moduli data of the blends is shifted vertically upwards for better clarity. The tan delta values (G''/G') values are also shown below the moduli data. It is difficult to distinguish any difference between the PS129k and the PS129k blend moduli simply by visual inspection. The same applies to the PS182k linear and blends (Figure 4.36). However, the differences are more easily distinguished in the more sensitive tan δ curve. A second minimum in tan δ which indicates a secondary relaxation process is clearly visible in the PS129k 10% and PS182k 10% blend curve. However, it is evident that as the Mw of the linear PS is increased, the secondary relaxation process of the H polymer in the mixture becomes more weak and harder to detect. The TMA fits of the PS129k 3% and 10% (Figure 4.35) and PS185k 1.5%, 3% and 10% (Figure 4.37) are in agreement with the experimental data. Again, in a similar fashion as the PS51k blends, there is no influence on the concentration of H polymer in the mixture on the respective linear, arm and backbone relaxation times. The only difference is depicted in the storage modulus curve, where a higher concentration of H polymer results in higher G'(ω) values at frequencies above the inverse relaxation time of the linear polymer.



Figure 4.34: Linear rheology data (above) of PS 129k (\circ) and blends with 3% H3A1 (shifted vertically upwards by a factor 10) (\Box) and 10% H3A1 (shifted vertically upwards by a factor 100) (\bigcirc) and respective tan delta (G''/G') (below)



Figure 4.35: Storage G'(ω) and loss G''(ω) modulus data of PS129k and 3% (above) and 10% H3A1 mixture (below). The experimental data are plotted along with the TMA fit and the deconvoluted linear, arm and backbone relaxation curves.



Figure 4.36: Linear rheology data (above) of PS 182k (\circ) and blends with 1.5% PS H3A1 (shifted vertically upwards by x10) (Δ), 3% H3A1 polymer (shifted vertically upwards by x100) (\Box) and 10% H3A1 polymer shifted vertically upwards by 1000 (\bigcirc) and respective tan delta (G''/G') (below).



Figure 4.37: Storage G'(ω) and loss G''(ω) modulus data of PS182k (a) 1.5%, (b) 3% and (c) 10% mixture of probe H3A1. The experimental data (circles) are plotted alongside the TMA fit (solid lines) as well as the deconvoluted linear, arm and backbone predictions.

4.13 Dilution of combs by well-entangled linear chains

The storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ of the linear PI22k at 25°C and the 10% comb blend mixture is displayed in Figure 4.39. The moduli data of the 10% blend and comb data is shifted vertically upwards for better clarity. Additionally, the loss tangent tand values are also plotted below. The arm retraction of the combs is clearly distinguished in the tan δ peak. Moreover, we also plot the stress relaxation modulus G(t) and distinguish quite clearly three relaxation processes, the first, related to the relaxation of the linear PI22k at 1E-3s, the second, to the comb arm retraction at 0.014s and the third, to the dynamically diluted backbone relaxation at 0.1s. The hierarchy of relaxation mechanisms in the blend is quite clear and depicted in Figure 4.40 by a schematic representation. The well-entangled linear chains are the first to relax by CLF/reptation. They will act as a solvent for both the early and activated arm time fluctuations due to the well separated relaxation time scales between the PI22k and the comb PI254k. The backbone relaxation time is even more accelerated than the comb arms, since it undergoes a double dilution process, first by static dilution by the linear chains and second, by DTD associated with the slow arm retraction process. In addition, the linear viscoelastic data of PI96k blended with 10% vol. fraction of comb PI254k is depicted in Figure 4.41. In this case, the relaxation of the linear PI96k occurs after the relaxation of the comb arms and before the relaxation of the comb backbone. The relaxation of the comb arms is depicted as a change of slope in the tan δ and the relaxation of the comb backbone as the low frequency minimum in $tan\delta$. As depicted in the schematic of Figure 4.42, the comb arms are retarded by the linear chains and the comb backbone is accelerated by the linear chains.



Figure 4.38: Linear rheology data at 25°C (above) of PI 22k (\circ) and comb PI254k (shifted vertically x 100) (Δ) and blend of PI 22k with 10% PI254k comb polymer (shifted vertically x10) (\Box) and respective tan delta (G''/G') (below).



Figure 4.39: Stress relaxation log G(t) data at 25°C (above) of PI 22k (\circ) and comb PI254k (Δ) and blend of PI 22k with 10% PI254k comb polymer (\Box). Indicated by arrows are the respective linear, arm and backbone relaxation times.



Figure 4.40: Schematic depiction of the hierarchical relaxation process associated with the linear PI22k blended with the comb PI254k. The entangled linear chains relax by reptation/CLF. The fluctuations of the comb arms are accelerated by the linear chains which act like a theta solvent. The backbone relaxation is accelerated by an even greater factor than the arms since it experiences both static dilution and DTD.



Figure 4.41: Linear rheology data at 25°C (above) of PI 96k (\circ) and comb PI254k (Δ) (shifted vertically upwards by x100) and blend of PI 96k with 10% PI254k comb polymer (shifted vertically upwards by x10) (\Box) and respective tan delta (G''/G') (below)


Figure 4.42: Schematic depiction of the hierarchical relaxation process associated with the linear PI96k blended with the comb PI254k.

4.14 Dilution of H polymer in long linear chains

In Figure 4.43 (above), the storage and loss modulus associated with the PS483k 10% blend experimental data and TMA model fit is depicted. In Figure 4.43 (below), the moduli of the PS1M blend and model fit is shown. In both cases, the TMA model predicts a weak G'' minimum associated with the H polymer arm relaxation. This relaxation feature is not captured in the experimental data most likely due to polydispersity in the sample. In the case of the PS483k blend, the arm relaxation time of the H polymer in the blend is exactly the same as in the probe. Most likely, this is due to the similar relaxation times of the linear PS483k matrix and the H polymer arm probe. In the case of the PS1M blend however, the model shows that the arm relaxation time is delayed, approximately 10 times, indicating the effect of the CR.



Figure 4.43: top: Storage G'(ω) and loss G''(ω) modulus data of 90% vol.fraction PS483k and bottom: 90% vol. fr. of PS1M with 10% vol.fr. of H3A1 mixture. The experimental data (circles) is plotted with the TMA fit (lines) as well as the deconvoluted branches (blue) and backbone (green) relaxation curves.



Figure 4.44: Schematic depiction of the hierarchical relaxation process associated with the linear PI96k blended with the comb PI254k.

4.15 Dilution of comb polymer in long linear chains

In the same fashion as the PS H mixtures, the long linear chains, act to suppress tube motion (CR) of the probe PI254k comb polymer. The fluctuations of the arms are delayed by the long linear PI1.5M which acts similarly to a permanent network and suppresses CR and tube motion. This is evident when comparing the loss modulus G''(ω) of the PI1.5M with the G''(ω) of the mixture (Figure 4.45). The delayed arm retraction process in the mixture is clearly observed on frequency scales between 1 rad/s and 1000 rad/s. The backbone relaxation is only slightly delayed by the presence of the long linear chains due to the rather small separation between their time scales. Unfortunately, the very low frequencies were not reached in the SAOS experiments as depicted in Figure 4.45, in order to avoid degradation effects that occur at high temperatures. The hierarchical process is depicted in Figure 4.46. The arms fluctuations of the combs are retarded by the long linear chains. The backbone is also retarded by the long linear chains but to a lesser degree. The PI 1.5M is the last component to relax.



Figure 4.45: Linear rheology data (above) of PI 1.5M (\circ), comb PI254k (Δ) and blend of PI 1.5M with 10% PI254k comb polymer (\Box) and respective tan delta (G''/G') (below)



Figure 4.46: Schematic depiction of the hierarchical relaxation process associated with the linear PI1.5M blended with the comb PI254k.

4.16 Acceleration factor of the H arms and backbone

Depicted in Figure 4.47, the acceleration factor (ratio between τ_d of the H polymer arms and backbone in the melt versus τ_d of the arms and backbone in the mixture) is plotted versus the number of entanglements of the linear polymer. In order to be consistent, the relaxation times determined by using the TMA model were used in our analysis. The higher the number of entanglements of the linear matrix, the less significant is the acceleration factor of both the arms and backbone of the H polymer. The acceleration factor of the H polymer backbone is greater (on average about 30 times) than the H polymer arms. This is intuitive since the backbone has a larger time scale separation than the arms. We notice the exact same acceleration factor curve for both the H polymer arms and backbone. This demonstrates that the CR mechanisms involved in both the arms and backbone relaxation are the same. We notice a transition zone at approximately 10 entanglements, which is equivalent to the dilution of the H polymer by the PS linear 182k. This can be explained by the CR influence on the relaxation. We are moving from a regime of acceleration by CR mechanisms to a regime of suppression by CR mechanisms. It is evident that the acceleration by CR is much more pronounced than its suppression. The transition zone most likely corresponds to the point at which static dilution by the linear chains is no longer applicable and the interaction of linear chains with the H polymer chains becomes active.



Figure 4.47: Acceleration factor of H polymer arms and backbone versus Z the number of entanglements of the linear chains.

4.17 Acceleration factor of the comb arms and backbone

In a similar fashion, we plot the acceleration factor of the comb arms and backbone in the mixture versus the number of entanglements of the linear matrix in order to determine the effect of CR on their relaxation dynamics. These acceleration factors are more approximate since the relaxation times were not determined from the TMA model for the simple reason that the model has not yet been fully adapted specifically for the dilute comb blends. We used more approximate methods of determination of arm and backbone relaxation times based on the graphical methods which were explained in more detail previously. Again, it is evident from Figure 4.48 that as the number of entanglements is increased, the acceleration factor of the branched components is reduced. Again, there is a transition region (at around 10 entanglements) where the relaxation times are not accelerated but rather retarded due to the effects of CR. Moreover, again similarly to the H polymer, the acceleration factor is always greater for the backbone in comparison with the comb arms. However, the difference between the acceleration factor of the respective arm and backbone is much greater in the mixture with the blend PI22k in comparison to the other mixtures. In this specific blend, the PI22k acts as a solvent, diluting the entanglements of the comb arms and backbone and acting to enhance the acceleration factor to a greater degree. In the other comb blends, the linear polymers do not act as simple theta solvent and therefore, reptation occurs in a skinny tube rather than a

dilated tube. The similarities between the H and comb relaxation behavior in their respective mixtures, conforms to a universal behavior.



Figure 4.48: Acceleration factor of H polymer arms and backbone versus Z the number of entanglements of linear chains.

Chapter 5

Conclusions

The thesis reports on the investigation of the effects of well-controlled polymer architecture on the molecular rheology of model branched polymers and blends. We focus on the right combination of state-of-the-art synthesis – characterization – and theoretical modeling on order to be able to link the molecular structure of complex polymers to their rheological behavior.

We address the physical origin of strain hardening for well-defined linear and complex branched polymers such as H and comb. In the case of monodisperse linear homopolymers, the prediction of the onset rate of strain hardening (the macroscopic consequence of chain stretch) is straight forward and corresponds to the inverse Rouse time and is due to the friction of the chain retracting within its tube. The experimental uniaxial extensional rheology obtained using a Sentmanat Extensional Fixture of a linear polystyrene of M_w =262k confirms that the onset rate of strain hardening is equivalent to this simple theoretical prediction. The molecular picture becomes more and more complex as the level of branching complexity increases.

We demonstrate experimentally that the inner segments between branch points of two well-defined H polymers (Roovers, 1981) result in an earlier onset rate of stretch and a larger magnitude of strain hardening compared to a linear analog. In effect, strain hardening is even observed at rates lower than the inverse of crossover relaxation time. Moreover, an increase in the number of entanglements of arms and backbone will also lead to a higher amount of chain stretch. Although the pom-pom model of (McLeish and Larson, 1997) seems to fit reasonably well the tensile stress growth coefficient data, the limitation is that the magnitude of strain hardening is not well predicted by simply using q=number of arms. Moving on to a higher order level of complexity, we study a well-defined series of combs with large M_b and

varying number of branches, synthesized by J. Roovers, 1979 and characterized by state-ofthe-art temperature-gradient interaction chromatography recently by (Chang et al. 1999). We systematically vary the molecular characteristics of the combs. In general, the larger the number of entanglements of the segments between branches and/or of the branches, the stronger the strain hardening and the smaller the characteristic rate for its onset. The key molecular parameter appears to be the number of entanglements per branch. By varying it, one can tailor the amount and onset of strain hardening. This can be rationalized by accounting for the combined effect of backbone tube dilation and extra friction, brought about by the branches. In fact, we define an effective "stretch time" of the comb as the timescale for stretch relaxation along the dilated backbone tube when accounting for the large friction that comes from the branches and suggest that extension hardening occurs at rates equal to or greater than its inverse. The good comparison of this prediction to experimental data indicates that despite its simplicity, it is a robust rationalization.

In order to quantitatively model the extensional data, two approaches are compared (a) the original pom-pom model of McLeish and Larson (b) a modified pom-pom model which accounts for the comb architecture. The fit provided by the former is in agreement with the experimental data, however, there are too many free parameters and hence the model fails to offer any meaningful physical interpretation. Rather, the latter, also results in good agreement with the experimental data with no free parameters. In order to account for the comb structure, the stretch evolution equation of the original pom-pom model is modified. The key assumptions made is that the tube is fully aligned in the direction of flow, that the comb backbone segments can be equally separated into two symmetric halves, that the maximum stretch occurs in the middle section of the comb and that the free backbone ends do not contribute to the stretch. For H polymers, invoking the pom-pom model rationalization, branch point withdrawal occurs when the maximum stretch is equal to the number of arms fixed to each branch point, $\lambda_{max}=q$. Contrarily, for comb polymers, invoking the comb model, branch point withdrawal occurs when $\lambda_{max}=n_s/2$ where n_s is equal to the number of backbone segments and occurs from the outer segments inwards. A new characteristic time τ_{seg} corresponding to the stretch relaxation time of each backbone segment is introduced. This new parameter free comb model which takes into account all relevant tube theory concepts

such as hierarchical relaxation and dynamic tube dilution can predict well the extensional rheology data of a variety of model comb polymer systems.

We report on the role of constraint release on CLF/reptation in a dilute blend of model H and comb blended with a linear matrix. We use the model of TMA (Time-Marching Algorithm) and BOB when applicable to fit the linear rheology data and try to understand the effects of the environment (length of linear chains) on the dynamics of the model polymer. Very short un-entangled linear chains act only as a solvent and dilute the branched polymer and speed up its relaxation considerably. As the length of the linear chains increases, shortlong chain entanglements are formed. If the reptation time of the linear chains is significantly slower than the retraction time of the arms but faster than the reptation time of the backbone, the linear chains will act as a solvent for the backbone and at the same time, slow down slightly the relaxation of the arms by the effect of constraint release. If the reptation time of the linear chains is slower than the arm retraction and the backbone relaxation, the branched polymer relaxation will be slowed down due to the effect of constraint release. The long linear polymer chains will act as a type of permanent network, thus suppressing the effects of For both comb and H molecules in the mixture, the acceleration factors of arm and CR. backbone relaxation times decrease with the number of entanglements of the linear matrix, pointing to the role of CR.

5.1 Questions and Recommendations

The key to improving one's own knowledge and also the general knowledge of the scientific community is to continuously frame the right questions.

This notion of two tubes, one tube contained within another tube has been invoked particulary when modelling two or more blend components. Watanabe and colleagues have used this molecular picture also to correct some of the deficiencies inherent in the full DTD which in itself is perhaps too simplified a picture for polydisperse systems. Is the picture of two tubes absolutely necessary or is it just complicating the molecular tube dynamic picture? Can the molecular rheology framework of complex blends and complex flows be described by simply using one tube?

As was mentioned previously, most theoretical models assume that the slow relaxing component in blends can simply be taken as a solvent. However, as was demonstrated by us and others, this is not the case. Can the Struglinsky-Graessley (r_{SG}) parameter, initially proposed for simple bidisperse blends be expanded also for more complex blends. Is there a universal behavior for this transition point? For example, can the r_{SG} parameter also be applied for example to star polymers. Can a transition point also be defined when CR competes with arm fluctuations? Should the relaxation by fluctuations also be made environment dependent? Another important related question is how to expand the Struglisnky-Graessley parameter also in the non linear regime.

The subject of parameter consistency is of great concern in tube model theories. Can a universal rule be applied to the dilation parameter α and the friction parameter p^2 , independent of the specific molecular tube model, ie BOB, Hierarchical, TMA, etc.?

The subject of strain hardening is of great industrial industrial, especially for packaging film produced from film blowing industrial processes. The goal is to tailor the molecular structure of the polyethylene resin in order to produce a highly strain hardening material and this would offer a greater bubble stability. Therefore, a relevant industrial question to ask is how can one design the molecular structure of complex polymers to provide for the greatest amount of chain stretch. The two relevant parameters used to define stretch are the amount of strain hardening in reference to the linear viscoelastic enveloppe which is often referred in industry as strain hardening factor and the onset of chain stretch, the rate at which strain hardening first appears. The higher the amount of strain hardening and the lower rate at which it first appears are both positive indicators. For the most simple case of branched polymer, an H or pom-pom, the maximum amount of stretch sustainable upon applying deformation is a function of the number of arms and the onset of stretch is a function of the arm retraction time, the number of entanglements of the backbone and the number of arms (McLeish and Larson, 1998). From our own work, for comb polymers, an increase in the number of entanglements of the backbone and more importantly, in the number of entanglements of the arms will lead to greater amount of chain stretch and an earlier onset rate. Evidently, the more the arm retraction process is delayed, the more stretch is sustainable in the backbone. Moreover, in our modified pom-pom model for combs, the maximum amount of stretch is approximately equivalent to half the number of arms. From the work of (Kempf et al., 2013), they demonstrated that increasing the number of comb arms increases the amount of stretch. However, in the range of 15 to 29 branches, a limit for the number of branches is reached, where a further increase no longer has an effect on the strain hardening. In the work of (van Ruymbeke et al.,2010), it has been demonstrated that increasing the number of generations in a Caylee tree will lead to a greater amount of strain hardening. Three generations of Caylee trees results in three levels of relaxation hierarchy observed in SAOS data and three levels of strain hardening. From (Nielsen et al., 2006), it is known that asymmetric stars will also strain harden appreciably, due to the separation of time scales of the relaxation processes associated with each respective arm length. (Auhl et al., 2009), demonstrated that a small amount of high M_w polymer in a bidisperse blend will lead to a greater amount of stretch since the onset of strain hardening is related to the effective stretch relaxation of the long chains. Therefore, clearly increasing the level of hierarchical complexity of the branching components and number of components with very slow relaxation times has a significant influence on increasing the amount of chain stretch and enables the design of a polymer resin with superior processing ability.

Although TGIC was used as a characterization tool for the branched polymer, the method was not utilized to the full of its potential. Although more exhaustive, it would be preferable to use TGIC in combination with SEC to identify all possible side products, to fractionate these products out of the original system and also identify the differences in rheological responses of both the clean and polydisperse product. Thus, following the methodology of others such as Larson and colleagues (Larson, 2001), van Ruymbeke and colleagues (Snijkers et al., 2011) and Hutchings and colleagues (Hutchings et al., 2012), we would be more assured of having an accurate and complete rheological picture of truly monodisperse polymers.

Moreover, there is some evidence that the theoretical tube models with some modifications can be applied to other more complicated systems such as supramolecular polymers or other self-healing materials. Associating polymers differ from simple polymers since they contain a fair amount of weaker bonds which form what is known as "sticky bonds" with each other via associative interactions weaker than covalent bonds. The terms sticky Rouse and sticky Reptation model have been coined to describe associative polymer networks (Rublinstein and Semenov, 2001; Leibler et al., 1991). It is clear that in these systems, there is a more complicated interplay than just polymer physics.

Moreover, we and others make the assumption of uniform grafting of the combs. Is it a truly vaild assumption? It would be relevant to synthesize model comb polymers with equal spacing between branches and perform rheological experiments in the linear and non-linear regime to test this assumption further.

Rheology is a purely macroscopic experimental characterization method and an indirect probe of branch point motion. In order to fully understand for branch point dynamics, microscopic probes are needed in addition to rheological methods. For example, selectively labeling the branch point region (having the rest deuterated) and performing neutron scattering rheology experiments in addition to non-linear rheology experiments would allow a more complete study of branch point dynamics.

Although performing uniaxial extensional rheology experiments is quite difficult which is evident by the few studies on model polymers which exist in literature, it is a rather simplified depiction of real extensional flows encountered in industrial processes. The study of model polymers under biaxial flows would be for example, more industrially relevant.

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