NONLINEAR RHEOLOGY OF LONG-CHAIN BRANCHED POLYMERS

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NONLINEAR RHEOLOGY OF LONG-CHAIN BRANCHED POLYMERS

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ABSTRACT

Entangled polymers show significant nonlinear rheological behaviors. Those studies on the mechanical behaviors of polymer melts and solutions not only promote our understanding on polymer dynamics, but also guide the application of polymers and establish principals to design polymeric materials. Recently emerged interpretations on nonlinear rheology of linear polymers proposed by Dr. Shi-Qing Wang emphasize the network nature of entangled polymers.

This dissertation studies the nonlinear rheology of long-chain branched (LCB) polymers. A new synthetic method is developed and implemented to overcome the limitation of previous methods for not being able to synthesize long enough branches. This method can produce ultra-high molecular weight LCB polymers with branches of identical length and uniform spacing between branch points.

Polymers with multiple long branches show remarkable resistance to the elastic-driven decohesion comparing to linear polymers. In startup uniaxial extension, they are extraordinarily more stretchable. An empirical rule shows that the failure of entangled network, as characterized by the overshoot of engineering stress, is proportional to the square root of number of entanglements. Polymers with LCB are also more resistant to failure in stepwise extension (withstand a larger stretching ratio), which would be part of film blowing process.
Historically, strain hardening stands for the upward deviation of transient extensional viscosity comparing to zero-rate transient viscosity, which typically shows up on branched polymers. Under the newly emerged conceptual framework, such behavior is due to three factors: firstly, the shrinking cross-section area leads to a factor of extension ratio in calculating true stress and transient extensional viscosity; secondly, the introduction of branches suppresses the breakdown of entangled network; lastly, the entanglement network is strengthened at sufficient high Hencky rates during extension.

Entangled polymeric liquids have so far only shown strain softening upon startup shear, signified by stress overshoot. However, solutions of polystyrenes with LCB exhibit strain hardening upon startup shear at high shear rates, undergoing non-Gaussian chain stretching and reaching finite extensibility limit. The stronger than linear increase of the shear stress ends with a sharp decline, forming a cusp. At intermediate shear rates, stress overshoots always occur at the same strain, which is explained also by the length of backbone. The LCB polymers show a rich variety of transient responses to startup shear at different rates and open a large window of dynamics to meet practical applications.
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CHAPTER I

INTRODUCTION

High molecular weight polymers have several unique mechanical properties that

distinct them from other materials\(^7-11\). For example, the viscosities of polymers increase
even faster when their molecular weights (M\(_w\)) are higher than a critical value. After
deformation, they can recover back at least partially. Thirdly, when we watch the decay

of stress with time of a deformed polymer, we see a flat region of stress. In 1930s
researchers suggest that high molecular weight polymers are acting as if they are
crosslinked. They start to use the word entanglement\(^12,13\). The M\(_w\) between the spacing

of such entanglements is M\(_e\) and is related the modulus of the polymer as. Other
indications of the proved by re-entangle process from freeze-dry state or during welding.

Early theoretical treatment used temporary “cross-links”\(^14\) or additional friction to
represent entanglement effect. Nobel Laureate de Gennes introduced the concept of
“reptation”\(^15\), polymer chains moving only by one-dimensional diffusion within a tube
formed by topological constrains\(^16\) – entanglements. Sir S. Edwards and M. Doi\(^17-20\)
continued to complete a detailed mathematical formulation for polymer dynamics which
became the mainstream of tube-based model.
Various amendments, contour length fluctuation (CLF), constraint release (CR), convective constrain release (CCR) and chain stretching were proposed to adjust the numerical predictions of tube model, so that tube model can be applied to not only linear rheology but also nonlinear rheology of polymer melts and solutions.

However, as Karl Popper\textsuperscript{21} suggested that science is to reject hypothesis, not to find evidence that support one idea over another and Thomas Kuhn\textsuperscript{22} states that we may not defend the paradigm and treat others as heterodoxy, it is proper to keep open minded and be caution to exam the evidence. Tube-based models have gone a long journey trying to giving good numerical outcome of stress-strain curves, yet there is no convincing conclusion. To understand the rheology of polymers is not just finding better and better numerical results, but an academic challenge because the behavior of entangled polymers is a many-body problem. Polymers are used in every aspect of our life. However, there are many questions that we can only empirically solve, not as rocket science that we can predict exactly where the rocket goes.

To study the nonlinear rheology of long-chain branched polymers, I will try to answer what stress-strain curve will branched polymers show, why branched polymers behave differently against linear polymers, how we should conceive the dynamics of those branches, and what are the key parameters we should use when we want to evaluate branched polymers. These progresses are built on newly emerged interpretations on nonlinear rheology proposed by Dr. Shi-Qing Wang since 2006.\textsuperscript{23-26} To begin my stories, the background knowledge about polymer rheology will be briefly stated in CHPATER II.

CHAPTER III studies the stress relaxation behavior of several entangled polystyrene (PS) solutions with the help of particle-tracking velocimetry (PTV).
Entangled polystyrene solutions have been studied in the past four decades in terms of their stress relaxation behaviors\textsuperscript{27-52}, by step strain experiments on whether we can separate stress into two term-strain part and time part, and been compared with the theoretical description based on the tube model\textsuperscript{5}. In fact, these previous studies have built a consensus that the tube model is a successful molecular theory for not only linear viscoelastic properties but also nonlinear rheological behavior of entangled polymers. Specifically, the agreement between some data and the theoretical damping function\textsuperscript{5,15} has been regarded as the validation of the tube theory despite the fact that a significant fraction of the data shows deviation from the theoretical formula.

PTV, a more simple technique comparing to other Particle Image Velocimetry (PIV)\textsuperscript{53,54}, is developed to study the deformation field of entangled polymers, and results show that on various polybutadiene solutions the relaxation is not quiescent, meaning the tracking particles may still in motion even after the stop of external applied deformation\textsuperscript{23,55,56}. To validate the generality of such anomaly, we systematically study the behaviors of PS solutions, which were traditionally used as a model system for polymer rheology.

Consistent with the previous PTV studies of other solutions, the classical PS solutions (a) also undergo non-quiescent relaxation after stepwise shear and (b) show stress relaxation behavior that deviates significantly from the tube model description. The macroscopic motions during stress relaxation affect the stress decay in a way that cannot be depicted by the tube model since the damping function is derived under the condition of quiescent relaxation. The observed macroscopic motions also suggest that even this slowly-imposed step shear involves significant chain stretching. It is the elastic
retraction associated with the chain stretching that overcome the cohesion or entropic barrier associated with the chain entanglement.  

In CHAPTER IV, we illustrate the origin of the so called "strain hardening". Strain hardening stands for the phenomena that the transient extensional viscosity, measured from a startup uniaxial extension of finite rate, deviates upward from zero-rate transient viscosity. Our analysis shows that polymer melts would always exhibit strain hardening at sufficient high Hencky rates because the entanglement network can be effectively strengthened during extension and can only be weakened during shear. The kinematic difference between simple shear and uniaxial extension has two effects: (a) the force resulting from the startup deformation is measured from an increasingly shrinking area in uniaxial extension instead of a constant area as in simple shear; (b) the tendency of the entanglement network to yield, i.e., to undergo chain disentanglement is partially suppressed during startup extension at high Hencky rates.

In short, the phenomenon of strain hardening reflects the reality that entangled melts are not fluids but temporary solids and that the conventional description of their uniaxial extension in terms of the Cauchy stress contains a geometric condensation factor. Both linear chains and polymers containing LCB show strain hardening when the uniaxial extension involves sufficiently high strain rate. Furthermore, polymers with LCB may make this kinematic difference more dramatic by delaying the eventual breakdown of entanglement network during extension so as to amplify the effect of the geometric condensation.

In CHAPTER V, We designed and explored a new synthetic strategy for ultra-high molecular weight long-chain branched (LCB) polymers with equal spacing between
adjacent branch points. While the branched samples provided by our collaborators don’t have enough long and multiple branches which are limited by the available synthetic methods, our method is straightforward to conduct and can synthesize LCB polystyrene (LCB-PS) with total molecular weight of 4.9 million g/mole, 16 branches of 140 kg/mole and polydispersity index of 1.5.

LCB-PS shows remarkably different nonlinear rheological responses to fast startup and stepwise uniaxial extensions, compared with the linear PS. The introduction of multiple branch points with long side chains allows the LCB-PS to resist the elastic-driven decohesion. These LCB-PSs are also extraordinarily more stretchable during startup uniaxial extension, with the maximum engineering stress emerging at stretching ratio $\lambda_{\text{max}} \approx 4\sqrt{M_{bb}/M_e}$, where $M_{bb}$ is the molecular weight of backbone and $M_e$ is the molecular weight between entanglements. Stepwise extension experiments reveal improved strength of the entanglement network. Specifically, even after a large step extension of stretching ratio $\lambda = 7.4$, the specimen would not undergo elastic breakup. In contrast, linear PS samples undergo elastic breakup at a stretching ratio of only 2.7. Thus, present study demonstrates that chain architecture can be an important molecular-design parameter to affect polymer dynamics and improve processing behavior.

In CHAPTER VI, continuing to study the solution behavior in shear on the LCB we synthesized, we show for the first time that entangled polymeric liquids containing LCB can exhibit strain hardening upon startup shear at high $Wi$. At intermediate $Wi$, we observe another bizarre behavior that stress overshoots occur at a constant strain. As the significant LCB impedes chain disentanglement, Gaussian coils between entanglements can deform to reach the finite extensibility limit where the intra-chain retraction force
exceeds the value expected from the usual conformational entropy loss evaluated based on Gaussian chain statistics. The non-Gaussian response is made possible by the presence of LCB that defers chain disentanglement. The LCB PS solutions show a rich variety of transient responses to startup shear at different rates and those dynamics requires further theoretical development.

In CHAPTER VII, a summary of this dissertation and an outlook of the development of nonlinear rheology on branched polymers will be presented.
CHAPTER II

BACKGROUND

To illustrate my progress on nonlinear rheology of long-chain branched (LCB) polymers, I will in this chapter lay the basics of polymers dynamics, linear rheology, then. Detailed knowledge can refer to various books.

2.1 Fundaments of linear rheology

2.1.1 Deformation

Assume we have a 3-dimension body, and it is being deformed. The first type of deformation called shear is applied on xz-plane as shown in Figure 2.1 (b) while extension is only applied on the x-direction as shown in Figure 2.1 (c). As we would encounter different kind of sample with different dimensions, normalization of the amount of deformation and force $F$ is necessary, while $A$ is the area that force is applied on, $L_0$ is the initial length in x-direction, $L$ is the length after deformation, $H$ is the height in y-direct while $\Delta x$ is the largest displacement in x-direction.

shear: strain $\gamma_{yz} = \frac{\Delta x}{H}$ \hspace{1cm} (2.1)

extension: Hencky strain $\varepsilon_{xx} = \log_e \lambda$, stretching ratio $\lambda = \frac{L}{L_0}$ \hspace{1cm} (2.2)
stress: \[ \sigma = \frac{F}{A} \]  \hfill (2.3)

Figure 2.1 Schematic illustration of a sample (a), being deformation as in simple shear (b) or in uniaxial extension (c).

2.1.2 Maxwell model

There two extreme type of response to deformation, purely elastic (a spring) or purely viscous (water, oil, honey). In the elastic deformation, all the input energy would be stored, and the force, or stress \( \sigma \), is only proportional to the amount of deformation, or strain \( \gamma \). The factor is the modulus of the sample, \( G \). On the other hand, in the viscous deformation, all the input energy would be dissipated, and the force, or stress \( \sigma \), is only
proportional to the rate of deformation, shear rate \( \dot{\gamma} = \frac{d\gamma}{dt} \) or extension Hencky rate as \( \dot{\epsilon} = \frac{d\epsilon}{dt} \).

\[
\sigma = G\dot{\gamma} \quad (2.4)
\]

\[
\sigma \propto \eta \dot{\gamma} \quad (2.5)
\]

If the material exhibits both elastic and viscous characteristics, we call this property as viscoelasticity. Linear viscoelasticity is a simple case of viscoelasticity, when there is a linear relationship between strain history and stress. An example of linear viscoelasticity is Maxwell model, a purely elastic spring with modulus of \( G \) and a purely viscous dashpot with viscosity of \( \eta \), connected in series as shown in Figure 2.2 so that to exhibit transient elasticity and terminal viscosity. As the spring and dashpot are connected in series, they share the same stress and deformation is the sum of each part.

\[
\dot{\gamma} = \frac{\dot{\sigma}}{G} + \frac{\sigma}{\eta} \quad (2.6)
\]

\[
\dot{\gamma} = \frac{\dot{\sigma}}{G} + \frac{\sigma}{\eta \tau}, \quad \tau = \frac{\eta}{G} \quad (2.7)
\]

\( \tau \) is the characteristic time of this system, and typically called as “relaxation time”, but it doesn’t mean the system relaxes within \( \tau \). Now we can apply types of deformation and examine the response of Maxwell model:

2.1.3 Stress relaxation

A sudden deformation is imposed on the sample and stress starts to decay with time, as \( \dot{\gamma} \) is 0 and sudden deformation is responded by the elastic part, the right side of Eq. 2.7 becomes:
Solving Eq. 2.8 gives:

\[ \sigma(t) = \sigma_0 e^{-t/\tau} \]  

(2.9)

Figure 2.2 Schematic illustration of a Maxwell model with modulus of \( G = 10^4 \) Pa and viscosity of \( \eta = 10^6 \) Pa.s.

Calculated stress during relaxation is presented in Figure 2.3. The response within \( \tau \) is mainly elastic, as the stress is proportional to strain and present a plateau against time. The response after \( \tau \) is mainly viscous, as the stress is decaying toward 0. \( \tau \) marks the transition from elastic response to viscous response. A further analysis can be performed by normalizing \( \sigma(t) \) with \( \gamma \) to get relaxation modulus \( G(t) \). In the linear rheology region, for example the Maxwell model here, \( G(t) \) would be identical regardless
of the \( \gamma \) applied. This is also the character of linear rheology, a linear relationship between strain history and stress. Nonlinear relationships are the character of nonlinear rheology and will be discussed in detail in Chapter III as stress-strain separability and damping function.

![Graph showing stress relaxation after sudden deformation](image)

Figure 2.3 Stress relaxation after sudden deformation of \( \gamma = 0.1, 1, \) and 10 calculate from Maxwell model with modulus of \( G=10^4 \) Pa and relaxation time \( \tau = 100 \) s.

2.1.4 Stress growth during start-up shear

The second type of test is keep shear rate constant, can watch stress grow from startup. By solving Eq. 2.7, we have the following equation that depicts the stress:

\[
\sigma(t) = [1 - e^{-t/\tau}] \dot{\gamma} \eta
\]  

(2.10)

Figure 2.4 present \( \sigma(t) \) with three different \( \dot{\gamma} \). Stress grows first linearly with \( t \) or \( \gamma \), then transient from this initial elastic response to viscous response, settles at the constant
value of $\dot{\gamma} \eta$. Especially in Figure 2.4 (b), that the initial elastic response are clapping on the same curve of $\sigma(t) = G \times \gamma(t) = G \dot{\gamma} \times t$. As the relaxation time is constant, the higher shear rates, the larger strain can the initial elastic response goes to. Although $\sigma(t)$ is higher at higher shear rates, that difference can be normalized by transient viscosity $\eta^+ = \sigma(t) / \dot{\gamma}$ which is plotted in Figure 2.4 (c) as all different shear rates result the very same transient viscosity curve.

The third type of test is creep and we will skip it here.
Figure 2.4 Stress growth from startup shear at $\dot{\gamma} = 0.1$, 1, and 10 calculate from Maxwell model with modulus of $G=10^4$ Pa, viscosity of $\eta=10^6$ Pa.s and relaxation time $\tau =100$ s. Plotted against time $t$ (a) and strain $\gamma$ (b). Transient viscosity plotted against time $t$ (c).
2.1.5 Small Amplitude Oscillatory Shear (SAOS)

Only one strain, strain rate, or stress is tested in previous three kind of test, stress relaxation, stress growth, or creep. At least a few tests has to be run to obtain the information on the dynamics and properties of the material, let alone more complicated materials. In order to obtain more information in a single test, SAOS is designed to use frequency (a similar concept as strain rate) as the variable, and the result is a map of linear responses at different frequency.

In a SAOS measurement, deformation is applied at angular frequency of $\omega$:

$$\gamma(t) = \gamma_0 \sin \omega t$$  \hspace{1cm} (2.11)

Mathematically we can rewrite that as and assume that:

$$\gamma(t) = \gamma_0 e^{i\omega t}$$  \hspace{1cm} (2.12)

$$\sigma(t) = G^* \times \gamma(t)$$  \hspace{1cm} (2.13)

Combining with Eq. 2.7, we have:

$$G^* = \frac{i\omega \tau}{1+i\omega \tau} G = \frac{(\omega \tau)^2}{1+(\omega \tau)^2} G + i \frac{\omega \tau}{1+(\omega \tau)^2} G$$  \hspace{1cm} (2.14)

We define $G^* = G' + i \times G''$ as the complex modulus, and real part as storage modulus $G'$ and image part as loss modulus $G''$ as:

$$G' = \frac{(\omega \tau)^2}{1+(\omega \tau)^2} G \hspace{1cm} \text{and} \hspace{1cm} G'' = \frac{\omega \tau}{1+(\omega \tau)^2} G$$  \hspace{1cm} (2.15)

We also define phase angle $\delta$ as:

$$\tan \delta = \frac{1}{\omega \tau} = \frac{G''}{G'}$$  \hspace{1cm} (2.16)
From Eq. 2.14, we also define complex viscosity as:

\[ |\eta^*| = \frac{|G^*|}{\omega} = \frac{\sqrt{G'^2 + G''^2}}{\omega} \]  

(2.17)

So at \( \omega_{\text{crossover}} = \frac{1}{\tau} \), we have \( \tan \delta = 1 \) and \( \delta = 45^\circ \) and \( G' = G'' \). It means the oscillatory deformation performance at this frequency will have equal contribution from the elastic response and viscous response. This crossover will be how we experimentally define relaxation time \( \tau \), which we often note as \( \tau_d \).

Figure 2.5 (a) presents the oscillatory deformation, elastic response which is in-phase and viscous response which is out-of-phase at one particular frequency. The results are \( G' \) and \( G'' \) at that frequency. We repeat such oscillatory deformation at different and get a map of \( G' \) and \( G'' \) at various frequency as shown in Figure 2.5 (b). , elastic response is dominant with a plateau of elastic modulus and \( G' > G'' \) for frequency above \( \omega_{\text{crossover}} \), while viscous response will dominate with constant \( |\eta^*| \) and \( G'' \propto \omega \). Also, there is this relationship that link Figure 2.5 (b) with Figure 2.4 (c):

\[ |\eta^*| \rightarrow \eta^+ \text{, by: } 1/\omega \rightarrow t \]  

(2.16)

These are the characteristics of linear viscoelasticity.
Figure 2.5 (a) Sinusoidal deformation $\gamma(t)$ as the black line. Red lower triangles mark the elastic response $\sigma' = G' \times \gamma(t)$ as which follows the same phase as $\gamma(t)$. Green upper triangles mark the viscous response $\sigma'' = G'' \times \gamma(t)$ which is cosinoideal and $90^\circ$ out of phase with $\gamma(t)$. The combined response is the sum of $G'$ and $G''$ and is $\delta$ degree out of phase. (b) Plot of SAOS.
2.2 Linear rheology of entangled polymers

Now with enough introductions on linear viscoelasticity and rheological experiments, we can extend to real systems. Linear rheology or linear viscoelasticity is only valid at low deformation rate or small deformation for complex systems, for example entangled polymers. For example, Figure 2.6 shows the SAOS of entangled linear polystyrenes at 150 °C in melt state. For linear PS with Mw of 1 million g/mole at frequency from $10^{-5}$ to 1, or for linear PS with Mw of 176 kg/mole at frequency from $10^{-2}$ to 10, the SAOS looks very similar to the outcome of Maxwell model with similar Modulus, but different relaxation time as shown in Figure 2.5 (b).

![Figure 2.6 Small amplitude oscillatory shear (SAOS) measurements of linear-PS 176k and 1M at a reference temperature of 150 °C.](image)
2.2.1 Plateau modulus and entanglement molecular weight (Me)

This common plateau modulus $G_{pl}$, regardless of the Mw of polymers (as long as they are above a threshold value), means there is a fixed density of network within polymers.

$$G_{pl} = \frac{\rho RT}{M_e}$$  \hspace{1cm} (2.17)

This equation relates the plateau modulus with as that each type of polymers would have their own characteristic $M_e$. A list of $M_e$ can be found in various references.\textsuperscript{57-59} So we can define number of entanglement per chain:

$$Z = \frac{M}{M_e}$$  \hspace{1cm} (2.18)

The SAOS of blends is discussed in Chapter V with BSW model.

2.2.2 Terminal relaxation time, rouse time and different regions of dynamics

However the real dynamics of polymers are not as simple as described by Maxwell model. The deformation slower than $1/\tau_d$ or $\omega < 1/\tau_d$ is the terminal region. $\tau_d$ is also the time scale that the polymer chain to reptate away the distance of its own coil size R. Polymer chains are always in a relaxed state. The time scale for the onset of strong chain stretching is $\tau_R \approx \tau_d/3Z$, which is the diffusion time for each entanglement. The shared high frequency crossover regardless of Mw denotes $\tau_e$, which has the relation that $\tau_d \approx \tau_e 3Z^3$. This relation means the spacing between $1/\tau_d$ and $1/\tau_e$ scales to the third power of Mw or Z.
For a startup deformation, the initial response is elastic with slope as plateau modulus. If $\dot{\gamma} < 1/\tau_d$, as the deformation goes and reaches steady state, the response is viscous with viscosity as $|\eta^*|$ at $\omega < \frac{1}{\tau_d}$, which we call as zero-shear viscosity. The situation becomes more complex when rate is higher.

2.3 Nonlinear rheology of entangled polymers

For entangled polymers, when deformation rate is high ($\dot{\gamma} > 1/\tau_d$) or deformation is large, stress strain relations are not as simple as in linear rheology shown in Figure 2.4. Weissenberg number is defined as $W_i = \dot{\gamma} \times \tau_d$ to indicate how much chain orientation has changed and and rouse Weissenberg number as $W_{IR} = \dot{\gamma} \times \tau_R$ indicates whether chain stretching is dominate. Next we will several characteristic behaviors of nonlinear rheology of entangled polymers.

2.3.1 Stress overshoot

Firstly, there will be an overshoot as the transition between initial elastic responses to final viscous response as shown in Figure 2.7. Various data suggests that the deformation before the overshoot point is elastic (the deformation is almost fully recoverable) while the deformation become more and more irrecoverable as the deformation passes the overshoot point. So it is also called as “yield” point.
Figure 2.7 Scheme of stress response

Figure 2.8 shows a set of real stress strain curves on a polystyrene solution. An phenomena to notice is that the position of overshoot strain, and the value of stress increase with shear rate, which is discussed in various references\textsuperscript{61,62}. 
2.3.2 Shear thinning

While the steady state viscosity is always the same in linear rheology as shown in Figure 2.4 (c), the steady state viscosity is lower with higher shear rates when $\dot{\gamma} < \frac{1}{\tau_d}$ in nonlinear region as plotted in Figure 2.9.
Stress relaxation behavior will be discussed in Chapter III and extensional behavior will be discussed in Chapter IV.

2.3.3 Finite extensibility and chain stretching

It is well known in rubber elasticity\textsuperscript{63} that force is proportional to the deformation, until the deformation is large enough that the polymer chains start to be straightened. The force will increase radically when the chain are close to straighten. These cases will be discussed in Chapter IV, V and VI.
2.3.4 Numerical models

As it is impossible to precisely capture the nonlinear rheological behaviors of real polymer systems, many models are being developed and improved. Early developments are various network models, such as Edwards-Vilgis slip-link model (EV model\textsuperscript{14,64-66}). Later, Doi-Edward tube model\textsuperscript{17-20} gets most of the attention. Many other models include Molecular Stress Function (MSF\textsuperscript{67}), GLaMM model\textsuperscript{68}, Rolie-Poly model\textsuperscript{69} also use the concept of tube and reptation\textsuperscript{16}. EV model is discussed in Chapter V.

As anionic polymerization is not the mainstream of this dissertation, the background is given in Chapter V.
CHAPTER III

STRESS RELAXATION BEHAVIOR OF ENTANGLED POLYSTYRENE SOLUTIONS AFTER STEPWISE SHEAR

3.1 Introduction

To have a baseline of nonlinear rheology of linear polymers, in this chapter, we start from studying the stress relaxation behavior of several entangled polystyrene (PS) solutions with the help of particle-tracking velocimetry (PTV). Similar to other entangled polymer solutions found to undergo macroscopic motions after step strain, we also observed non-quiescent relaxation during large deformation of PS solutions regardless of whether or not the rheometric data are in agreement with the theoretical description of the tube model. Our PTV observations imply that many classical step-strain rheological experiments based on entangled PS solutions\textsuperscript{44, 45}, could involve the same complications associated with the inhomogeneous breakdown of the entanglement network. Since the Doi-Edwards (DE) damping function is computed for a step-strained (entangled) polymer undergoing quiescent stress relaxation, the present study raises the question of whether it is meaningful to compare experimental data and the tube model for large deformations.
3.2 Background on damping function

Since the arrival of the Doi-Edwards tube model for polymer rheology\textsuperscript{17-20} there have been numerous experimental studies performed to validate the model. The most well-known agreement between the theory and experiment in the nonlinear regime involves the stress relaxation behavior after stepwise shear. The tube model anticipates two-step relaxation dynamics for well-entangled polymers after a large step strain. Specifically, there would be a kink in the time dependence of the relaxing stress.\textsuperscript{70} The sharp stress drop would occur quiescently around the Rouse relaxation time $\tau_R$ due to the chain retraction, which is assumed in the tube model to take place in a barrier-free manner. This ansatz of the tube model hash the consequence that the chain orientation would relax on the time scale of reptation, decoupled from the fast dynamics associated with chain stretching. Thus, the structure of the tube model automatically insures that there would be time-strain separability, i.e., the relaxing stress would have the same time dependence beyond the Rouse time $\tau_R$, independent of the magnitude of the applied step strain. In particular, the strain softening would take place, due to the assumed barrier-free chain retraction. In other words, the residual shear stress arises entirely from the surviving chain orientation

$$\sigma(\gamma, t) = G_{eq}(t)\gamma h(\gamma), \text{ for } t > \tau_R, \quad (3.1)$$

so that the relaxation modulus $G(\gamma, t) = G_{eq}(t)h(\gamma)$ actually decreases with the magnitude of $\gamma$ beyond a certain value of $\gamma$. Here the damping function $h(\gamma)$ captures the essence of the strain softening as\textsuperscript{18}

$$h(\gamma) = 1/(1 + \gamma^2/5), \text{ for } t > \tau_R, \quad (3.2)$$
where $G_{eq}(t)$ is the equilibrium relaxation modulus that describes the stress relaxation $\sigma(t)$ in the regime of linear response, i.e., $\sigma(t) = G_{eq}(t)\dot{\gamma}$, for $\gamma \ll 1$.

Experimental reports of stress relaxation behavior first appeared in 1970s.\(^{30-32}\) The systems under study were typically polystyrene solutions capable of undergoing wall slip.\(^{28,40,50,71}\) Such solutions indeed show two-step relaxation upon large stepwise strain in remarkable agreement with the theoretical depiction based on the Doi-Edwards tube model\(^{70}\). Some of the sharp stress decline was actually so severe that the data actually showed ultra strain softening, deviating downward from eqs 1 and 2, such as those of Osaki and coworkers\(^{44}\) in 1980 and of Vrentas and Graessley\(^{72}\) in 1982. But a subsequent 1982 paper from Osaki's lab\(^{45}\) produced stress relaxation behavior in quantitative agreement with the tube model prediction. It is this match between the experiment and theory that is well-known in the community\(^5\) and hailed as the great triumph of the tube model.

In the past 40 years, there have been two dozens of papers published on step strain of entangled polystyrene (PS) solutions,\(^{27-40,42-46,48-52}\) making the PS solutions a classical system to study nonlinear rheology of entangled polymers. Whenever, the data were in disagreement with the tube model, it was suggested\(^{40,50}\) that wall slip or other material instabilities or even instrument limitations were the cause. Indeed, in the case of ultra strain softening\(^{72}\), wall slip could be the origin of the steep stress decline at short times, leading to the two-step characteristic. But we were still left with the question of whether we fully understand the nature of the nonlinear responses when there is agreement between experiment and theory given by the damping function of eq 2.
Nearly all of the two dozen papers\textsuperscript{27-40, 42-46, 48-52} and other studies on other polymer solutions measured the damping function to compare with eq 2 instead of presenting the raw data of the actual relaxing stress as a function of time. We were not made aware of the fact that even the normal strain softening, as defined by eqs 1 and 2 and known as type B behavior\textsuperscript{40}, already involves too much softening. In other words, any data in agreement with the damping function of eq 2 would suggest that at long times \((t > t_k)\) the residual shear stress actually shows a maximum at \(\gamma > \sqrt{5}\) and eventually declines as \(1/\gamma\), as described by eq 1. When the experimental data of \(\sigma(\gamma, t > t_k)\) actually obeys eq 1, showing a decrease with \(\gamma\), we were alarmed and prompted to apply a particle-tracking velocimetric technique (PTV) in conjunction with the simultaneous rheometric measurements to answer the following questions. Did the reduced shear stress reflect a breakdown of the strained entanglement network? For well-entangled polymer solutions, could such a structural breakdown take place homogeneously?

Based on several entangled polybutadiene solutions, the recent PTV observations revealed\textsuperscript{73} that the stress relaxation after a sizable stepwise shear was non-quiescent, contradicting the wide-held perception that a shear-strained polymeric liquid should always relax quiescently upon shear cessation. A subsequent PTV study confirmed that macroscopic motions were still present during stress relaxation even when the imposed stepwise shear occurred at a rate too low according to the tube model to produce chain stretching.\textsuperscript{74}

The objective of the present study is to determine whether the previously observed non-quiescent relaxation is universal, in particular, whether the classical system of entangled polystyrene solutions\textsuperscript{27-40, 42-46, 48-52} would also show macroscopic motions
during stress relaxation if they are sufficiently entangled and possessive of a sizable slip length $b$.\textsuperscript{75}

3.3 Experimental

The material characteristics of the corresponding solvents and polymer solutions, and the experimental methods will be discussed in this Section.

3.3.1 Materials

Entangled polystyrene (PS) solutions were prepared by first dissolving a desired wt % of high molecular weight polystyrene in carbon disulfide. To this solution either tricresyl phosphate (TCP) or diethyl phthalate (DEP) was added to form a uniform solution. All previous PS solutions solutions\textsuperscript{27-40, 42-46, 48-52} used to study stress relaxation behavior were based on either TCP or DEP. For the present study, we prepared three solutions: two made of 7 volume % of PS-20M in TCP and DEP respectively, and the other of 20 volume % PS-2M in TCP. They are labeled as PS20M(7%-TCP), PS20M(7%-DEP) and PS2M(20%-TCP) respectively. Table 3.1 lists the basic information about the materials used in the present study.

The silver-coated particles (HGS-10) from Dantec Dynamics are polydisperse with the diameter ranging from 5 to 30 μm (were first ultrasonicated in CS$_2$ and then added to the PS solutions. The final loading of the particles was at a level of 200-500 ppm. Since the vapor pressure of TCP and DEP are rather high, carbon disulfide can readily evaporate under ambient conditions for nearly a week under a hood. The remaining carbon disulfide was removed in vacuum oven over several days.
Table 3.1. Molecular Characteristics of PS and solvents

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn</th>
<th>Source</th>
<th>Mw/Mn density</th>
<th>Pa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene-20M</td>
<td>20,000,000</td>
<td>Polymer Standard</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>Polystyrene-2M</td>
<td>2,000,000</td>
<td>Pressure Chemical</td>
<td>1.30</td>
<td></td>
</tr>
<tr>
<td>Polystyrene-20K</td>
<td>19,600</td>
<td>Polysciences</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>TCP(tricresyl phosphate)</td>
<td>368.37</td>
<td>Aldrich 1330-78-5</td>
<td>1.17</td>
<td>0.1</td>
</tr>
<tr>
<td>DEP(diethyl phthalate)</td>
<td>222.24</td>
<td>Aldrich 84-66-2</td>
<td>1.12</td>
<td>0.012</td>
</tr>
</tbody>
</table>

3.3.2 Apparatus

Step shear experiments of PS20M solutions were carried out on an Advanced Rheometric Expansion System (ARES) using a cone-plate geometry with diameter of 25 mm and cone angle of 4 degrees. The particle-tracking velocimetric (PTV) setup on ARES as depicted in Figure 3.1 allows simultaneous determination of the rheometric information and corresponding deformation field and is a key apparatus in the present study. The surfaces of the cone and plate were covered with black sand papers to minimize light reflection during the PTV observation, except for the PTV glass window. The sand paper was Waterproof silicon carbide P1000 Grid. Past studies have shown that topographically rough surface improves the mechanical coupling between the sample and shearing surfaces. The present study also revealed the effect of surface condition.

The PTV experiments on the PS2M(20%-TCP) solution were carried out on an Anton Paar MCR301 rotational rheometer based on parallel-plate geometry with diameter of 25 mm and a gap of 1 mm. The PTV setup on MCR301 involves wrapping a
transparent PET film around the meniscus with the CCD camera peeking horizontally through the film, as depicted previously. No sand papers were used in the parallel-plate setup.

In the PTV setup, the silver-coated particles embedded in the sample are illuminated by a sheet of laser light (cross-section 2 mm by 0.15 mm). The laser beam was incident into the sample at an appropriate angle as shown in Figure 3.1 so that a CCD camera (30 frames per second) can record through the same optical window. Movements of the particle were recorded by a Toshiba DR 430 recorder onto a DVD disc. To have a field of view around 1.5 mm by 1 mm, a DIN objective lens (3.2x) was mounted on the CCR camera through an adaptive tube (Edmund Optics: U54-868). The distance traveled by a particle can be determined frame by frame using Ulead VideoStudio SE DVD software. These PTV observations were made at a radial distance of 4 mm from the edge. The spatial resolution of our PTV is around 30 μm.

To make stepwise shear, we employ different protocols, including the stress relaxation mode where the prescribed strain of various magnitudes are applied within the same amount of time ca. 0.04 s, and a truncated startup shear that produces the various strains at the same shear rate.
3.4 Results and discussions

3.4.1 Characterization of linear viscoelastic properties

Small-amplitude oscillatory shear (SAOS) measurements were carried out at strain amplitude $\gamma = 4\%$ to determine linear viscoelastic properties of these PS solutions based on an Anton Paar MCR301 rotational rheometer coupled to a cone-plate assembly with 25 mm diameter and $2^\circ$ cone angle. Figure 3.2 (a) and Figure 3.2 (b) respectively show the storage and loss moduli as a function of the oscillation frequency $\omega$ for the two solutions of PS20M(7%-TCP) and PS2M(20%-TCP). From such SAOS measurements the basic linear viscoelastic properties such as the elastic plateau modulus $G_{pl}$, the reptation time $\tau_d$ and zero-frequency viscosity $\eta_0$, can be obtained as listed in Table 3.2
including the reptation time or terminal relaxation time $\tau$ and the Rouse relaxation time $\tau_R$.

Figure 3.2. (a) Small amplitude oscillatory shear measurements of storage (red circles, $G'$), loss moduli (blue squares, $G''$), and the complex viscosity, green solid triangles, $|\eta^*|$, as a function of frequency $\omega$, for PS20M(7%-TCP). (b) Small amplitude oscillatory shear measurements of storage (red circles, $G'$), loss moduli (blue squares, $G''$), and the complex viscosity, green solid triangles, $|\eta^*|$, as a function of frequency $\omega$, for PS2M(20%-TCP).
In particular, the Rouse relaxation time $\tau_R$ can be estimated in two ways, related either to the zero-shear viscosity $\eta$ or to the frequency dependence of storage modulus $G'$ in the Rouse regime.\textsuperscript{41,47} Specifically, we employ the following two formulas\textsuperscript{35} in our evaluation of $\tau_R$:

$$\tau_R = \frac{6M\eta}{\pi^2cRT} \left(\frac{M_c}{M}\right)^{2.4}$$

(3.4)

and

$$\tau_R = \left(\frac{aM}{1.111cRT}\right)^2$$

(3.5)

We also need to estimate the sample's ability to undergo wall slip by evaluating the slip length $b$ according to

$$b = (\eta/\eta_i)a,$$

(3.6)

where $\eta$ is the zero-shear solution viscosity, $\eta_i$ is the viscosity at the polymer/wall interface in absence of chain entanglement between adsorbed and unbound bulk chains, and the thickness of the entanglement-free interfacial layer $a$ is the entanglement spacing of the PS solution, which can be related\textsuperscript{38} to the entanglement spacing $l_{\text{ent}}$ of the pure PS melt and the polymer volume $\phi$ fraction in the solution as $a = l_{\text{ent}}\phi^{2/3}$. Here the entanglement spacing $l_{\text{ent}}$ is 7.2 nm for the PS melt.\textsuperscript{59,77,78} Since PS slows down the solvent dynamics, we cannot use the solvent viscosity as the interfacial viscosity $\eta_i$. We prepared two solutions based on a lower molecular weight PS as listed in Table 3.2 and measured their viscosity as listed in Table 3.1 to be used as $\eta_i$ in eq 6. The estimated values of $b$ are the upper bounds.
Table 3.2. Linear viscoelastic characteristics of the PS Solutions

<table>
<thead>
<tr>
<th>Solution samples</th>
<th>$\varphi, Z$</th>
<th>$\tau_d$ (s), $\tau_R$ (s)</th>
<th>$G_p$ (Pa)</th>
<th>$\eta_0$ (Pa.s)</th>
<th>b (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS20M(7%-TCP)</td>
<td>0.07 50</td>
<td>487 s, 3.68 s$^1$/4.88 s$^2$</td>
<td>447</td>
<td>122,940</td>
<td>3.8</td>
</tr>
<tr>
<td>PS2M(20%-TCP)</td>
<td>0.20 19</td>
<td>17.5 s, 0.278 s$^1$</td>
<td>4,700</td>
<td>40,000</td>
<td>0.11</td>
</tr>
<tr>
<td>PS20M(7%-DEP)</td>
<td>0.065 42</td>
<td>15.0 s</td>
<td>353</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS19.6K(20%-TCP)</td>
<td></td>
<td></td>
<td></td>
<td>2.58</td>
<td></td>
</tr>
<tr>
<td>PS19.6K(7%-TCP)</td>
<td></td>
<td></td>
<td></td>
<td>0.23</td>
<td></td>
</tr>
</tbody>
</table>

$^1$Calculated based on eq 4. $^2$Calculated based on eq 5.

3.4.2. Stress relaxation from conventional rheometry

The aim of this study is to characterize the nature of the stress relaxation behavior of entangled polystyrene solutions that are very similar to those studied in the past by rheometric measurements. However, the present study differs from those of the past in that the rheometric measurements are coupled with in situ PTV observations of the deformation field. Moreover, most measurements involved cone-plate and sand papers as the shearing surfaces. When either smooth steel surfaces are used or parallel-plate geometry is involved, we explicitly indicate such conditions within the figures.
PS20M(7%-TCP) stress relaxation mode

(a)

(b)

PS20M(7%-TCP)
shear rate = 5 s$^{-1}$
Figure 3.3 (a) Shear stress growth and relaxation of PS20M(7%-TCP) during and after discrete step shearing of different magnitudes by a similar time, where the effective shear rate ranges from 2 s\(^{-1}\) to 100 s\(^{-1}\). (b) Shear stress growth and relaxation PS20M(7%-TCP) during and after discrete step shearing of different magnitudes with same shear rate of 5 s\(^{-1}\), corresponding to a Weissenberg number \(Wi = 2435\). In (a) and (b), the shearing surfaces are sand papers. (c) Shear stress growth and relaxation of PS2M(20%-TCP) during and after discrete step shearing of different magnitudes with the same shear rate of 5 s\(^{-1}\), corresponding to \(Wi = 88\). (d) Shear stress growth and relaxation of PS2M(20%-TCP) during and after discrete step shearing of different magnitudes at two different shear rates of 1 and 10 s\(^{-1}\) respectively. In the (c) and (d), the shearing surfaces are smooth and metallic.
Our first experiment adopts the standard protocol used to study stress relaxation. In this stress relaxation mode, the prescribed strain is produced within a very short period around 0.04 s on the ARES rheometer. In a second experiment, we use a fixed shear rate to produce the prescribed strains. This amounts to terminating a startup shear test and conducting stress relaxation upon the shear cessation. For the PS20M(7 %-TCP) solution that has a reptation time τ = 487 s, a shear rate of 5 s⁻¹ is exceedingly fast, corresponding to a Weissenberg number of 2435. Figure 3.3 (a) and (b) respectively show the shear stress as a function of time during the stepwise shear and after shear cessation, involving the two different ways to produce the prescribed strains. A similar solution based on DEP as the solvent, i.e., PS20M(7 %-DEP), shows the same trend. We omit the actual stress relaxation data to spare some space. It is clear that the relaxing stress at any given time only increases with the imposed strain within the explored strain range, deviating significantly from the type B behavior depicted by eq 1. Osaki classified this as type A behavior⁴⁰. Note that these experiments involved sand papers glued onto the cone-plate to minimize any possible wall slip.

In contrast, for the less entangled solution of PS2M(20%-TCP), no sand papers were used to shear the sample. Shearing to different strain amplitude at a shear of 5 s⁻¹, involves Wi = 88. Figure 3.3 (c) shows the actual stress build-up and relaxation data as a function of time for the various strain amplitude from 0.5 to 8. Contrary to Figure 3.3 (b), the shear stress at the long times is lower for γ = 4 than for γ = 2 in Figure 3.3 (c).

Thus, it appears clear that the surface condition plays a role in these nonlinear relaxation experiments. To illustrate this effect, the same PS-20M(7 %-TCP) was stepwise sheared, based on smooth metallic cone-plates. Figure 3.3 (d) presents the stress
build-up and relaxation data for seven different strains, ranging from 0.1 to 15, where for
the two highest strains, a shear rate of 10 s\(^{-1}\) was used to ensure that the stepwise shear
was completed fast enough relative to the reptation time \(\tau\).

From plots such as Figure 3.3 a-d we can extract the damping function according to
its definition given by the first equality in eq 2. Figure 4 shows the damping function
obtained from the four stepwise shear experiments. It is interesting to note that the more
entangled solution of PS20M(7%-TCP) shows weaker strain softening when the sander
papers were used as the shearing surfaces. In other words, for smooth steel surfaces the
solution produces strain softening that falls onto the DE damping function, whereas the
same solution show type A behavior\(^{10}\) in presence of sand papers.

For PS solutions, it was found that the product of polymer concentration \(c\) (proportional to the weight fraction \(\phi\)) and molecular weight \(M\) dictates whether a sample
can be described by the DE damp function of eq 2 or not. Normally, a PS solution with
higher \(cM\) is more strain softening. Specifically, it was reported\(^{32}\) that the experimental
data were consistent with the tube model calculation of eq 2 only for \(cM < 10^6\),
corresponding to a relatively weak level of chain entanglement. When \(cM > 10^6\), the
solutions typically showed type C behavior, i.e., ultra strain softening, with their damping
function deviating downward from the DE damping function of eq 2. Indeed, the
PS2M(20%-TCP) satisfies \(cM < 10^6\) and happens to display its damping function in
agreement with eq 2 though we caution that this set of data was collected with parallel-
plate and therefore cannot be quantitatively compared with the tube model. On the other
hand, PS20M(7%-TCP) meets the condition of \(cM > 10^6\). But instead of type C
behavior\(^{10}\) found in the literature that usually involve metallic plates, we observed type A
behavior, i.e., the (open and filled) squares and circles are above the DE damping function. We attribute this to the use of sand papers as the shearing surfaces.

3.4.3 In situ PTV observations revealing non-quiescent relaxation

To explore the nature of the observed stress relaxation behavior, we conducted simultaneous PTV observations corresponding to the actual rheometric data presented in Figure 3.3 (a) to (c). We first present the PTV measurements after the various stepwise shear depicted in Figure 3.3 (c). Figure 3.5 shows that the stress relaxation depicted in Figure 3.3 (c) did not occur quiescently. Without the use of sand papers as the shearing surfaces, the step-strained PS2M(20%-TCP) appeared to have suffered "arrested" wall slip\(^79\) at the low strain of 2 as well as internal breakup at the high strains. In other words, the strained solution showed some failure at the sample/stationary-plate upon shear cessation for \(\gamma = 2\). There were also significant motions in the bulk at \(\gamma = 3\) and 4. Such breakup greatly relieved the residual shear stress and produced the strain softening shown in Figure 3.3 (c) and Figure 3.4. Similarly, the stress relaxation of the PS20M(7%-TCP) solution also involved macroscopic motions as shown in Figure 3.6. Non-quiescent relaxation is obvious in the first 60 s.
Figure 3.4 Damping function $h$ that represents the normalized stress relaxation at long times from the different tests involving different methods and different solution samples, along with the Doi-Edwards damping function as the thin line.

Figure 3.5 Particle-tracking velocimetric (PTV) detection of macroscopic motions after various discrete step strains, showing the displacements of tracked particles during a period of 20 seconds immediately after shear cessation. The displacements are normalized by the gap distance. Quiescent relaxation was found for strain equal to 1 and below.
3.4.4 Motions inside and outside

Admittedly, the experimental setup was imperfect in the sense it is a finite system, with a rim of free surface at the edge. Edge instability could complicate nonlinear rheological experiments. However, it is not an issue for the present step strain experiments because there is no edge fracture during the stepwise shear. Specifically, the PTV observations of the edge indicate a uniform deformation field up to the point of shear cessation. Moreover, during the stress relaxation the PTV observations only detected weaker macroscopic motions on the rim than inside the sample.
Specifically, we set up two cameras to observe both inside the sample and at the edge during stress relaxation for two discrete stepwise shear of the PS20M(7%-TCP) solution. Figure 3.7 show that there were the greater motions inside the sample than there were at the edge. Thus, this result is consistent with a previous conclusion that the non-quiescent relaxation took place without any edge instability. The previous study built and employed a special costumer-made cone-plate apparatus to insure that during the large step strain the edge did not suffer sufficient strain and remained motionless.

![Figure 3.7 Particle-tracking velocimetric (PTV) detection of macroscopic motions going on both inside the parallel plate as well as on the free-surface edge.](image)

3.4.5 Non-quiescent relaxation at Wi_R<0.1

Conventional step strain involves the application of the stress relaxation mode, i.e., to achieve the prescribed strain amplitude within a period negligibly shorter than the
reptation time $\tau$. Thus, step strain would definitely involve chain stretching. The strain softening shown in eq 1 and eq 2 occurs because the fast barrier-free chain retraction would take place on the Rouse time scale according to the tube model. The preceding stepwise strain experiments revealed macroscopic motions upon shear cessation. This was not anticipated by the tube theory because the chain retraction was thought to occur uniformly while the chain entanglement is preserved to assure quiescent relaxation.

We may note that numerical efforts$^{81, 82}$ have been made based on some version of the tube model. However, any discussion of their merits is beyond the scope of the present work and will be present elsewhere. In this subsection, we consider a slowly produced stepwise shear involving a rate so low that there would be no chain stretching according to the tube model. Consequently, there should not be any chain retraction during the stress relaxation, eliminating any molecular mechanism conceivable within the tube model framework to explain non-quiescent relaxation. In other words, after cessation from a stepwise shear involving a shear rate of 0.02 s$^{-1}$ corresponding to a Weissenberg number $Wi = 9.7$ and Rouse-Weissenberg number (the product of shear rate and Rouse relaxation time) $Wi_R = 0.074$, as shown Figure 3.8 (a), the stress relaxation should be quiescent according to the tube model. However, our in situ PTV observations show considerable motions after shear cessation as shown in Figure 3.8 (b).
Figure 3.8 (a) Shear stress growth and relaxation during and after discrete step shearing of different magnitudes at a low shear rate 0.02 s⁻¹, where the Rouse Weissenberg number is less than 0.1. (b) Particle-tracking velocimetric (PTV) detection of macroscopic motions after various discrete step strains, showing the displacements of tracked particles during a period of 60 second immediately after shear cessation. The displacements are normalized by the gap distance.
3.4.6 Inhomogeneity in LAOS

Well-entangled polymers with appreciable slip length undergo strain localization as an effective way to respond to large deformation that causes yielding through chain disentanglement. To show that there is nothing special about the present PS solutions, we also carried out large amplitude oscillatory shear (LAOS) experiments. Figure 3.9 (a) shows the steady-state Lissajous plots corresponding to strain amplitude ranging from 1 to 3. Our in situ PTV observations confirm that there is shear banding during the LAOS as shown in Figure 3.9 (b), similar to previous PTV observations of polybutadiene solutions.\textsuperscript{83} Thus, homogenous shear may not be a correct assumption for entangled polymeric systems under LAOS. When there is shear banding, theoretical analysis of LAOS\textsuperscript{84-86} becomes less perceptible.
Figure 3.9 (a) Lissajous plots in steady state, where sand papers were used as the shearing surface. (b) Particle-tracking velocimetric (PTV) measurements of the velocity field at different moments of a cycle during LAOS in steady state. The magnitude of the velocity is normalized by the gap distance.
3.5 Conclusion

Entangled polystyrene solutions have been studied in the past four decades in terms of their stress relaxation behaviors\textsuperscript{27-52} and been compared with the theoretical description based on the tube model\textsuperscript{5}. In fact, these previous studies have built a consensus that the tube model is a successful molecular theory for not only linear viscoelastic properties but also nonlinear rheological behavior of entangled polymers. Specifically, the agreement between some data and the theoretical damping function\textsuperscript{5,15} has been regarded as the validation of the tube theory despite the fact that a significant fraction of the data shows deviation from the theoretical formula of eq 1 and 2.

The present work is the first PTV study of the entangled PS solutions to show that they are not different from the other entangled polymer solutions. Although the PS is not monodisperse in the molecular weight distribution (MWD), the MWD is not too broad to suppress strain localization. Consistent with the previous PTV studies of other solutions,\textsuperscript{32} the classical PS solutions (a) also undergo non-quiescent relaxation after stepwise shear and (b) show stress relaxation behavior that deviates significantly from the tube model description. The macroscopic motions during stress relaxation affect the stress decay in a way that cannot be depicted by the tube model since the damping function is derived under the condition of quiescent relaxation. Also consistent with a past experiment,\textsuperscript{33} we observed non-quiescent relaxation even for a stepwise strain that was imposed so slowly that there would be no chain stretching according to the tube model. In absence of chain stretching, there would be no chain retraction after shear cessation to explain the emergence of non-quiescent relaxation within the framework of the tube model. The observed macroscopic motions seem to suggest that even this
slowly-imposed step shear involves significant chain stretching. It is the elastic retraction associated with the chain stretching that overcome the cohesion or entropic barrier associated with the chain entanglement.\textsuperscript{47}
CHAPTER IV

THE ORIGIN OF "STRAIN HARDENING": BASIC DIFFERENCE BETWEEN EXTENSION AND SHEAR; DIFFERENCE BETWEEN LINEAR AND BRANCHED POLYMERS

4.1 Introduction

In this chapter, we illustrate the origin of the so called "strain hardening" observed when comparing the transient stress response of entangled melts to uniaxial extension with that to simple shear. Strain hardening occurs when the transient extensional viscosity measured from a startup uniaxial extension of finite rate deviates upward from zero-rate transient viscosity. Our theoretical analysis shows that polymer melts would always exhibit strain hardening at sufficient high Hencky rates because the entanglement network can be effectively strengthened during extension and can only be weakened during shear. The kinematic difference between simple shear and uniaxial extension has two effects: (a) the force resulting from the startup deformation is measured from an increasingly shrinking area in uniaxial extension instead of a constant area as in simple shear; (b) the tendency of the entanglement network to yield, i.e., to undergo chain disentanglement is partially suppressed during startup extension at high Hencky rates.
In short, the phenomenon of strain hardening reflects the reality that entangled melts are not fluids but temporary solids and that the conventional description of their uniaxial extension in terms of the Cauchy stress contains a geometric condensation factor.

The subject of polymer rheology investigates respective mechanical responses to both simple shear and uniaxial extension. Traditionally, the two experimental fields of shear and extensional rheology have developed nearly independently partially because different instruments are required. On the other hand, for rheology to guide polymer processing, it is necessary to compare rheological behaviors of entangled polymer melts upon startup shear and extension. Indeed, from the beginning $^{87-89}$, the shear properties of polymer melts have been used as a reference when investigating the extensional rheological characteristics of low-density polyethylene (LDPE).

The phrase “strain hardening” was introduced to recognize an essential difference in the transient responses of entangled melts to startup shear and extension. Specifically, a difference arises when examining the rate dependence of the time-dependent transient viscosity in shear and extension: The transient shear viscosity $\eta_s^+(t)$ at a finite rate is always lower than that obtained in the zero-rate limit, $\eta_s^0(t)$, whereas the transient extensional viscosity $\eta_e^+(t)$ can deviate upward from the zero-rate elongational viscosity $3\eta_e^0(t)$. This upward deviation is known as strain hardening, whereas the downward trend is known as strain softening, as schematically illustrated in Figure 4.1 and Figure 4.2. A prominent example for such strain hardening behavior is LDPE $^{88,90-92}$. 
Figure 4.1 Schematic depiction of strain softening in shear and hardening in extension in terms of the transient viscosity $\eta^+$ and $\eta_{E}^+$ respectively, where the curve in the middle represents the response in the limit of vanishingly low Weissenberg number $Wi \ll 1$. 

Figure 4.2 Schematic depiction of the stress responses to startup shear (any rate) and extension (low rates) as well as extension (high rates), designated by the lower non-monotonic curve and the upper monotonic curve respectively. Here the stress is either the shear ($\sigma_{12}$) or the engineering extensional stress ($\sigma_{\text{engr}}$). The initial elastic stiffness is indicated by the dashed line with a slope equal to $G_{pl}$. With increasing deformation the effective modulus $G$ becomes lower, as shown for the case beyond the stress maximum.
It is usually thought\textsuperscript{93} that this feature of strain hardening is due to long chain branching (LCB) in LDPE\textsuperscript{87-97} because linear polyethylene such as high density polyethylene (HDPE) fails to display such upward deviation. The opposing trends in the transient rheological responses to shear and extension presented a great theoretical challenge when it was recognized that the popular K-BKZ model\textsuperscript{98,99} could not describe both the strain softening in shear and hardening in planar extension\textsuperscript{100}. A pom-pom model was subsequently developed by\textsuperscript{101} to offer a theoretical account of strain hardening. It is commonly perceived\textsuperscript{101-105} that chain stretching in extension is responsible for the observed "strain hardening" in startup extension.

Meanwhile, many experimental studies showed that linear melts with broad molecular weight distribution (MWD), and particularly linear polymers with bidisperse MDW could also show "strain hardening"\textsuperscript{103, 106-111}, invalidating the idea\textsuperscript{93} that LCB needs to be present for strain hardening to take place. More recently, even fairly monodisperse melts were found to show a upward deviation at high enough rates\textsuperscript{112,113}.

Nevertheless, strain hardening has been regarded as a feature indicative of specific chain architecture\textsuperscript{93,101,102}. Moreover, it was speculated that strain hardening is desirable and required to ensure good processability\textsuperscript{114}. For example, in fiber spinning it is often suggested that polymer melts should have strain hardening characteristic to enhance spinnability as if strain hardening is a material property of certain polymer materials\textsuperscript{115}. 

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4.2 Experimental

Our uniaxial extension experiments are based on three polymer melts: one linear 3,4-polyisoprene (ca. 60% 3,4-content), one dendritic PI with the same microstructure, and a linear styrene-butadiene rubber (SBR). The synthesis of the dendritic polyisoprene is rather involved and has been described in the literature\textsuperscript{116}. We first carried out small amplitude oscillatory shear measurements using a Physica MCR 301 rotational rheometer equipped with 15mm parallel plates. Figure 4.3 (a), 5(b) and 5(c) show the storage and loss moduli $G'$ and $G''$ as a function of the oscillation frequency $\omega$, from which we obtain basic linear viscoelastic characteristics such as the reptation time $\tau$ and the elastic plateau modulus $G_{pl}$, as listed in Table 4.1. The number of entanglements per chain $Z$ can be estimated as $Z = \frac{M_w}{M_e} = \frac{M_w}{(\rho RT/G_{pl})}$. 
\( G'_p = 0.32 \text{ MPa} \)
\( G''_p = 0.53 \text{ MPa} \)
\( \tau = 2533 \text{ s} \)
\( T_{\text{ref}} = 25 \degree \text{C} \)
\( G\text{pl} = 0.32 \text{ MPa} \)
\( \eta^* \)
\( \omega \) (rad/s)
\( T_{\text{ref}} = 25 \degree \text{C} \)
\( \eta^* \)
\( \omega \) (rad/s)
\( G\text{pl} = 0.53 \text{ MPa} \)
\( \tau = 2532 \text{ s} \)
\( T_{\text{ref}} = 25 \degree \text{C} \)
\( \eta^* \)
\( \omega \) (rad/s)

(a)

(b)
Figure 4.3 Small amplitude oscillatory shear measurements of linear (a) polyisoprene and (b) SBR melts, and (c) a dendritic polyisoprene melt at a reference temperature $T_{\text{ref}} = 25$ °C.

Table 4.1 The Molecular Characteristics of polymer Melts

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$ (kg/mol)</th>
<th>$M_w/M_n$</th>
<th>$\tau$ (s)</th>
<th>$G_{pl}$ (MPa)</th>
<th>$Z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear PI</td>
<td>356</td>
<td>1.08</td>
<td>2533</td>
<td>0.32</td>
<td>50</td>
</tr>
<tr>
<td>Dendritic PI</td>
<td>176</td>
<td>1.08</td>
<td>11.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBR</td>
<td>161</td>
<td>1.05</td>
<td>2532</td>
<td>0.53</td>
<td>37</td>
</tr>
</tbody>
</table>

All the uniaxial extension experiments were carried out at room temperature (approximately 23°C) using a first generation SER fixture $^{117,118}$ mounted on a Physica MCR 301 rotational rheometer or a strain control rheometer ARES-LS at a constant Hencky strain rate $\dot{\varepsilon}$, as well as Instron Material Testing System (model 5543, maximum velocity: 1000 mm/min) that stretches the samples according to Eq. (11)-(13). The specimens for extension experiments were made by first preparing solutions based on toluene and then casting the solutions on a PTFE plate at room temperature. The cast
solutions were left under a hood for days to allow solvent evaporation before placed in a vacuum oven to remove residual toluene. The typical dimension of the sample was 21 mm × 2 mm × 0.4 mm. The stretching was video-recorded at the rate of 30 frames per second to allow post-experiment analyses.

4.3 Theoretical analysis and experimental results

4.3.1 Theoretical analysis

4.3.1.1 Origin of strain softening in startup shear: yielding

Monodisperse entangled melts may be treated as a “uniformly crosslinked network” on time scales much shorter than their terminal relaxation times, also known as the reptation time $\tau$ in the literature. Such a Gaussian chain network may exhibit a simple linear relationship between the stress and strain in startup simple shear, involving an elastic plateau modulus $G_{pl}$, according to

$$\sigma_{12}^{\text{ideal}}(t) = G_{pl} \dot{\gamma}(t) = G_{pl} \dot{\gamma} t,$$

where the imposed strain grows linearly with time at a given shear rate: $\dot{\gamma}(t) = \dot{\gamma} t$. It is well known that the stress growth of entangled melts (at temperatures well above the glass transition temperature) upon a startup shear cannot be stronger than linear with time, i.e., Eq. (1) is the upper limit.

In the zero-shear limit, i.e., for the Weissenberg number $Wi = \dot{\gamma} \tau \ll 1$, the shear stress grows essentially linearly with time $t$ up to a time scale comparable to $\tau$ before molecular diffusion prevents any further elastic deformation and corresponding stress
increase. It is customary to depict the stress response in a normalized manner, i.e., in terms of the so called transient shear viscosity, rewriting Eq. (1) as

$$\eta_0^*(t) = \sigma_{12}^{ideal}(t) / \dot{\gamma} = G_{pl} t. \quad (4.2)$$

Eventually $\eta_0^*(t)$ reaches a plateau given by $\eta_0^*(t \approx \tau) = \eta_0 \approx G_{pl} \tau$, which is the so called zero-shear viscosity.

On the other hand, for a startup shear with $Wi > 1$, the shear stress $\sigma_{12}(t)$ no longer grows linearly with the imposed strain $\gamma(t)$ after a certain time $t_y$ as depicted in Figure 4.2. In an entangled melt, the intermolecular interactions are never strong enough to prevent yielding of the entanglement network in simple shear at $t_y$. Such yielding occurs when the intrachain elastic retraction force grows to reach a limiting magnitude of the intermolecular gripping force. At and beyond this moment, chains start to slide past one another at the entanglement points $^{119,120}$. As the number of load-bearing entanglement strands decreases, the elastic plateau modulus $G(\gamma)$ is reduced from the equilibrium value $G_{pl}$ as shown in Figure 4.2 for $t > t_y$. In other words, Eq. (1) becomes generalized as

$$\sigma_{12} = G(\gamma) \dot{\gamma}, \quad (4.1')$$

where $\gamma = \dot{\gamma} t$. The transient shear viscosity for a finite $Wi$ is then given by

$$\eta^*(t) = \sigma_{12}(t) / \dot{\gamma} = \eta_0^*(t) h(\gamma), \quad (4.3a)$$

where the strain softening function $h$ is given by

$$h(\gamma) = G(\gamma) / G_{pl} < 1, \quad (4.3b)$$
which is the ratio of the two slopes according to Figure 4.2, and equals to unity for \( t < t_y \).

Therefore, there is always strain softening in simple shear, i.e., \( \eta^+(t) < \eta_y^+(t) \), whose physical origin is yielding of the entanglement network. Eventually, more load bearing entanglement strands disappear so that the further elastic deformation of the surviving strands cannot compensate for the loss of elastic retraction from the vanishing strands, causing \( \sigma_{12}(t) \) to decline at \( t > t_{\text{max}} \) as shown in Figure 4.2. We have suggested this non-monotonic behavior to signal yielding \(^{112, 119}\).

4.3.1.2 Origin of “strain hardening” in startup extension: geometric condensation

Let us examine, in parallel, the response of an entangled melt to startup uniaxial extension. Specifically, the uniaxial extension is typically carried out at a constant Hencky rate \( \dot{\varepsilon} \). As a Gaussian chain network, at short times before occurrence of any structural rearrangement, an entangled melt could display a stress vs. strain relation similar to that anticipated by the classical theory of rubber elasticity

\[
\sigma_{\text{engr}}(\lambda) = G_p(\lambda-1/\lambda^2),
\]

where the engineering stress \( \sigma_{\text{engr}} \) is defined as the total tensile force divided by the sample’s initial cross-sectional area \( A_0 = A(\lambda=1) \), and the stretching ratio \( \lambda \) is related to the Hencky strain \( \varepsilon \) as

\[
\varepsilon = \dot{\varepsilon} t = \ln\lambda
\]

or
\[ \lambda = \exp(\varepsilon) = 1 + \varepsilon + O(\varepsilon^2). \quad (4.6) \]

In the limit of \( Wi << 1 \), the tensile force (i.e., \( \sigma_{\text{engr}} \)) tends to grow as the elastic deformation of the entanglement network increases until times close to \( \tau \) when the molecular diffusion becomes dominant. Insertion of Eq. (6) into Eq. (4) gives

\[ \sigma_{\text{engr}}^{\text{ideal}} (Wi << 1) = (3G_{pl}) \varepsilon = 3G_{pl} \dot{\varepsilon} t, \quad (4.7) \]

which follows because for \( Wi << 1 \) we have \( \varepsilon << 1 \) up to \( t \sim \tau \). Eq. (7) states that both \( \sigma_{\text{engr}}^{\text{ideal}} \) and Cauchy stress \( \sigma_{\text{engr}}^{\text{ideal}} = \sigma_{\text{engr}}^{\text{ideal}} \lambda = \sigma_{\text{engr}}^{\text{ideal}} \) increase linearly with time. Thus, we can show that the zero-rate transient elongational viscosity \( \eta_{E0}^+(t) \) grows linearly in time with a slope equal to the Young’s modulus \( 3G_{pl} \)

\[ \eta_{E0}^+(t) = \sigma_{\text{engr}}^{\text{ideal}} (Wi << 1) / \dot{\varepsilon} = 3G_{pl} t, \text{ for } t < \tau. \quad (4.8) \]

At long times, i.e., \( t \sim \tau \), the zero-rate transient viscosity saturates to the steady-state value \( \eta_{E0}^+(t \approx \tau) = \eta_{E0} = 3G_{pl} \tau \), which is simply \( 3\eta_0 \).
Figure 4.4 Numerical plots of the $g(\lambda)$ of Eq. (9d), $g(\lambda)/\lambda$ and $(\lambda^2+\lambda+1)/3$ as a function of the stretching ratio $\lambda$, where the inset shows how $g$ scales with $\lambda$.

On the other hand, for a startup extension with $Wi > 1$, the elastic deformation would last until significant yielding takes place at the peak of $\sigma_{\text{engr}}$ at time $t_{\text{max}}$. The deviation from the ideal elastic behavior of Eq. (4) starts at $t_y$ as depicted in Figure 4.2 when some load bearing entanglement strands start to disappear. The consequence of such partial yielding is softening of the entanglement network, so that an effective elastic modulus $G(\lambda)$ replaces the equilibrium $G_{\text{pl}}$ in Eq. (4), i.e.,

$$\sigma_{\text{engr}}(\lambda) = G(\lambda)(\lambda - 1/\lambda^2).$$

(4.4')

Thus, we have the following expression of the transient extensional viscosity $\eta^e_\ell(t)$ for a finite $Wi$, noting $\sigma = \sigma_{\text{engr}}\lambda$. 
\[ \eta^*_E(t) = \sigma(t)/\dot{\varepsilon} = \eta^*_E(t_0) f(\lambda), \]  
\( (4.9a) \)

where the factor \( f(\lambda) \) is given by

\[ f(\lambda) = h(\lambda) g(\lambda), \]  
\( (4.9b) \)

with the strain softening function given by

\[ h(\lambda) = G(\lambda)/G_{pl}, \]  
\( (4.9c) \)

analogous to Eq. (3b), and the geometric enhancement function defined by

\[ g(\lambda) = \lambda \left[ \frac{\lambda - 1/\lambda^2}{3\ln(\lambda)} \right]. \]  
\( (4.9d) \)

In contrast to the case of strain softening in simple shear depicted in Eq. (4.3a-b) by

\[ h < 1, f(\lambda) \text{ could be greater than unity, i.e., we could have } \eta^*_E(t) > \eta^*_E(t_0) \text{ because } g(\lambda) > 1 \]

and grows with \( \lambda \). An upward deviation would occur when the geometric enhancement factor \( g(\lambda) \) offsets the decline of \( h(\lambda) \) that arises from yielding. Specifically, Figure 4.4 shows how the various factors change with \( \lambda \). Thus, whether the “strain hardening” shows up depends on the yielding characteristic depicted by \( h(\lambda) \).

On the other hand, because of their extremely low glass transition temperature, HDPE resins possess fast relaxation dynamics. Typical experimental conditions correspond to modest values of \( Wi \), for which yielding occurs readily at a rather low degree of extension. In other words, \( h(\lambda) \) soon decreases before \( g(\lambda) \) increases significantly so that \( f(\lambda) \) of Eq. (4.9b) never gets to rise above unity. Consequently, HDPE typically shows no “strain hardening”. In contrast, if an entangled melt can be
extended rapidly so that only partial yielding occurs as sketched in Figure 4.2 (in green), we showed that \( \eta_E^+(t) > \eta_{E0}^+(t) \) can happen during startup extension\(^{112,113}\).

When the response is evaluated in terms of so called engineering transient viscosity

\[
\eta_{\text{engr}}^+(t) = \frac{\sigma_{\text{engr}}(t)}{\dot{\varepsilon}} = \eta_{E0}^+(t) j(\lambda),
\]

where the function \( j \) is given by

\[
j(\lambda) = f(\lambda)/\lambda,
\]

with \( f \) defined in Eq. (4.9b). The plot in Figure 4.4 shows that \( j(\lambda) \) is approximately equal to \( h(\lambda) < 1 \) because \( g(\lambda)/\lambda \) stays around unity for a wide range of \( \lambda \). Therefore, it is this engineering viscosity \( \eta_{\text{engr}}^+(t) \) that could be a suitable measure to reflect the fact that actually strain softening takes place, not strain hardening.

The comparison between Eq. (4.9a-d) and Eq. (4.10a-b) has allowed us to indicate that the origin of the upward trend of \( \eta_E^+(t) \) arises primarily from the extra factor of \( \lambda \) associated with the areal shrinkage. Now we would like to examine whether the “strain hardening” would also occur in an Instron-style extension that grows only linearly in time, analogous to the evolution of shear strain \( \gamma(t) = \dot{\gamma} t \), having the two ends of a specimen displaced away in opposite directions with velocity \( V^*/2 \) so that the stretching ratio \( \lambda \) increases linearly in time as

\[
\lambda(t) - 1 = V^*/L_0 = \dot{\varepsilon}_0 t \quad (4.11)
\]

where \( L_0 = L(t = 0) \), and the initial Hencky rate is given by
\[ \dot{\varepsilon}_0 = \frac{V^*}{L_0}. \]  

(4.12)

In terms of \( \dot{\varepsilon}_0 \), the time-dependent Hencky rate is given by

\[ \dot{\varepsilon}(t) = \frac{V^*/L(t)}{\lambda(t)} = \frac{\dot{\varepsilon}_0}{1 + \dot{\varepsilon}_0 t}, \]  

(4.13)

where use is made of Eq. (11). In this case, the transient extensional viscosity would be given by

\[ \eta^+_{\varepsilon}(t) = \sigma(t)/\dot{\varepsilon} = G(\lambda)(\lambda^2 - 1/\lambda)(\dot{\varepsilon} / \dot{\varepsilon}_0) = \eta^+_{\varepsilon0}(t) h(\lambda) \left[ \frac{(\lambda^2 + \lambda + 1)}{3} \right], \]  

(4.14)

where \( h \) is defined in Eq. (4.9c). Here for notational simplicity, we do not differentiate the strain softening function \( G(\lambda) \) produced under a variable Hencky rate from that corresponding to a constant Hencky rate. Figure 4.4 shows that \( (\lambda^2 + \lambda + 1)/3 \) goes significantly above unity for \( \lambda > 2 \). Thus, the “strain hardening” could show up even in Instron style melt stretching.

In summary, the shear stress never grows with time more strongly than it does (linearly) at low strains or at vanishingly low rates. This is not the case for uniaxial extension. At vanishingly low rates, the Cauchy stress \( \sigma \) is linear in time and saturates around \( t = \tau \). But at high rates, i.e., for \( Wi >> 1 \), \( \sigma \) can grow faster with time than linearly due to the shrinkage of the cross-sectional area. Consequently, when characterized in terms of the transient extensional viscosity, opposing trends could emerge in response to startup deformation, as depicted in Figure 4.1.
Figure 4.5 A molecular picture depicting the consequence of startup uniaxial extension, where the dots represent the load-bearing entanglement strands (LBES) in the cross-section. During the initial elastic deformation from (a) to (b), all LBES are present, leading to the depicted geometric condensation. Note that the drawing does not violate the mass density conservation since we did not draw strands in the cross-section that are not load-bearing: the percentage of LBES in the cross-section increases before yielding at the expense of the non-LBES. Yielding corresponds to loss of LBES in the cross-section, as illustrated in (c).

Specifically, the real difference between simple shear and uniaxial extension is as follows. Shear stress $\sigma_{12}$ is measured from the force exerted on the shear plane of a constant area whereas the Cauchy stress $\sigma$ is evaluated from the tensile force on an ever shrinking cross-sectional area. Thus, during elastic deformation in the initial phase of startup extension, i.e., before any massive yielding takes place, there is some obvious geometric condensation: the same number of load-bearing entanglement strands is condensed to a reduced cross-sectional area as depicted in Figure 4.5. The geometric condensation is bound to occur and produces noticeable “strain hardening” if yielding only takes place after a significant degree of extension.

The transient extensional viscosity in the zero-rate limit, $\eta_{\text{ext}}(t)$, involves a negligible amount of stretching so that the shrinkage of the cross-sectional area is negligible, and therefore there is little geometric condensation. In contrast, the transient extensional viscosity $\eta_{\text{ext}}(t)$ for $Wi > 1$ may be enhanced due to the geometric
condensation. As long as entangled melts undergo partial elastic deformation so that the strain softening function $h$ of Eq. (4.9c) does not drop as quickly as the areal shrinkage, i.e. as long as $\lambda h(\lambda) > 1$, $\eta_{\text{E}}(t)$ of Eq. (4.9a) would necessarily deviate upward from $\eta_{\text{E}0}(t)$ in startup uniaxial extension because Figure 4.4 shows that $g(\lambda)/\lambda$ is always above unity.

In the reminder of this paper, we will use both linear and dendritic polymer melts to verify the theoretical analysis, i.e., to show by experiment that the difference sketched in Figure 4.1 arises as long as the number of the load-bearing strands does not decreases as rapidly as the shrinkage of the cross-sectional area during startup uniaxial extension. In other words, it is the geometric condensation elucidated in Figure 4.5 that causes us to see monotonic rises of the Cauchy stress and transient extensional viscosity with time, in contrast to the non-monotonic behavior of the shear stress associated with the overshoot.

4.3.2 Breakdown of time-temperature equivalence at high rates and low temperatures

4.3.2.1 Yielding-to-rupture transition

We first present uniaxial extension measurements on the linear PI356K melt. Figure 4.6 shows that at low rates the engineering stress $\sigma_{\text{enr}}$ is non-monotonic, reflecting yielding due to force imbalance between the rising intrachain elastic retraction force and intermolecular gripping force $^{120}$. At high enough rates, the initial yielding ceased, and the surviving entanglement network can further stretch until the point of window-glass like rupture, which has recently been studied in some detail in our lab $^{113, 121, 122}$. This rupture behavior is preceded by non-Gaussian chain stretching, as most noticeably seen
in the data of rate 1 s⁻¹ in Figure 4.6. To show that yielding has taken place, corresponding to the emergence of the overshoot in $\sigma_{\text{engr}}$, we replot a typical set of data obtained at the Hencky rate of $\dot{\varepsilon} = 0.03$ s⁻¹. Figure 4.7(a) indicates several characteristics associated with the yielding behavior. First, the tensile force measured in terms of $\sigma_{\text{engr}}$ shows a peak around $t_{\text{max}} = 40$ s after the startup extension. This is a time scale much shorter than the reptation time $\tau = 2533$ s, within which the entanglement network cannot relax appreciably in quiescence. The deviation from the ideal elastic deformation of Eq. (4.4), which is designated by the straight line in Figure 4.7(a), occurred a few seconds after the start of the experiment. A quantitative measure of the degree of yielding has been defined in the preceding Section II in terms of the strain softening function of Eq. (4.9c)

$$ h(\lambda) = \frac{G(\lambda)}{G_{\text{pl}}} \equiv \frac{\sigma_{\text{engr}}(\lambda)}{[G_{\text{pl}}(\lambda-1/\lambda^2)]}, $$

(4.15)

which can be experimentally evaluated in the example of the startup extension with $\dot{\varepsilon} = 0.03$ s⁻¹, where the initial slope $G_{\text{pl}}$ in Figure 4.7(a) is indeed the shear plateau modulus equal to 0.323 MPa as listed in Table 1. Figure 4.7(b) shows the strain softening function $h(\lambda)$ based on the data of Figure 4.7(a). The inset of Figure 4.7(b) indicates that $h(\lambda)$ drops more deeply than $1/\lambda$ at large values of $\lambda$ because $\sigma_{\text{engr}}$ eventually decreases with $\lambda$ as shown in Figure 4.7(a).

According to the theoretical analysis of Section II, i.e., Eq. (4.9a-d), such significant yielding, starting rather early during the startup extension, makes it difficult to see any "strain hardening", i.e., $f(\lambda)$ of Eq. (4.9a) is hardly above unity as $h(\lambda)$ drops more steeply than $1/\lambda$. although the geometric factor $g(\lambda)$ also scales with $\lambda$ more strongly than linearly,
as indicated in the inset in Figure 4.4. Therefore, we may expect the data at \( \dot{\varepsilon} = 0.03 \text{ s}^{-1} \) to produce no appreciable upward deviation of \( \eta^e_\varepsilon(t) \) from \( \eta^e_{\varepsilon_0}(t) \) before the sample undergoes non-uniform extension. Moreover, because of the geometric condensation effect we do not usually see appreciable downward deviation either, in sharp contrast to the case of simple shear, despite occurrence of yielding.

![Figure 4.6](image)

Figure 4.6 Engineering stress \( \sigma_{\text{engr}} \) as a function of extensional deformation factor \( (\lambda - 1/\lambda^2) \) for the linear PI356K melt at different Hencky rates ranging from 0.001 to 1 \text{ s}^{-1}. For rates 0.3 \text{ s}^{-1} and higher above, the tensile force grows monotonically until rupture.
Figure 4.7 (a) At the applied rate of 0.03 $s^{-1}$, engineering stress $\sigma_{\text{engr}}$ is seen to show an overshoot at $t_{\text{max}} = 40$ s. Confirming the sketch of Figure 4.2, the data deviate from the ideal elastic deformation denoted by the straight line with slope equal to $G_{\text{pl}}$ to show the characteristic of yielding. (b) Plot of the strain softening function $h(\lambda)$ defined by Eq. (15) where $\sigma_{\text{engr}}$ is taken from the data in (a) and $G_{\text{pl}}$ is determined from the initial slope as shown in (a). The inset shows that $h(\lambda)$ eventually decreases with $\lambda$ more steeply than $1/\lambda$. 
Figure 4.8 Transient viscosity $\eta^*_E(t)$ and transient engineering viscosity $\eta^*_\text{engr}(t)$ as a function of time $t$ for the linear PI356K melt at different Hencky rates, replotted from Figure 4.6, where all the data of bend downward. The linear response data are taken from the small amplitude oscillatory shear measurements according to $^{123} \eta^*_\text{engr}(t) \big|_{t=1/\omega} = 3|\eta^*(1/\omega)|$.

Conversely, if we remove the geometric compression factor $\lambda$, i.e., represent the transient response in terms of the transient engineering viscosity defined in Eq. (4.10a-b), only "strain softening", i.e., a downward trend can be expected. Figure 4.8 illustrates the two different ways to describe the transient responses at the various Hencky rates. In particular, it confirms a basic conclusion that "strain hardening" is usually absent in startup uniaxial extension of linear entangled melts that cannot be stretched fast enough. In the other words, at rates that allow yielding to fully develop, there is sufficient strain softening to overcome the geometrical factor associated with the definition of Cauchy stress $\sigma$, involving an ever shrinking area in the denominator.
This is the sole reason why high-density polyethylene (HDPE) has not shown "strain hardening". HDPE does not show strain hardening because a typical uniaxial extension is not fast enough for it to avoid catastrophic yielding, not because long-chain branching must be there, as asserted in the literature. When represented in terms of the transient engineering viscosity $\eta^\text{engr}(t)$ that removes the effect of geometric condensation, there is only the sign of strain softening. For the present 3,4-PI linear melt with an extremely long reptation time, it is straightforward to reach a different regime where yielding is only partial and a sufficient amount of chain entanglement survives to allow continued elastic deformation and rising tensile force until the point of rupture. Consequently, at the high rates equal to and above 0.1 s$^{-1}$, we see a noticeable amount of "strain hardening" in Figure 4.8.
Figure 4.9 Transient extensional viscosity $\eta_E(t)$ obtained from either constant Hencky rate extension or Instron style extension where the initial Hencky rate $\dot{\varepsilon}_i = 0.03, 0.1, 0.3, 0.8, 1.2, \text{ and } 1.6 \text{ s}^{-1}$ respectively. Also plotted are the linear response data taken from the small amplitude oscillatory shear measurements according to $\eta^{*}(1/\omega)$. 
Figure 4.10 (a) The engineering stress $\sigma_{\text{engr}}$ as a function of extensional deformation for the dendritic PI176K melt at four different Hencky rates. (b) Transient extensional viscosity of the dendritic PI176K melt as a function of time at the four different Hencky rates of 0.03, 0.1, 0.3 and 0.75 s$^{-1}$. The linear response data from small amplitude oscillatory shear measurements also presented as a reference according to $\eta^*_{\text{Eo}}(1/\omega) = 3|\eta^*(1/\omega)|$. For comparison also plotted is transient engineering viscosity at 0.03 s$^{-1}$.
Our theoretical analysis in Section II shows that the exponential rise of uniaxial
deformation in Eq. (4.6) is not necessary to observe "strain hardening". Even when the
stretching ratio grows linearly in time as shown in Eq. (4.11), the geometrical factor \( \lambda \)
involved in the definition of the transient extensional viscosity \( \eta_{\varepsilon}(t) \) can still produce an
upper deviation from the linear time dependence, provided that the yielding does not
produce massive decline in the tensile force. In Figure 4.9 we show a comparison of
constant-Hencky-rate extension (in filled symbols) with Instron style extension (in open
symbols) involving six different rates, based on a second entangled melt of linear SBR
chains. Here the Instron style extension involves an initial Hencky rate \( \dot{\varepsilon}_0 \) defined in Eq.
(4.12), taken to have the same values as those used in the constant Hencky rate extension,
equal to 0.03, 0.1, 0.3, 0.8, 1.2 to 1.6 s\(^{-1}\) respectively. At these rates, the elastic
deformation ensues for a significant degree of extension, allowing the upward deviation
to be observed before the yielding eventually brought down the Cauchy stress at the three
lowest rates of 0.03, 0.1 and 0.3 s\(^{-1}\) in Instron style extension.

Finally, we examine the uniaxial extension behavior of a long-chain-branched (LCB)
polyisoprene melt. Because of the dendritic chain architecture\(^{97, 104, 116}\), it is far more
difficult, upon reaching the point of force imbalance and yielding\(^{62}\), for chain retraction
to take place rapidly. Consequently, the chain disentanglement leading to the eventual
structural breakdown can be significantly delayed during extension so that the tensile
force can remain appreciable at high stretching ratios. Figure 4.10(a) shows the
engineering stress \( \sigma_{\text{engr}} \) as a function of deformation. These data remind us of the similar
rheological responses of LDPE melts. Such melts with LCB show extraordinary upward
deviation as shown in Figure 4.10(b). But in reality, the d-PI melt actually is undergoing
significant yielding. Otherwise, the tensile force would have grown up monotonically with the applied strain. Thus, much of this “strain hardening” is a result of the conventional representation based on the transient extensional viscosity. We show in Figure 4.10(b) that in terms of the engineering transient viscosity, $\eta_{\text{engr}}^+(t)$, analogous to Figure 4.8, there is only a downward deviation, reflecting the fact that yielding has occurred.

4.5 Summary

When comparing nonlinear rheological responses of entangled melts to their linear viscoelastic characteristics, it is important to have a clear depiction of the rheological state in the limit of vanishing rate. Upon startup deformation in the zero-rate limit, i.e., for $Wi \ll 1$, the entanglement network would remain intact at all times. It renews its entanglement structure when the time approaches the reptation time $\tau$. Thus, the initial (transient) response is elastic deformation of the initial equilibrium entanglement network. Consequently, the zero-rate transient viscosity is given by Eq. (4.2) for simple shear and by Eq. (4.8) for uniaxial extension, showing that it grows linearly with time $t$ up to $\tau$ with a slope characteristic of the maximum strength of the entanglement network, i.e., the equilibrium elastic plateau modulus $G_{\text{pl}}$. Upon startup shear with $Wi > 1$, the entanglement network can only become softer over time with a lower elastic modulus $G(\gamma)$ as shown in Figure 4.2. Therefore, the growth of transient shear viscosity $\eta^+(t)$ with time $t$ is only weaker than that depicted by Eq. (4.2).
The situation is rather different for uniaxial extension. The zero-rate transient viscosity $\eta_{e0}^+(t)$ is evaluated as follows: Up to $\tau$ when $\eta_{e0}^+(t)$ approaches $3\eta_0$, there is little cross-sectional area shrinkage as the Hencky strain would be no higher than $\varepsilon \tau = \tilde{W}i << 1$, and thus $\eta_{e0}^+(t)$ involves little geometric condensation. At sufficiently high rates of extension, the entanglement network may still remain partially intact even after a significant amount of extension. Because of the corresponding cross-sectional area shrinkage, the system is actually in effect strengthened, going from Figure 4.5(a) to (b). The upward deviation of $\eta_{e}^+(t)$ from $\eta_{e0}^+(t)$ amounts to involvement of a higher elastic modulus than $3G_{pl}$, which arises from the geometric condensation illustrated in Figure 4.5(b) relative to (a). In other words, despite the fact that the same kind of yielding observed in simple shear has also taken place during the startup uniaxial extension the effect of the geometric condensation is present and can cause the appearance of “strain hardening”.

In conclusion, the so called strain hardening takes place when comparing the transient responses of entangled melts to simple shear with uniaxial extension. The phenomenon originates from the difference in the kinematics between shear and extension. Both linear chains and polymers containing LCB show strain hardening when the uniaxial extension involves sufficiently high strain rate. Indeed, polymers with LCB may make this kinematic difference more dramatic by delaying the eventual breakdown of entanglement network during extension so as to amplify the effect of the geometric condensation.
CHAPTER V

SYNTHESIS AND MELT EXTENSION OF ULTRA-HIGH MOLECULAR WEIGHT LONG-CHAIN BRANCHED POLYSTYRENES

The branched samples provided by our collaborators don’t have long and multiple branches which are limited by the available synthetic methods. We designed and explored a new synthetic strategy for ultra-high molecular weight long-chain branched (LCB) polymers with equal spacing between adjacent branch points. This method can synthesize LCB polystyrene (LCB-PS) with total molecular weight of 4.9 million g/mole, 16 branches of 140 kg/mole and polydispersity index of 1.5. The introduction of multiple branch points with long side chains allows the LCB-PS to resist the elastic-driven decohesion. Even after a large step extension of stretching ratio $\lambda = 7.4$, the specimen would not undergo elastic breakup that occurs in linear PS even at $\lambda = 2.7$. These LCB-PSs are also extraordinarily more stretchable during startup uniaxial extension, with the maximum engineering stress emerging at stretching ratio $\lambda_{max} \approx 4\sqrt{\frac{M_{bb}}{M_e}}$, where $M_{bb}$ is the molecular weight of backbone and $M_e$ is the molecular weight between entanglements.
5.1 Introduction

Long-chain branching (LCB) can greatly influence processing and rheological behavior of polymers as demonstrated in previous studies on low-density polyethylene (LDPE)\textsuperscript{89, 93, 124-129}. Branched polymers show stronger "strain hardening" in uniaxial extension and better processability in film blowing\textsuperscript{131} than linear polymers. They are also important viscosity modifiers\textsuperscript{132-134}. Since the chain architecture in LDPE is rather irregular\textsuperscript{135}, recent rheological studies focused on model LCB polymers with well-defined branching structures to study the dynamics of branches. These polymers, mostly polystyrenes and polydienes, have defined branch architectures such as hyper-branch\textsuperscript{97, 116, 136, 137}, comb\textsuperscript{138-143}, H-shape\textsuperscript{144-146}, and pom-pom\textsuperscript{147-149} (arm\textsubscript{q}-backbone-arm\textsubscript{q}, a long backbone connecting with another q arms). In this notation, an H-shaped chain is arm\textsubscript{2}-backbone-arm\textsubscript{2}, i.e., q equals 2. Grafting\textsuperscript{138} usually cannot control spacing between two branch points thus the branch structure is rather irregular. There are mainly two methods to synthesize H-shape and pom-pom polymers (mostly q=3). The first well-controlled synthetic method\textsuperscript{142-145, 148} uses bifunctional initiator to make a backbone with two living chain ends, which react with excess SiCl\textsubscript{4} (or MeSiCl\textsubscript{3}, etc. for H-shape) to form Cl\textsubscript{3}Si–backbone-SiCl\textsubscript{3}. Then, linear chains having one living chain end arm-Li are coupled to the Cl\textsubscript{3}Si–backbone-SiCl\textsubscript{3}, resulting in a pom-pom polymer, arm\textsubscript{3}-Si

backbone-Si-arm\textsubscript{3}. The second widely used method uses 4-(chlorodimethylsilyl) styrene (CDMSS) or its derivatives\textsuperscript{140, 141, 146} to couple linear living chains with CDMSS, resulting in arm\textsubscript{q}-CDMSS-Li. Subsequently, half of the backbone grows from CDMSS-Li. Finally, a bifunctional coupling agent couples two of such asymmetric stars arm\textsubscript{q}-(backbone)\textsubscript{0.5} to form a pom-pom chain, i.e., arm\textsubscript{q}-backbone-arm\textsubscript{q}. Although higher
molecular weight of such LCB polymers can be made with these precise methods, no literature reported arms longer than 10 $M_e$.

McLeish and co-workers$^{102}$ used rheology and neutron scattering to study 4 model H-shaped polyisoprenes (arm length 20 to 60k, backbone length 100 to 200k, with k indicating kg/mole). The highest molecular weight H-shaped PI had four 60k arms and one 200k backbone, with PDI of 1.3. Archer and Juliani$^{149}$ carried out step strain tests on one pom-pom of arm$_3$-backbone-arm$_3$ with six 21k arms and 89k backbone and PDI of 1.2. Gary also used step strain tests to study a series of short-branched comb polymers$^{150}$. Nielsen et al.$^{147}$ synthesized one arm$_{2.5}$-backbone-arm$_{2.5}$ polystyrene sample with 28k arms (five, in average) and 140k backbone and PDI of 1.1. Vlassopoulos and co-workers$^{130}$ investigated several grafted comb polymers with short branches to show that more and longer (3 Me) branches produce stronger strain hardening at much lower rates than $\tau^{-1}_{R,comb}$. Previous studies mainly focus on stress relaxation behavior after large deformation in shear (damping function) and continuous uniaxial extension (strain hardening).

McLeish et al.$^{151-153}$ developed the pom-pom model to theoretically relating the branched structure to chain dynamics. Pom-pom model shows strain hardening in extension and strain softening in shear of LCB polymers as well as strain softening of linear polymers in both shear and extension. The key understanding and assumptions from the pom-pom model$^{151,152}$ are: 1) each Gaussian strand of end-to-end distance $a$ is associated with thermal entropic force $kT/a$ in equilibrium, and 2) chain alignment in shear suppresses chain stretching and greatly reduces projected stress (strain softening). The consequence of the former is that backbone can sustain a tension of $qkT/a$ between
two branch points where there are $q$ arms at each branch point regardless of the length of branches. It asserts that the backbone can only be stretched to a strain of $q^{151, 152}$. Comparison between experiments and theory is not in perfect agreement$^{102, 147}$. The effect of long-chain branching is still quantitatively unclear since the current theoretical treatment does not explicitly consider the branch length, and experimental information remains limited.

Herein we report one-pot anionic synthesis of ultra-high molecular weight centipede-like polymers (e.g., polystyrene) with controlled LCB by coupling the living poly(styryl)lithium with 1,3-bis(1-phenylethenyl)benzene$^{154, 155}$ (DDPE) as illustrated in Scheme 5.1. Each branch point induced by DDPE has two branches that are of equal length. In our reaction scheme, coupling is only between two free chain ends, allowing the easy synthesis of multiple longer branches. This method is kinetically much more favorable than the coupling among three or more chain ends$^{142-144, 147}$. Consequently, our method produces extremely high molecular weight LCB polymers with the same spacing between branch points, and all branches are of equal length, although the total number of coupled four-arm stars is less controllable which is a compromise to study dynamics of multiple long branches. In this work, we show how LCB alters nonlinear dynamics of polymer melt in extension and makes the polymer super-stretchable without failure.
5.2 Experimental Section

5.2.1 Materials

Benzene (ACS grade, EMD; 99%) was stirred with freshly crushed calcium hydride, then stirred with sodium dispersion inside and distilled under vacuum into a storage round-bottom flask equipped with a Rotoflo® stopcock that contains an orange solution of poly(styryl)lithium made from s-butyllithium (sec-BuLi) with a small amount of styrene monomer (about 4 mL). The benzene was impurity-free as long as the color stays orange (or red, depending on the concentration of sec-BuLi). THF (ACS grade, Fisher scientific; >95%) was stirred with freshly crushed calcium hydride, and then stirred with sodium dispersion inside for two days. Then the THF was vacuum distilled into round-bottom flask equipped with sodium mirror inside. The THF should look bluish and was
impurity-free as long as shiny sodium mirror remained. Styrene (Aldrich; 99%) was stirred with freshly crushed calcium hydride, and then distilled into the storage flask with Dibutylmagnesium (FMC Lithium Division; 17% in heptane). The styrene was stirred until it turned red and then stored in the refrigerator. The purified monomer was then vacuum distilled into calibrated ampoules as needed. Methanol (Fisher Scientific, reagent ACS, 99.8%) was degassed three times on the vacuum line before being distilled into ampoules that were then flame-sealed from the vacuum line. DDPE $^{156}$ was purified by recrystallization from methanol/acetone (2: 1 by vol.) for 3 times and then vacuum dried and kept in glove box (VAC, Model # HE-43-2) before weighted and sealed in the glass apparatus. This weighing process would cause most of the experimental error on the feed ratio of DDPE: PS-Li.
5.2.2 Polymerization and Coupling

The synthesis started from purging the reactor to get a fully clean environment. 2 mL $n$-BuLi was injected into the purge section under nitrogen atmosphere, and the side arm was flame-sealed. After the vacuum was established, about 260 mL of benzene was distilled into the reactor and then the reactor was flame-sealed off the vacuum line. The reactor was then cooled by icy water from outside and then the condensed solvent inside was poured back to the purge section. Cleaning was repeated 3 times. The purge section was then flame-sealed off after complete cooling down by either an icy water or dry ice/i-propanol bath. Procedures of polymerization are: A) Smash sec-BuLi; B) Smash 1st styrene, the color of the solution is orange; overnight; C) Take a sample. Freeze and seal off sample ampule (1); D) Smash 1th DDPE and THF, the color of the solution is vivid
red; overnight; E) Take a sample. Freeze and seal off sample ampule (2); F) Smash 2nd styrene. The color of the solution gradually turns into orange; after 6 hours, take a sample. Freeze and seal off sample ampule (3); G) Smash 2nd DDPE, the color of the solution is vivid red; overnight; H) Smash methanol; and the reaction is finished (4). The final product was obtained by terminating the polymeric organolithiums with degassed methanol. The precipitated polystyrene was then dried and characterized by SEC. Fractionation was done using a mixture of toluene and methanol at 1 wt % in toluene/methanol.

5.2.3 Chromatography Characterization

Size exclusion chromatography (SEC) analyses for the synthesized polymers were performed using two mixed B columns (Agilent) at a column temperature of 40 °C. THF (Samchun, HPLC grade) was used as eluent at a flow rate of 0.8 mL/min. SEC chromatograms were recorded with a light scattering/refractive index/viscometer triple detector (Viscotek TDA 305, labeled as R_90) and a UV absorption detector (TSP, UV2000 at 260 nm wavelength) for on-line determination of absolute molecular weight of polymers. The dn/dc value for the PS samples in THF is 0.185 mL/g. Polymer samples were dissolved in THF at a concentration of ca. 1 mg/mL and the injection volume was 100 μL.

Temperature gradient interaction chromatography (TGIC) separations were performed by C18 bonded silica column (Nucleosil C18, 7 μm, 1000 Å pore, 250 x 4.6 mm I.D.). A CH2Cl2/CH3CN mixture (58/42, v/v, Samchun, HPLC grade) was used as eluent at a flow rate of 0.5 mL/min. The temperature of the column was controlled by circulating the fluid from a programmable bath/circulator (Julabo, F25-HL) through a
homemade column jacket. Sample solutions for injection (2~4 mg/mL) were prepared by dissolving the polymer in a small volume of the eluent and the injection volume was 100 μL. TGIC chromatograms were recorded with a LS detector (Wyatt, TREOS, labeled as R90), an RI detector (Wyatt, Optilab T-rEX) and a UV detector (Younglin, UV730D) for on-line determination of absolute molecular weight. The $dn/dc$ value for the PS samples in the mixed solvent was measured as 0.221 mL/g from TGIC of PS 1arm 110k by setting absolute MW to the MW from GPC. MWs obtained from TGIC are very similar to MW from GPC by using 0.221 mL/g for PS.

5.2.4 Rheological measurements

Small amplitude oscillatory shear (SAOS) measurements were carried on ARES-LS with 8 mm parallel plates at a gap distance around 0.7 mm from 120 °C to 240 °C. Uniaxial extension experiments at constant Hencky strain rates $\dot{\varepsilon}$ were carried out mostly at 150 °C using a first generation SER fixture mounted onto a TA ARES-G2. Together with uniaxial extension, we record the stretching process through the viewing window on the forced-convection-oven by using an EverFocus EQ200E camera with a zoom lens. The failure of specimen was video-recorded at 30 fps to allow post-experiment analyses that determine the onset of non-uniform uniaxial extension. The specimens were made by solution casting of a THF solution (with antioxidants, BHT, IRGAFO8108, IRGANOX1010 at 0.1%) into sheet, and the solvent in the sheet was allowed to slowly evaporate for a week and then slowly heat up to 140 °C in a vacuum oven for another week. The final sheet was 0.3 mm thick and then cut to the desired dimensions to mount onto the SER.
Figure 5.1 (a) SEC curves showing the doubling of molecular weights as proof that the coupling based on DDPE has taken place as designed. (b) TGIC profile of the branched polymer after fractionation shows a relatively small amount of various low molecular weight species (e.g., two four-arm stars) in addition to the dominant component, which is the LCB-PS involving three four-arm stars. $\Delta n$ (blue curve, recorded by RI detector) represents the concentration of the polymer while $R_{90}$ (red curve, by light scattering detector at 90° scattering angle) represents molar mass $\times$ concentration (weight average $M_w$).
5.3 Results and discussions

5.3.1 Synthesis and characterization of LCB-PS1M and LCB-PS4M

As the first step, a linear living poly(styryl)lithium (PS-Li) 1 in Scheme 5.1 was synthesized as 110k shown in the SEC-LS profile in Figure 5.1 (a). Upon the addition of DDPE to a little less than a half of the moles of PS-Li 1, the sample's color changed slowly from bright orange 1 to ruby red 2, indicating the coupling of two PS-Li chains to form two diphenylalkyllithium sites. DDPE was used to synthesize star polymers and is superior to divinylbenzene (DVB) in making the star 3 because DDPE-Li 2 will stop further polymerizing with DDPE while DVB tend to oligomerize. From Figure 5.1 (a) and Figure 5.2 (b), we can see that insufficient DDPE resulted in uncoupled PS-Li 1. A calculated amount of styrene monomer was then added to form four-arm stars 3. Then the color of solution changed back to bright orange, and 3 is 377k (peak position from LS on SEC) or 488k (peak position from LS on TGIC), with \( M_w/M_n = 1.2 \), suggesting that each arm is approximately 120k. At the same time, some of the uncoupled PS-Li 1 from the previous step were dead and some also grew from 105k to 243k as shown in Figure 5.2 (c). Four-arm stars 3 have two living PS-Li chain ends available for the final coupling by the second addition of DDPE at a molar ratio of 1:4 to PS-Li. At this step, not only two four-arm stars 3 may couple, but three of them may also couple together as determined by the molecular weight of 4. Some residue living linear PS-Li may also couple with with four-arm stars to form byproduct 6 as shown in Scheme 5.3.
Scheme 5.3 One possible kind of impurities during synthesis LCB-PS1M.
Figure 5.2 Detailed TGIC analysis of intermediate and products during synthesis LCB-PS1M and assumed Molecular weights from TGIC.

Fractionation can remove some of these low molecular weight impurities in Figure 5.2 (d) in comparison to Figure 5.1 (b). Such high molecular weight LCB polymers are not very distinguishable even by TGIC. Fractionated LCB-PS1M still has low molecular weight substances with $M_n = 450k$, $M_w = 1.1$ million g/mole and $M_{peak}$ at 1.3 (peak position from LS) or 1.5 (TGIC) million g/mole with branches having an average $M_n = 110k$. Thus, $M_w/M_n$ (PDI) is 2.6. $M_{peak}$ is more close to three coupled 4-arm-stars and we assume the resulting product is a mixture of two coupled 4-arm-stars and three coupled 4-arm-stars as well as lower molecular substances. In general, this kind of coupling is not suitable for getting only two four-arm stars coupled. We also made two
linear PS (L-PS 160k and L-PS 1M) by anionic polymerization having $M_n = 161k$ (PDI=1.01) and 1010k (PDI =1.02) respectively.

As shown in Scheme 5.1, at DDPE: living PS-Li molar ratio of 1:2, more four-arm stars (3) will be coupled. Since each star has only two living PS-Li chain ends available for coupling, the final product is centipede-like as 5 shown in the Scheme 1, with well-defined long-chain branching (blue, online) and well-defined spacing (black, online). As shown in Figure 5.3 (a), the initial PS-Li 1 is 140k and two of them coupled by DDPE is 2, 272k or 290k according to the TGIC profile in Figure 5.4 (b). Upon the addition of styrene monomers, the living polystyrene 2 grows on the two diphenylalkylithium sites to become 668K four-arm stars 3 or (615k as in Figure 5.4 (c) ), with $M_w/M_n =1.15$. Therefore, the average spacing between each branch point in final product is $615k-140k \times 2 = 335k$, while the length of branches is 140k. After fractionation, LCB-PS4M 5 has $M_n$ of 3,300k , $M_w$ of 4,900 and $M_{peak}$ at 4,900k With $M_w/M_n = 1.5$. Average number of four-arm stars that are coupled together is calculated from $4700k/615k \approx 8$. The tail at longer times in the TGIC profile, Figure 5.3 (b), suggests there are substances of more than 8 four-arm stars coupled together which are not distinguishable in current TGIC measurements. Detailed TGIC analyses of intermediate products are in Figure 5.4.
Figure 5.3 (a) SEC curves of LCB-PS4M and four intermediate products. (b) TGIC profile of branched polymer after fractionation shows a relatively small amount of low molecular weight precursors. Peak molecular weight corresponds to coupling of 8 four-arm stars.
5.3.2 Linear Viscoelasticity

Small amplitude oscillatory shear (SAOS) measurements, as shown by the open cycles and squares in Figure 5.5, of linear l-PS1M and l-PS170k reveal terminal relaxation time $\tau$ of $2.6 \times 10^3$ s and 3.4 s respectively at a reference temperature of 150 °C, where there is an obvious plateau of at $G_{pl}(\phi = 1.0) = 270$ kPa. The Rouse relaxation time $\tau_R$ of l-PS is listed in Table 5.1, estimated from the zero shear viscosity following $^{161}$. The Rouse time of LCB-PS may be crudely estimated as $\tau_{R,\text{centipede}} = \frac{\tau_{R,\text{lin}} Z_{bb}}{Z_{total}} = \ldots$
\( \tau_{R, lin}/2 \) following \(^{130}\), where \( \tau_{R, lin} \) is the Rouse relaxation time of a linear polystyrene with the same \( M_w \) as LCB-PS by extrapolating from \( \tau_r \) of 1-PS1M according to \( \tau_r \sim M_w^2 \). SAOS of LCB-PS1M and LCB-PS4M did not reach terminal crossover in the accessible frequency range because the dynamics of LCB are so slow and thermal instability limits the application of time-temperature superposition to 240 °C. Terminal dynamics can be observed when LCB-PSs were diluted with solvent\(^1\). Because the chain dynamics associated with arms are widely separated from those with the backbone, there should be a second lower plateau at lower frequencies around \( G_p(\phi = 0.5) = \phi^{2.2} G_p(\phi = 1.0) = 0.5^{2.2} \times 270 \text{ kPa} = 59 \text{ kPa} \). Since the terminal region was inaccessible, the lower plateau could hardly show up. We use the BSW model to extract a dominant relaxation time that we associate with the dynamics of arms from the relaxation spectrum. \(^{147, 161-163}\)

Specifically, given the BSW spectrum in

\[
G'(\omega) = n_e \sum_{i=1}^2 \left( \frac{G^{0}_{N,i}(\omega \tau_{max,i})}{n_e} \int_0^{\omega \tau_{max,i}} \frac{x^{1+n_e}}{1+x^2} dx + G_{N,i}(\omega \tau_c)^{-1/n_e} \int_0^{\omega \tau_{max,i}} \frac{x^{1-n_e}}{1+x^2} dx \right)
\]

\[
G''(\omega) = n_e \sum_{i=1}^2 \left( G^{0}_{N,i}(\omega \tau_{max,i})^{n_e} \int_0^{\omega \tau_{max,i}} \frac{x^{n_e}}{1+x^2} dx + G_{N,i}(\omega \tau_c)^{-n_e} \int_0^{\omega \tau_{max,i}} \frac{x^{-n_e}}{1+x^2} dx \right)
\]

we use Matlab to carry out least square fitting to the \( G' \) and \( G'' \) data in Figure 5.5, i.e., to minimize

\[
\sum_i \left( \frac{G'(\omega)}{G'_{i, \text{exp}}} - 1 \right)^2 + \left( \frac{G''(\omega)}{G''_{i, \text{exp}}} - 1 \right)^2
\]

with most suitable values of \( n_e, n_g, G^{0}_{N,i}, \tau_{max,i}, \tau_c \) as shown in Figure 5.6 to 5.8. According to \(^{147, 161}\), overall relaxation time for arms is given by \( \tau_{arm}^{BSW} \approx \tau_{max,1}/2 \). We find, as listed in Table 5.1, \( \tau_{arm}^{BSW} \) are 21.9 and 68.8 s respectively.
Figure 5.5 Small amplitude oscillatory shear (SAOS) measurements of l-PS and LCB-PS at a reference temperature of 150 °C. Because of the limited thermal stability, the SAOS can only obtain data at frequencies lower than $10^{-5}$ rad/s.

Table 5.1 Molecular and linear Viscoelastic Characterization of Polystyrenes at 150 °C.

<table>
<thead>
<tr>
<th></th>
<th>$M_w \times 10^6$</th>
<th>PDI</th>
<th>Arm $M_w$</th>
<th>$\eta_0$ (Pa.s)</th>
<th>$\tau$ (s)</th>
<th>$\tau_{BSW}^{arm}$ (s)</th>
<th>$\tau_{R,lin}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>l-PS170k</td>
<td>0.167</td>
<td>1.01</td>
<td></td>
<td>$5.95 \times 10^5$</td>
<td>3.4</td>
<td></td>
<td>0.41</td>
</tr>
<tr>
<td>l-PS1M</td>
<td>1.01</td>
<td>1.02</td>
<td></td>
<td>$2.95 \times 10^8$</td>
<td>$2.6 \times 10^3$</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>LCB-PS1M</td>
<td>1.10</td>
<td>2.6</td>
<td>$2 \times 120k$</td>
<td></td>
<td></td>
<td></td>
<td>21.9</td>
</tr>
<tr>
<td>LCB-PS4M</td>
<td>4.90</td>
<td>1.5</td>
<td>$2 \times 140k$</td>
<td></td>
<td></td>
<td></td>
<td>68.8</td>
</tr>
</tbody>
</table>
Figure 5.6 BSW fitting to the data in the frequency range from $3 \times 10^{-3}$ to $4 \times 10^{3}$ rad/s for LCB-PS1M. Green dot line is mode 1. Red dot line is mode 2. Black curves are the fitting curves by summation of mode 1 and 2.

Figure 5.7 BSW fitting by data from 0.1 to $3 \times 10^{3}$ rad/s for LCB-PS4M. Green dot line is mode 1. Red dot line is mode 2. Black curves are the fitting curves by summation of mode 1 and 2.
5.3.3 Start-up of uniaxial extension

All extension is visibly uniform up to the last presented data point. Figure 5.9 (a) shows the extensional rheological response of the linear polymer, l-PS1M melt, at 150 °C for a wide range of Hencky rates. The characteristics are consistent with a recent study of entangled linear styrene-butadiene random copolymer (SBR) melts\cite{164,165}, revealing rupture-like tensile decohesion at lower rates (below 0.01 s\(^{-1}\)), shear yielding initiated non-uniform extension (unstable necking) at intermediate rates (between 0.01 s\(^{-1}\) and 1 s\(^{-1}\)), and sharp rupture at higher rates (1 to 10 s\(^{-1}\)). These three types of failures\cite{164} corresponds to the last three regions (transition, rubbery and glass-like zone) of the master curve summarized by Malkin and Petrie\cite{166} and discussed by others\cite{167,168}.

Figure 5.8 BSW fitting for l-PS1M shown as the black curves.
Figure 5.9 (b) shows that the LCB-PS1M sample also undergoes tensile decohesion at the lowest rates (0.003 s\(^{-1}\) to 0.1 s\(^{-1}\), open symbols at low rates) and show distinct maxima at the higher rates (0.3 s\(^{-1}\) to 10 s\(^{-1}\), filled symbols) at the same reference temperature. In the tensile decohesion regime, the LCB-PS1M takes an unusually large Hencky strain of 3 or more to break whereas the linear melts\(^{164}\) normally fails at a strain around 1.5 as shown in Figure 5.9 (a). Figure 5.9 (c) shows the uniaxial extensional behavior of LCB-PS4M with tensile decohesion at an equivalent rate of 0.0005 s\(^{-1}\) at 150 °C (0.03 s\(^{-1}\) at 190 °C) and LCB-PS4M also goes beyond Hencky strain of 3. At rates higher than 0.0005 s\(^{-1}\), the engineering stress shows a plateau (from strain 0.8 to strain 2.6) before peaks again at higher strains 3.5 ~ 4. LCB-PS1M has similar plateau (from strain 0.9 to strain 2.1) and overshoots at strains 3 ~ 3.5. The linear PS (l-PS1M) hardly displays a stress plateau and does not show another peak at high strains. Samples will overwrap on SER\(^{158}\) clamp after Hencky strain of 4 when approaching one cycle of rotation. This causes a brief perturbation on torque by increases extension rates about 5% and back to normal at Hencky strain of 5. This effect does not change the conclusion that LCB-PS can extend much longer than l-PS. Clearly, the presence of LCB enhanced the cohesion of the entanglement network against the tensile decohesion, as expected. The maximum engineering stress of LCB-PS1M at rates from 0.3 to 10 s\(^{-1}\) occurs at a remarkable high and similar Hencky strain of \(\varepsilon_{\text{max}} = 3.3\), corresponding to a stretching ratio of \(\lambda_{\text{max}} = 27\) in a range of rates from 0.3 s\(^{-1}\) to 10 s\(^{-1}\). This contrasts strongly with the responses of linear polymers. The engineering stress of LCB-PS4M reaches a strain higher than 4, i.e., \(\lambda_{\text{max}} \sim 55\), in a range of rates from 0.01 to roughly 0.3 s\(^{-1}\).
Some characteristics of the data in Figure 5.9 (a) to (c) can be interpreted in terms of the description of the Edwards-Vilgis slip-link model\textsuperscript{64-66}. The model envisions a double-network, one involving crosslinks with a corresponding modulus $G_c$ from crosslinks and the other due to the slip-links with modulus $G_s$, such that the initial elastic modulus is given by $G_c + G_s = G_{pl} (\phi=1) = 270$ kPa. The slip parameter $\eta$ is chosen to be 0.2. The condition of $G_c = G_{pl}$ with $G_s=0$ and $\alpha=0$ is the same as the classical rubber elasticity formula and mimics the situation when all entanglements from both backbone and arms are in effect. The condition of $G_c = G_{pl} (\phi=0.5)$ with $G_s=0$ and $\alpha=0$, equivalent to swollen rubber elasticity with reduced modulus $G_{pl} (0.5)$, corresponds to a PS solution at 50 % with all entanglements from backbone in effect and all arms are acting as solvent for $\dot{\epsilon} \tau_{arm} < 1$). Up to 0.01 s$^{-1}$ for LCB-PS1M and 0.003 s$^{-1}$ for LCB-PS4M, the stress responses are bounded by the curve with $G_{pl}(\phi=0.5)$, indicating that the applied rate is too low to probe any participation of arms in entanglement networking. At rates from 0.1 to 10 s$^{-1}$ of LCB-PS1M (Figure 5.9 (b)), the stress-strain curves are bounded between the two sets of curves with $G_{pl} (\phi=1)$ and $G_{pl} (\phi=0.5)$, suggesting that the initial deformation of entanglement network involves entanglements from arms. This is consistent with the fact that $\dot{\epsilon} \tau_{arm}^{BSW} = 0.1 \times 21.9 > 1$. The initial elastic response of LCB-PS4M (Figure 5.9 (c)) is above the curve with $G_{pl} (\phi=0.5)$ for 0.01 s$^{-1}$ and higher, as $\dot{\epsilon} \tau_{arm}^{BSW} = 0.01 \times 68.8 \sim 1$. The progressive loss of entanglement\textsuperscript{165} in both linear and LCB PS produces stress-strain curves that can be crudely described by the Edwards-Vilgis model: slip-links depict the group of weaker entanglements that vanish first. The arms of LCB-PS naturally first disentangle, or pulled in the tube\textsuperscript{147, 152} to produce strain softening. We
show in Figure 5.9 (a) to (c) some fitting of the Edward-Vilgis model to the data at the highest rates with various values for parameters $\alpha$ and $G_c$. 

![Graph (a)](image1)

![Graph (b)](image2)
The amount of extension required to straighten a Gaussian entanglement strand is $\lambda_{ent}^* \approx l_{ent}/l_{Kuhn} = 4$ for PS. Since there are 18 entanglements in the strand of 240k between the two neighboring branch points ($b_p$) in LCB-PS1M, the stretching ratio needed to straighten the Gaussian coil of $M_w = 240k$ is $\lambda_{bp}^* \approx \sqrt{18} \times \lambda_{ent}^* = 17$. For the LCB-PS4M with 21 entanglements between two branch points, we have $\lambda_{bp}^* = 20$. Since the entire backbone of LCB-PS1M is three times the length between the branch points, the stretching ratio to straighten the whole backbone ($b_p$) is $\lambda_{bb} = \sqrt{3} \lambda_{bp}^* = 29$, and $\varepsilon_{bb} = 3.4$. There are eight branching points in LCB-PS4M, separated by 335k. Therefore, to
straighten the backbone requires a stretching ratio of \( \lambda_{bb} = \sqrt[8]{8} \lambda_{bp}^* = 57 \), or \( \varepsilon_{bb} = 4 \). These two numbers are nearly the same as \( \lambda_{\text{max}} \) seen in Figure 5.9 (b) and (c), respectively. This is not a coincidence and suggests that there can still be one entanglement per chain at \( \lambda_{\text{max}} \).

In Nielsen et al. \(^{147}\) they also found their 140+28×2=196k backbone to show \( \lambda_{bb} = 15 \) or \( \varepsilon_{bb} = 2.7 \), which is much higher that the prediction of branch point retraction by the pom-pom model \(^{152}\). The discrepancy in the strain of stress maximum \(^{102}\) requires further theoretical consideration. On the other hand, for l-PS1M, \( \lambda_{bb} = \sqrt{1000/13.3} \times \lambda_{\text{ent}}^* = 34 \), i.e., \( \varepsilon_{bb} = 3.5 \). Experimentally, we observed from Figure 5.9 (a) \( \varepsilon_{\text{max}} \sim 3 < \varepsilon_{bb} = 3.5 \). Thus, massive chain disentanglement already occurs before the linear chain could become fully straightened. This rule is also true in the previous studies of linear SBR melt \(^{164}\) and solutions \(^{165}\), and polyisoprene melts \(^3\). Branches prevent material failures and inhomogeneity during stretching. Polymers with LCB show \( \sigma_{\text{max}} \) at stretching ratio proportional to the square root of Mw of backbone. In the current case, LCB-PS1M reaches stretching ratio of 29 while LCB-PS4M reaches 57. Thus, the molecular structure can be designed to increase stretchability of polymer melts, beneficial to industrial processes such as film blowing.
Hencky rates

LCB-PS1M 150 °C

(a)

LCB-PS4M 150 °C

(b)
Figure 5.10 Transient extensional viscosities of a) 1-PS1M, b) LCB-PS1M and c) LCB-PS4M as a function of time for different Hencky rates from 0.003 to 10 s\(^{-1}\). Also plotted are the linear response data taken from the small amplitude oscillatory shear measurements according \(^{123}\) to \(\eta_E^*(1/\omega)|_{\dot{\varepsilon}=1/\omega}=3|\eta^*(1/\omega)|\).

Analogous to the uniaxial extension behavior of LDPE, the transient extensional viscosity stays far above the zero-rate curve as shown in Figure 5.10 (a) and (b). \(\eta_E^*=\eta_{enr}\lambda/\dot{\varepsilon}\). This is a rheological characteristic\(^1,3,89,125,129,130,147,152,169\) of LCB polymers. Long branches postpone the complete breakdown of the entanglement network and allow the geometric condensation effect to dominate the transient responses.\(^3\) In startup uniaxial extension even linear melts can postpone chain disentanglement at high enough rates as shown Figure 5.10 (c) to display true strain hardening.\(^3,130\) At \(\dot{\varepsilon} \gg \tau_R^{-1}\), rupture occurs by non-Gaussian stretching within entanglement strands\(^3,164,165,170\) and is universally independent of chain architecture.
5.3.4 Stepwise extension and stress relaxation

Well-entangled linear polymer melts universally suffer elastic yielding and mechanical breakup upon a moderate step extension\textsuperscript{171-173} because the entropic barrier against the failure of entangled network is rather low\textsuperscript{24}, and linear chains can readily disengage from the entanglement network through two chain ends or as instability of monodisperse polymers\textsuperscript{173}. Such chain disentanglement would become much more difficult in presence of multiple branching points as depicted in Figure 5.11. For linear melts, we already knew that the elastic yielding produces specimen breakup after a stepwise-extension for amplitude of a Hencky strain as low as 0.8.\textsuperscript{171} Our stepwise extension of the 1-PS1M at a Hencky rate of 1 s\textsuperscript{-1} confirms our expectation as shown in Figure 5.12 (a) that the sample breaks during relaxation. At a mere amplitude of Hencky strain $\varepsilon = 1$, $\lambda = 2.7$, the sample broke up within a fraction of the terminal relaxation time $\tau$. In contrast, the LCB-PS1M resists against such an elastic breakdown as shown in Figure 5.12 (a). Even at a step-extension of $\varepsilon = 2$, corresponding to a large stretching ratio $\lambda = 7.4$, the LCB-PS1M does not undergo breakup during relaxation. All curves labeled as “no break up” mean there is no visual change of sample shape or cross section area during relaxation. Movies are available in Supplementary data to show that the stretched LCB-PS1M remains intact as long as 50 minutes while the same step extension of $\varepsilon = 2$ caused the 1-PS1M to break up very quickly after 1 min. LCB-PS4M can also sustain a step-extension strain of 2 without failure during relaxation. For the current architecture of long-chain branching, the elastic breakup still occur when the magnitude of the step extension is $\varepsilon = 2.5$, as shown both in Figure 5.12 (a) and (b). As mentioned in section 3.3, deformation of $\lambda_{bp}^* = 20$, $\varepsilon_{bp}^* = 3$ (LCB-PS4M) or $\lambda_{bp}^* = 17$, $\varepsilon_{bp}^* = 2.8$
(LCB-PS1M) will hypothetically straighten polymer chains between the two neighboring branch points. The transition from the stress plateau to the second stage of stress growth at $\varepsilon = 2.6$ and $2.1$ involves significant stretching. The intra-chain retraction force in the backbone could built up and exceed the entropic barrier associated with the arm retraction, allowing withdrawal of branch points and leads to the macroscopic failure during relaxation. Whether the number of arms per branching point, the number of branch points or the length of branches determines the magnitude of the entropic barrier to prevent the elastic breakup after large step extension remains as an open question.

Figure 5.11 Scheme of disentanglement of (a) linear polymers, (b) LCB polymers.
Figure 5.12 Engineering stress growth and relaxation during and after stepwise extension respectively, carried at Hencky rates of 1 s$^{-1}$, (a) involving l-PS1M and LCB-PS1M at 150 °C; (b) involving LCB-PS4M at 190 °C. The filled symbols denote step extensions that produce no breakup during relaxation, whereas open symbols denote breakup during relaxation. Elastic breakup occurs at $\varepsilon = 1$ for l-PS, whereas LCB-PS1M and LCB-PS4M show no breakup up to $\varepsilon = 2$. 
5.3.5 Stepwise extension on two branched polyisoprene melts

The present study also includes two branched polyisoprene (PI), which are H-shaped and comb-shaped, respectively. The H-PI was synthesized in Avgeropoulos’ lab in Greece. The comb-PI was synthesized in Dr. Mays’ lab in Tennessee with 3 randomly spaced branches. The linear viscoelastic properties of the PI melts were first evaluated by performing small-amplitude oscillatory shear measurements on an ARES-LS rotational rheometer from TA Instruments; the curves of storage and loss moduli ($G'$ and $G''$) as a function of angular frequency are shown in Figure 5.13. The linear viscoelastic measurements produce the molecular characteristics as listed in Table 5.2 for branched PI. The plateau modulus $G_N^0$ is found to vary from 0.30~0.35 MPa for the two PI melts. The number of entanglements per chain $Z$ can be estimated as $Z = M_w/M_e = M_w/(ρRT/G_N^0)$. The samples have terminal relaxation times $τ$ that can be estimated as the reciprocal of the crossover frequency $ω_c$, at which $G'(ω_c) = G''(ω_c)$.

Branched polyisoprene specimens were made from dense polymer/THF solution that slowly evaporated inside glass ring (3 cm radius) on the Kapton film. The polymer film was placed in vacuum oven for several days to remove any residue solvent before cut in to the same dimensions as other polymer samples. The PI melts are solution-casted as described before.

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1 This section 5.3.5 is reproduced with permission from Sun, H.; Lin, P.; Liu, G.; Ntetsikas, K.; Misichronis, K.; Kang, N.; Liu, J.; Avgeropoulos, A.; Mays, J.; Wang, S. Q. *J. Rheol.* **2015**, 59, (3), 751-767. Copyright © 2015 The Society of Rheology
Table 5.2 Microstructures and characterization of two branched polyisoprenes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn arm</th>
<th>Mn Backbone</th>
<th>Mn total</th>
<th>PDI</th>
<th>3,4 (%)</th>
<th>Tg</th>
<th>$\lambda_{\max}$</th>
<th>$\varepsilon_{\max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-PI 150K</td>
<td>25k</td>
<td>150k</td>
<td>210</td>
<td>1.1</td>
<td>63</td>
<td>-11</td>
<td>18</td>
<td>2.9</td>
</tr>
<tr>
<td>Comb-PI 700k</td>
<td>20k</td>
<td>700k</td>
<td>760</td>
<td>55</td>
<td>41</td>
<td>3.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.13 Small amplitude oscillatory shear measurements at room temperature for two PI melts with long chain branching.

The presence of long chain branches (LCB) completely changes the failure behavior of entangled polymers \(^1\text{-}^3\). For example, at a Hencky rate of 0.1 s\(^{-1}\), the critical amplitude of stepwise strain to produce any failure goes above Hencky strain of 2.5 as shown in Figure 5.14 (a) that involves the H-shape polyisoprene. The only failure mode observed at strains of 2.7 and 3 is tensile decohesion as shown by the IR temperature profile. LCB in comb-PI postpones specimen breakup after step extension from happening as shown in Figure 5.14 (b): For a range of Hencky rates from 10 to 0.1 s\(^{-1}\), the entangled comb-PI
did not fail during the relaxation from a large step strain of $\varepsilon = 2$, in obvious contrast to the failure behavior of entangled melts of linear chains.

![Graph showing tensile decohesion or no failure, depending on the amplitude of stepwise extension of H-PI 150K. These step strains were performed on Physica MCR301. The inset thermal image shows the moment of tensile decohesion, with little temperature change after startup extension for $\varepsilon = 3$, where the white lines mark the edges of the specimen. (b) No failure after stepwise extension on comb-PI 700K for step Hencky strain of 2 produced at different rates.](image)

Figure 5.14 (a) Tensile decohesion or no failure, depending on the amplitude of stepwise extension of H-PI 150K. These step strains were performed on Physica MCR301. The inset thermal image shows the moment of tensile decohesion, with little temperature change after startup extension for $\varepsilon = 3$, where the white lines mark the edges of the specimen. (b) No failure after stepwise extension on comb-PI 700K for step Hencky strain of 2 produced at different rates.
With significant LCB, entangled melts possess two different dynamical regimes, associated with side chains and the backbone respectively. The dynamical separation introduces a mechanism to delay structural collapse of the entanglement network. Since the side branches act like linear chains and have much faster dynamics, they can quickly undergo chain retraction and return toward their non-deformed states after significant extension, i.e., after a Hencky strain of 2. As long as the backbones remain in entanglement with one another, the disentanglement of side chains does not lead to a downfall of the overall entanglement network. At longer times when the backbones try to undergo disentanglement through chain retraction, they are confronted with a much higher entropic barrier than linear chains meet. The already-relaxed side chains must all undergo conformational changes in order to accompany backbone retraction. This amounts to a significant entropic loss. Unless the amplitude of stepwise extension is much higher than the threshold amplitude observed of linear polymers, elastic breakdown of the overall entanglement network would not occur, and the relaxation would remain quiescent, as is the case for $\varepsilon = 2.5$ and $\varepsilon = 2$ shown in Figure 5.14 (a) and (b) respectively.

5.5 Summary

In summary, we have demonstrated a straightforward synthetic route to make ultra-high molecular weight, well-entangled polymers with long-chain branching (LCB) longer than 10Me. Such LCB-PS has equal chain length between the branch points, which is twice the arm length in the current case. The present method is also effective to
synthesize grafted copolymers where the arms and backbone have different chemical structures, as they propagate at different stages.

LCB-PS shows remarkably different nonlinear rheological responses to fast startup and stepwise uniaxial extensions, compared with the linear PS. LCB-PS can stretch far more during startup extension before the specimen failure terminates the uniform extension. The strain at the maximum engineering stress correlates with square root of length of the backbone, rather than the number of branches. Stepwise extension experiments reveal improved strength of the entanglement network. Specifically, LCB-PS samples stay intact even after a stretching ratio of 7.4. In contrast, linear PS samples undergo elastic breakup at a stretching ratio of only 2.7. Thus, present study demonstrates that chain architecture can be an important molecular-design parameter to affect polymer dynamics and improve processing behavior.
CHAPTER VI

NONLINEAR RHEOLOGY OF LONG CHAIN BRANCHED POLYMER SOLUTIONS IN STARTUP SHEAR

We show for the first time that entangled polymeric liquids containing long-chain branching (LCB) can exhibit strain hardening upon startup shear. As the significant LCB impedes chain disentanglement, Gaussian coils between entanglements can deform to reach the finite extensibility limit where the intra-chain retraction force exceeds the value expected from the usual conformational entropy loss evaluated based on Gaussian chain statistics. The phenomenon is expected to lead to further theoretical understanding.

6.1 Introduction

Entangled polymeric liquids are extremely complex to model at a molecular level when they are subjected to external deformation at rates that match or exceed the molecular relaxation rates. On the other hand, it is fairly straightforward to carry out macroscopic rheological measurements of such viscoelastic fluids in simple shear and uniaxial extension. Considerable progress has been made in the past several decades to explain nonlinear behavior of entangled polymers in terms of molecular deformation.\(^\text{70, 174, 175}\)
For example, the tube model has been developed\textsuperscript{68, 176-179} to describe such nonlinear phenomena as stress overshoot upon startup shear and strain softening associated with the relaxation dynamics after step strain. Since particle-tracking velocimetric observations of strain localization such as shear banding during startup,\textsuperscript{23} and non-quiescent relaxation after step strain\textsuperscript{55} in entangled polymers of linear chains, the tube model has further demonstrated its versatility to claim that it captured all the essential physics associated with these and other instabilities\textsuperscript{81, 172, 180}. More remarkably, a subsequent extension of the tube theory for entangled polymers with long chain branching, e.g., low density polyethylene (LDPE) that has multiple, irregularly spaced long branches,\textsuperscript{181} attempted to explain why there is "strain hardening"\textsuperscript{91, 182} in startup uniaxial extension but only "strain softening" in response to startup shear.\textsuperscript{102, 151-153, 183}

\[
M_{\text{star}} = 615 \text{ kg/mol, PDI: 1.15} \\
M_{\text{crossbar}} = 308 \text{ kg/mol}
\]

Figure 6.1 A schematic depiction of a relatively monodisperse long-chain branched PS that is made of eight four-arm stars and has total molecular weight of \(8 \times 615 = 4,920\) kg/mol, as determined from temperature gradient interaction chromatography. Each of the seven crossbars has an average molecular weight of 335 kg/mol while each branch is 140 kg/mol.

Specifically, based on a simplest long-chain branching architecture involving one crossbar linked on each end to a star-like chains with \(q\) arms, a tube-based pom-pom model\textsuperscript{152, 183} explains that the \(q\) arms at the branch point provide an entropic barrier of
$q k_B T$ to enable stretching of the crossbar in terms of a stretching factor $\lambda$ up to the limit of $\lambda^* = q$. The retractive stress develops a quadratic dependence on $\lambda$ because it arises from both the extension of the crossbar and the tension within the backbone.\textsuperscript{152} Since the zero-rate limit is a linear response where the transient viscosity $\eta_{\text{EO}}(t)$ grows linearly in time, the quadratic arguments in the pom-pom model produce "strain hardening" in extension but still extreme strain softening in shear due to the coupling of orientation to chain stretching. Since the publication of the pom-pom model, several pom-pom-like systems including H-shaped polymers have been studied to compare with the model. Qualitative agreement between experiment and the model has generally been found\textsuperscript{102,147,152,182} for both startup shear and extension.

6.2 Experiments

In this chapter, we study a model LCB polystyrene (PS) made with a straightforward synthetic method as described in previous chapter.\textsuperscript{2} As shown in the schematic drawing in Figure 6.1, our comb-like PS(LCB-PS4M, as in previous chapter) has an extraordinarily high molecular weight so that even its 22 % (volume fraction) solution is sufficiently entangled. Small-amplitude oscillatory shear measurements in Figure 6.2 revealed its linear viscoelastic characteristics that resemble the previously reported $G'$ and $G''$ curves of other melts and solutions made of polymers with LCB.\textsuperscript{102, 147, 184, 185} This entangled PS solution is made with a non-volatile solvent, tricresyl phosphate (TCP) from Aldrich 1330-78-5 as used in Chapter III. The glass transition temperature of TCP is $-70 \, ^\circ C$ and has a high viscosity of 3 Pa.s at $-15 \, ^\circ C$. There are two visible plateaus, corresponding to two levels of chain entanglement. This can be anticipated from the
depicted chain architecture in Figure 6.1, characterized by a modulus \( G_0 = \phi^{2.2} G_N^0 \sim 7.1 \) kPa for \( \phi = 0.22 \) and \( G_N^0 = 0.2 \) MPa of PS, and \( G_{bb} = (\phi/2)^{2.2} G_N^0 = 1.56 \) kPa, associated with the backbone entanglement.

Figure 6.2 Small amplitude oscillatory shear (SAOS) measurements of the LCB PS solution at a volume fraction of \( \phi = 0.22 \) and reference temperature \( T_{ref} = 70 \) °C. The time-temperature equivalence principle was applied to obtain the linear viscoelastic characterization over nine decades of frequency. The data are presented on double X axes, with the lower given in terms of Deborah number \( D_e \), and the upper given in terms of the oscillation frequency \( \omega \). The lowest frequency portion of storage modulus \( G' \) and loss modulus \( G'' \) curves are collected at 80 °C and the highest frequency portion are obtained with SAOS at -15 °C. Other temperatures involved in the SAOS measurements are 70, 25, 0 and -10 °C.
Figure 6.3 Stress-strain curves of startup shear at various rates from 0.001 to 20 s\(^{-1}\) at 70 °C. Black open cycles marked stress maxima \(\sigma_{\text{max}}\). The coordinates \((\gamma_{\text{max}}, \sigma_{\text{max}})\) of the stress overshoot vary with the applied shear rates differently in the different regimes. (a) in log-log scale, (b) in lin-lin scale.
6.3 Results and discussions

We impose startup shear to examine nonlinear responses in the various dynamic regimes, using an Anton Paar MCR301 Rheometer equipped with 25 mm cone-plate of 2° cone angle (CP25-2-SN4294). As shown in Figure 6.3, around the end of the terminal regime ($Wi = \dot{\gamma} \tau_{bb} < 1$) and for $Wi < 10$ or so, i.e., in regimes I and II, the maximum shear stress occurs at a similar level of strain around 2 ~ 3, not much different from the characteristic of linear chains.\textsuperscript{61,186} At rates of $\dot{\gamma} = 0.3 \text{ s}^{-1}$ and higher (i.e., $Wi = 21 > 10$) in regime III, strong dependence of $\gamma_{\text{max}}$ on $\dot{\gamma}$ shows up. We summarize in Figure 6.4 (a)-(b) the coordinates of the overshoot in comparison to those of linear chains as a function of the applied rate. The much stronger scaling of $\gamma_{\text{max}} \sim \dot{\gamma}$ in regime III contrasts the scaling behavior of $\gamma_{\text{max}} \sim \dot{\gamma}^{1/3}$ observed in linear chains.\textsuperscript{186} This feature is clearly due to presence of the arms that postpone the onset of catastrophic disintegration of the backbone entanglement network in regime III so that the stress maximum emerges far more gradually than observed in linear chain systems. Another remarkable feature in Figure 6.4 (a) is a "plateau" in regime IV, where over a range of shear rate $\gamma_{\text{max}}$ reaches a massive value of 30 and remains essentially constant independent of $\dot{\gamma}$. 

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Figure 6.4 (a) The strain at the peak shear stress $\gamma_{\text{max}}$, plotted against the imposed shear rates given in double X axes, with the lower one given in terms of the Weissenberg number $Wi = \frac{\tau_{bb}}{\dot{\gamma}}$, and the upper one given in terms of the shear rate $\dot{\gamma}$, at the reference temperature of 70 °C. The data involve startup shear experiments at four different temperatures of 70, 25, 0 and -10 °C. The WLF shifting factor is 25 between 70 and 25 °C, 33 between 25 and 0 °C and 242 between 25 and -10 °C. (b) The peak shear stress $\sigma_{\text{max}}$, plotted against the imposed shear rate, given in the same double X axes as defined in (a).
The data in Figure 6.4 (a)-(b) offer us a first case to compare with the available pom-pom model\textsuperscript{152} that derives the stress in terms of a stretching factor $\lambda$ and orientation function $S$ as follows

$$\sigma(t) = (15/4)G_{bb} \phi_b^2 \lambda^2 (t^2) S(t), \quad (6.1)$$

where the orientation dynamics are given by

$$\frac{\partial}{\partial t} A(t) = K \cdot A + A \cdot K^T - \frac{1}{\tau_{bb}} \left( A - \frac{1}{3} I \right), \quad S(t) = \frac{A(t)}{\text{trace}[A(t)]}, \quad (6.2)$$

and the backbone stretching is described by

$$\frac{\partial}{\partial \lambda} \lambda = \lambda (K : S) - \frac{1}{\tau_s} (\lambda - 1), \quad \lambda \leq q. \quad (6.3)$$

A modified pom-pom model\textsuperscript{183} introduces drag-strain coupling to rewrite Eq. (3) as

$$\frac{\partial}{\partial \lambda} \lambda = \lambda (K : S) - \frac{1}{\tau_s} (\lambda - 1)e^{\nu^*(\lambda-1)}, \quad \nu^* = \frac{2}{q-1}. \quad (6.4)$$

These equations contain two relaxation times: the relaxation time of the backbone, $\tau_{bb} = \frac{4}{\pi^2} \tau_s s_b \phi_b$, and the stretching time, $\tau_s = s_b \tau_{arm} q$. Here $s_a$ and $s_b$ are the numbers of entanglement per arm and backbone respectively, and $K$ is the deformation rate tensor. The backbone volume fraction $\phi_b$ is defined as $\phi_b = s_b/(2q s_a + s_b)$.

Eq. (2), along with either Eq. (3) or Eq. (4), is solved by Matlab using the command ODE45, based on the following choices of the parameters: $q = 14$, $s_b = 28.7$, $s_a = 1$, $\tau_{arm} = 0.03$ s, $G_{bb} = 1560$ Pa, $\tau_{bb} = 71$ s, and $\tau_s = 12$ s, to achieve a good fit. The solutions are inserted into Eq. (1) to produce the solid curves according to Eq. (3) and dashed curves according to Eq. (4) in Figs. 4(a) and 4(b) respectively. The solid curve has a "plateau"
region where $\gamma_{\text{max}}$ is flat with increasing rate, matching the plateau of the data in Figure 6.4 (a). On the other hand, the data in Figure 6.4 (b) do not appear to level off as indicated by the theoretical solid line. The theoretical dashed lines from the updated pom-pom model do not reveal a plateau for either of the two figures. We presented these calculations only up to the rate of $1/\tau_{\text{arm}}$ since the pom-pom model did not make predictions for higher rates. In this range, the agreement between our data and the pom-pom model is rather promising, given the fact that our LCB is not a simple pom-pom molecule modeled by the theory. For linear chains, disentanglement always occurs in simple shear before the finite extensibility limit is approached. In contrast, entanglements can get locked-in during fast startup uniaxial extension\textsuperscript{187} to show true strain hardening.\textsuperscript{3}

Can LCB delay the disentanglement to the point where the finite extensibility limit is reached even in startup shear? In other words, is shear strain hardening due to non-Gaussian stretching possible in our LCB PS solution? Up to regime IV there is only the sign of strain softening. Moreover, the pom-pom model would only anticipate shear strain softening because of the coupling between chain orientation and stretching. But LCB is expected to play a greater role when the arms are engaged in entanglement. This means application of higher rates in the regime V. By conducting the startup shear experiments at -10 °C, Figure 6.5 shows a typical set of startup shear at equivalent rates from 1,815 (0.3) to 60,500 (10) s\textsuperscript{-1} for $T_{\text{ref}} = 70$ °C. Stress responses at these effectively very high rates are sharply different from the strain softening observed at the lower rates probed at 70 °C as shown in the inset. The initial response exhibits an elastic modulus comparable to $G_0$, confirming that the primary entanglement network with participation
of arms is undergoing elastic deformation. However, this network quickly yields after a few strain units, as expected from the relatively short arms, leaving the backbones to withstand further shearing, at the four lowest rates. The backbone network shows no sign of yielding, however. More remarkably, after a shear strain of ca. 10~15, \( \sigma \) takes an upturn to grow more strongly than linearly with \( \gamma \). In particular, the strain hardening, indicated by the upturn in the stress vs. strain plot on linear scales, implies that non-Gaussian stretching has occurred. In other words, the Gaussian coils between entanglements may have been straightened at such high strains. In the affine deformation limit, the condition to straighten the backbone entanglement strand (bes) can be readily estimated as requiring a strain of \( \gamma_{bes}^* = \frac{L_{bes}}{R_{bes}} = \left(\frac{N_e}{2}\right)^{1/2} = (\phi/2)^{0.6} \lambda_{eq}^* = 16 \), where \( N_e = N_{e0}(\phi/2)^{1.2} \), \( \phi = 0.22 \), and \( \lambda_{eq}^* = (N_{e0})^{1/2} = 4.3 \). Indeed, the upturns in Figure 6.5 take place around strains just below \( \gamma_{bes}^* \).
Figure 6.5 Stress vs. strain plot shows non-Gaussian stretching and "strain hardening" in startup simple shear at -10 °C. Inset is a re-plot from Figure 6.3 on the linear-linear scale to show the usual strain softening.

At the two highest rates, the primary network hardly yields because the shear stress follows closely $\sigma(t) = G_0\dot{\gamma}(t)$. For $\gamma > 11$, $\sigma$ deviates upward from the linear relation given by the inclined line, indicating strong non-Gaussian responses. Thus, depending on the value of the imposed shear rate, either the backbone network ($G_{bb}$) or the primary network ($G_0$) displays strain hardening, i.e., becoming stiffer with increasing external deformation. This is the first report of shear strain hardening for entangled polymeric liquids and thus has rather significant theoretical implications.

It is evident that the present solution can reach the finite extensibility limit because the LCB prevented chain disentanglement from taking place prematurely. Due to the presence of branch points, more severe molecular straining of the entanglement network
can take place before any eventual chain disentanglement. The observed strain hardening of the present system underscores that simple shear can effectively stretch the entanglement network made of LCB regardless of chain orientation. Given the mesh size of the entanglement network, on the order of $a = a_0(\phi/2)^{-0.6} \sim 30$ nm, the molecular tension $f$ within a backbone entanglement strand can be estimated as $f \sim a^2 \sigma_{\text{max}} \sim 0.1$ nN, whereas the force required to break the covalent bond is known to be several nN. Thus, the cause for the sharp strain softening beyond the peak stresses in Figure 6.5 remains elusive and needs to be explored in a future study.

In summary, the LCB PS solutions show a rich variety of transient responses to startup shear at different rates from regime I to V. At low rates, the arms act like solvent to swell the backbone entanglement network, and the comb-like molecules behave like linear chains. The nonlinear rheological responses at low rates can be qualitatively described using the pom-pom model although a different interpretation also exists for the origin of the stress overshoot. The most remarkable behavior is the shear strain hardening observed in regime V where the effect of LCB, i.e., the presence of branch points, is remarkable. We conclude that the observed strain hardening is a result of the molecular deformation reaching the finite extensibility limit. The non-Gaussian response is made possible by the presence of LCB that defers chain disentanglement. This first report of strain hardening upon startup shear of entangled polymeric liquids indicates that more theoretical development is needed.
CHAPTER VII

SUMMARY

Polymers are in every aspect of our daily life, yet we don’t governing equations to tell us how polymers behavior. Nonlinear viscoelasticity and nonlinear rheology still have a long journey to go (They are more like experimental science rather than equations).

In this dissertation, steps are made toward a better understanding of the dynamics of polymers, especially on polymers with long branches. A straightforward synthetic method to produce long chain branched polymers can help the utilization of branched polymers not only in academic research but also in industry applications. The traditional view of always strain softening in shear is overturned by our finding on long chain branched polystyrene solutions, in which strain hardening and non-Gaussian stretching can happen. The origins of strain hardening in extension are also identified as the shrinking of cross-section area in extension together with the postpone of yielding by the presence of branches. An empirical law on the stretchability of polymers is given by the square root of number of entanglements.

Besides those fascinating behavior of branched polymers, there will be more to study. In particular, on what direction should the theories to go, as the current models on branched polymers don’t seem to capture the dynamics of branches.
As the consumption of petroleum and development of nature-sourced polymers, better understanding on their nonlinear rheological behavior will play an important part and help the rational design and development of materials.

Remaining questions include:

What is the relationship between number of branches and the ability to resist elastic yielding; does more branches help or longer branches help;

How much long chain branched polymers blended in linear polymers would change the yielding of linear polymers; what is the magnitude of change and on what range of deformation rates;

How specific is the strain hardening behavior relates to polystyrene, a polymer with high Tg comparing to the experimental temperature of its solutions;
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