NONLINEAR BEHAVIOR IN STARTUP UNIAXIAL EXTENSION OF
ENTANGLED POLYMER MELTS

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NONLINEAR BEHAVIOR IN STARTUP UNIAXIAL EXTENSION OF
ENTANGLED POLYMER MELTS

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Dissertation

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ABSTRACT

It is recently established that transient nonlinear responses of entangled polymers to startup deformation always show a transition from the initial elastic deformation to irreversible deformation (flow). This yielding behavior varies with the applied rate: at a higher rate the entanglement network can be strained to a higher degree before the chain disentanglement causes a breakdown. Moreover, for extensional deformation, at sufficiently high rates, there will be a yield-to-rupture transition, and non-Gaussian stretching followed by brittle rupture will be present.

In this dissertation, we will show for highly entangled linear polymer melts, this yield-to-rupture transition could only occur during extensional deformation. In other words, at comparable rates, non-Gaussian stretching followed by brittle rupture is only available in extensional deformation, but absent in shear deformation. Moreover, at the same effective rate (e.g., the same Rouse–Weissenberg number $Wi_R$ equal to the product of the Hencky rate and the Rouse time) of uniaxial extension the nonlinear responses of entangled polymers are different as temperature changes, pointing out to an evident breakdown of the time-temperature superposition principle (TTS). Specifically, we will show that for the same $Wi_R$ well-entangled polymer melts rupture at relatively low temperatures, yet still 20–30°C above the glass transition temperature $T_g$, but undergo necking-like failure at higher temperatures. When we subject the various entangled melts and solutions to startup uniaxial extension at temperatures even closer to $T_g$, we will have the chance to access a range of unconventionally high rates. We will show the rheological
response is found to deviate significantly from the rubbery elastic deformation that is familiar at higher temperatures. Especially, we discover that a non-network (interchain) contribution dominates the stress response, showing initial Hookean solid-like deformation with stiffness $G_{\text{initial}}$ much higher than the rubbery plateau modulus and subsequent viscous flow comparable to the dissipative component observed with small amplitude oscillatory shear. The transition to viscous flow is found to occur at a time scale longer than typical $\alpha$-relaxation time. In absence of an adequate theory, the observations suggest the importance of the inter-segmental interactions and are inviting new theoretical development.
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CHAPTER I

INTRODUCTION

Polymers are macromolecules made by repeating small molecules\textsuperscript{1-4}. Polymeric materials are important in the daily life. Many of them have superior mechanical, optical or electronic properties\textsuperscript{5-8}, and therefore have become an essential part of the modern world. In this dissertation, several important phenomena of the mechanical properties of highly entangled polymeric materials have been discovered. In particular, we will discuss them in the context of the dynamics of highly entangled polymers during startup deformation.

Rheology is the science to study the deformation and flow of materials\textsuperscript{9-14}. Polymer rheology connects processing and applications of polymeric materials. Over the past several decades, numerous efforts have been made to understand the rheological behaviors of entangled polymeric materials. Since 2006, a new worldview has emerged\textsuperscript{15-16}, which has significantly altered our understanding of nonlinear rheology of entangled polymers.

In the following CHAPTER II, the background knowledge of polymer rheology, as well as recent developments of nonlinear rheology of entangled polymers, will be reviewed and discussed. The concepts introduced in CHAPTER II will be frequently used in the subsequent chapters.
CHAPTER III discusses a first study in the literature of similarities and differences between simple shear and uniaxial extension of entangled polymer melts. In recent years, our group has advocated the concept of yielding to describe the transition from the initial elastic deformation to irreversible flow during the startup deformation of entangled polymers\textsuperscript{15-19}. In CHAPTER III, we will show that such yielding occurs in both simple shear and uniaxial extension at low rates. On the other hand, at comparable higher rates, we find that yielding continues to prevail through chain disentanglement in startup shear, but sufficient entanglements become locked up, allowing non-Gaussian stretching to take place during startup extension, leading to sharp ruptures\textsuperscript{20-23}. In other words, in startup extension, as a function of the applied rate, there is a yield-to-rupture transition. In contrast, only yielding occurs in the same rate range during startup shear\textsuperscript{24}.

In CHAPTER IV, we report the first example of the breakdown of time-temperature equivalence during large uniaxial extension of entangled polymer melts\textsuperscript{20}. Time-temperature superposition principle has been widely used to access a broader dynamic spectrum for polymeric materials. Here, we will show while this principle is valid for linear viscoelastic properties and steady-state properties, it fails to describe some transient responses during startup extensional deformation. Specifically, we will show that the yield-to-rupture transition does not occur at the same effective rate under different temperatures. Also, different failure behaviors were observed, \textit{e.g.}, the material can undergo a much higher degree of extension at low temperatures before its macroscopic failure.

In CHAPTER V, we will explore the rheological responses at unconventionally high rates by conducting experiments closer to glass transition temperature $T_g$. Our
experiments confirm that an inter-segmental frictional contribution to the mechanical stress can be neglected where the deformation rate is well below $1/\tau_e$, which is situated at the second crossover frequency $\omega_e$. Conversely, on the time scale specified by $\omega_e$, a significant viscous component of stress emerges and dominates over the initial entanglement network response. More remarkably, the initial rheological response is found to be solid-like and can be characterized by an elastic modulus one or two orders of magnitude higher than the melt rubbery plateau modulus $G_N^0$. This is the first report to reveal the non-glassy inter-segmental association that emerges tens of degrees above the glass transition temperature $T_g$ and produces a measurable mechanical consequence.

In CHAPTER VI, a summary of this dissertation will be presented, and possible future directions will also be included.
CHAPTER II

BACKGROUND INFORMATION

In this chapter, relevant fundamental knowledge and concepts will be reviewed and discussed. We will first introduce basic knowledge of polymer rheology, and then we will discuss traditional understandings, as well as recent developments on the dynamics of entangled polymeric systems. We will then briefly talk about the glass transition of polymers.

2.1 Fundaments of polymer rheology

In this section 2.1, fundamental knowledge of polymer rheology and related concepts will be reviewed.

2.1.1 Mechanic deformations

The practical industrial processing usually involves complicated types of deformations. In lab research, two most fundamental deformations, namely, the simple shear and uniaxial extension, are usually the starting points.\textsuperscript{9-13}
Figure 2.1 Schematic illustration of a simple shear deformation.

Figure 2.1 is a schematic illustration of a simple shear deformation. The material is sheared between two plates, and the shear stress is defined as

$$\sigma = \frac{F}{A}$$  \hspace{1cm} (2.1)

where $F$ is the measured force and $A$ is the cross sectional area of the material. The strain unit $\gamma$ is defined as

$$\gamma = \frac{\Delta x}{H}$$  \hspace{1cm} (2.2)

where $\Delta x$ is the displacement the material suffered, and $H$ is gap between the two plates. The shear rate is defined as

$$\dot{\gamma} = \frac{d\gamma}{dt} = \frac{v}{H}$$  \hspace{1cm} (2.3)

where $v$ is the speed of the moving plate.

Another fundamental type of deformation is the uniaxial extension, which is schematically illustrated in Figure 2.2.
In a uniaxial extension deformation, the material is stretched along one axis, and the stretching ratio, $\lambda$, is defined as

$$\lambda = \frac{L}{L_0} \quad (2.4)$$

where $L_0$ is the initial length of the material, and $L$ is the instant length during the deformation. The extension rate, also known as Hencky rate, is defined as

$$\varepsilon = \frac{v}{L} = \frac{v}{L_0 + vt} \quad (2.5)$$

where $v$ is the relative moving speed between the two ends of the sample. We could further derive that

$$\frac{d\lambda}{dt} = \frac{d(L)}{L_0 dt} = \frac{1}{L_0} \frac{dL}{dt} = \frac{v}{L_0} = \frac{\dot{\varepsilon} L}{L_0} = \dot{\varepsilon} \lambda \quad (2.6)$$

so that

$$\frac{d\lambda}{\lambda} = \varepsilon dt \quad (2.7)$$

The integral shows that
\[ \lambda = \exp(\varepsilon) = \exp(\varepsilon_H) \]  
(2.8)

The parameter \( \varepsilon_H \) is called Hencky strain. The stretching ratio \( \lambda \) is the exponential of Hencky strain.

To measure the mechanical responses during a uniaxial extension, the engineering stress is defined as

\[ \sigma_{\text{engr}} = \frac{F}{A_0} \]  
(2.9)

where \( F \) is the measured force and \( A_0 \) is the initial cross sectional area of the sample. The true stress, also called the Cauchy stress, is defined as

\[ \sigma = \frac{F}{A} \]  
(2.10)

where \( A \) is the cross sectional area during the extensional deformation. Assuming the density (volume) of the material is constant during the deformation, we could derive

\[ \sigma = \frac{F}{A} = \frac{F}{A_0} \frac{A_0}{A} = \frac{F}{A_0} \frac{L}{L_0} = \lambda \cdot \sigma_{\text{engr}} \]  
(2.11)

So, the value of true stress is the production of stretching ratio and engineering stress.

For viscous liquids, Newton’s law\(^{9-13}\) could describe their mechanical response during external deformation. For example, during a simple shear, the shear stress could be described as

\[ \sigma = \eta \dot{\gamma} \]  
(2.12)

where \( \eta \) is the viscosity of viscous material.

For elastic solids, Hooke’s law\(^{9-13}\) could describe their mechanical response. Still taking the simple shear as an example, the shear stress is
\[ \sigma = G\gamma \] (2.13)

where \( G \) is the modulus of the elastic material.

Newton’s law and Hooke’s law describe the mechanical responses of the ideal viscous and elastic materials, respectively. Any stress-strain relationship that deviates from them shall be called nonlinear behavior.

2.1.2 Rheological measurements and concepts

Polymer material is known to have viscoelasticity. When the material is imposed a very small strain (i.e., \( \gamma \to 0 \)), or a very small deformation rate (i.e., \( \dot{\gamma} \to 0 \)), the intrinsic properties such as modulus and viscosity shall be independent of the strain and deformation rate. This region of test conditions is called linear region\(^9\text{-}^{13}\).

Small amplitude oscillatory shear (SAOS) is usually the starting point to probe the linear viscoelasticity. During SAOS measurement, a small oscillatory deformation is applied to the sample:

\[ \gamma(t) = \gamma_0 \sin \omega t \] (2.14)

where \( \gamma_0 \) is the amplitude of the oscillatory shear. The measurement is schematically shown in Figure 2.3.
Figure 2.3 Schematic show of SAOS measurement. (a) Experimental setup; (b) the strain and stress as the function of time
The corresponding stress response should have the same format, except for the existence of a phase difference.

\[ \sigma(t) = \sigma_0 \sin(\omega t + \delta) \]  \hspace{1cm} (2.15)

For ideal elastic material, the stress and strain would be in phase and therefore \( \delta = 0 \). For ideal viscous material, \( \delta = 90^\circ \). For viscoelastic polymeric material, \( 0 < \delta < 90^\circ \).

For an easier and more convenient mathematical description, the complex modulus is defined as

\[ G^*(i\omega) = G'(\omega) + iG''(\omega) \]  \hspace{1cm} (2.16)

where \( G'(\omega) = \frac{\sigma_0}{\gamma_0} \cos \delta \) is the storage modulus and \( G''(\omega) = \frac{\sigma_0}{\gamma_0} \sin \delta \) is the loss modulus. They represent the elastic component and viscous component of the viscoelasticity of the material, respectively.

The absolute value of complex modulus is therefore

\[ |G^*| = \sqrt{G'^2 + G''^2} \]  \hspace{1cm} (2.17)

and the complex viscosity is

\[ |\eta^*| = \frac{|G^*|}{\omega} \]  \hspace{1cm} (2.18)

the dynamic viscosity is defined as

\[ \eta' = \frac{G'}{\omega} \]  \hspace{1cm} (2.19)

In order to describe the viscoelasticity, models were proposed. Maxwell model\(^1,10\) is the combination of a spring and a dashpot in series, as shown in Figure 2.4.
Figure 2.4 Components of the Maxwell model.

The spring represents the elastic component of the material, and the dashpot represents the viscous component of the material. During the deformation, the spring and the dashpot would suffer the same amount of stress. Based on the structure of the model, we can write

\[ \gamma = \frac{\sigma}{G} + \frac{\sigma}{\eta} \]

(2.20)

A characteristic relaxation time, \( \tau \), is defined as \( \tau = \frac{\eta}{G} \). The above equation can be rewritten as
\[
\dot{\gamma} = \frac{\sigma}{G} + \frac{\sigma}{G\tau}
\]  

(2.21)

For a stress relaxation measurement, where a sudden small deformation is imposed on the sample and the stress decay is then measured, we have the condition of \( \dot{\gamma} = 0 \), so

\[
\dot{\sigma} + \frac{\sigma}{\tau} = 0
\]  

(2.22)

solving this differential equation, we have

\[
\sigma(t) = \sigma_0 \exp\left(-\frac{t}{\tau}\right)
\]  

(2.23)

where \( \sigma_0 \) is the stress at the moment \( t=0 \). Thus, Maxwell model predicts the exponential decay of the stress for a stress relaxation measurement.

Besides the stress relaxation, Maxwell model could also predict the SAOS measurement. In a SAOS measurement, we have

\[
\gamma = \gamma_0 e^{i\omega}, \text{ and } \sigma = \sigma_0 e^{i(\omega + \delta)}
\]  

(2.24)

combining with equation 2.21, and define \( \tau = \frac{\eta}{G} \), we have

\[
\sigma(1+i\omega\tau) = i\omega\tau \sigma_0 G
\]  

(2.25)

The complex modulus can be therefore written as

\[
G^* = \frac{\sigma}{\gamma} = \frac{i\omega\tau}{1+i\omega\tau} G = \frac{(\omega\tau)^2}{1 + (\omega\tau)^2} G + \frac{i\omega\tau}{1 + (\omega\tau)^2} G
\]  

(2.26)

so based on Maxwell model,

\[
G' = \frac{(\omega\tau)^2}{1 + (\omega\tau)^2} G \text{ and } G'' = \frac{\omega\tau}{1 + (\omega\tau)^2} G
\]  

(2.27)
The result is schematically shown in Figure 2.5, with key features labeled. The crossover of $G'$ and $G''$ occurs at the condition $\tau = \frac{1}{\omega_c}$, where $\omega_c$ is the crossover frequency.

![log G' and G''](image)

Figure 2.5 Schematic show of $G'$ and $G''$ as the function of $\omega \tau$ according to the Maxwell model.

Voigt model\(^1\) is another phenomenological model, which combines a spring with a dashpot in parallel. The structure is shown schematically in Figure 2.6.
Figure 2.6 The structure of Voigt model.

The same as in Maxwell model, the spring represents the elastic component of the material, and the dashpot represents the viscous component of the material. However, in Voigt model, during the deformation, the spring and the dashpot would suffer the same amount of strain, rather than stress.

Based on the structure of the model, we can write

\[ \sigma = G \gamma + \eta \dot{\gamma} \] \hspace{1cm} (2.28)

Consider a creep experiment where a constant stress \( \sigma_0 \) is applied, and define \( \tau = \frac{\eta}{G} \), we have
\[
\frac{d\gamma}{\sigma_0 - G\gamma} = \frac{dt}{\eta}
\]  
(2.29)

Solving this differential equation, we have

\[
\gamma(t) = \frac{\sigma_0}{G} (1 - e^{-\frac{t}{\tau}}) = \gamma(\infty)(1 - e^{-\frac{t}{\tau}})
\]  
(2.30)

where \(\gamma(\infty) = \frac{\sigma_0}{G}\) is the strain for \(t \to \infty\). Thus, Voigt model could be used to predict creep measurements. The prediction is schematically shown in Figure 2.7.

![Figure 2.7 Creep measurement based on Voigt model prediction.](image)

Investigations of the rheological properties of polymers show that there is a correlation between the shapes of the functions describing the steady-state properties and the dynamic properties. Cox-Merz rule\(^{9-10, 12-13}\) is a widely used empirical correlation between the dynamic and steady-state characteristics of polymers. Though there is no
strong theoretical background that it should work for all polymers, it is valid for many polymers.

Cox-Merz rule says the steady-state viscosity under a specific shear rate is equal to the complex viscosity under the frequency with the same value of the shear rate. It is expressed as

$$\eta(\dot{\gamma}) = \eta^*(\omega), \text{ at } \dot{\gamma} = \omega.$$  \hspace{1cm} (2.31)

Boltzmann superposition\textsuperscript{2, 9-13} principle is another important concept in polymer rheology. It states that the effects of mechanical history are linearly additive. For creep, this means each stress contributes to the strain independently and the total strain is the linear superposition of each stress contribution. Similarly, in stress relaxation measurement, each strain contributes to the stress relaxation process independently, and the total stress during the relaxation process is the linear superposition of the effects from all the strains. Suppose each stress or strain is imposed on the material at the moment of \( t=u \), for creep and stress relaxation respectively, we can write the mathematical expression of Boltzmann superposition principle as\textsuperscript{10}

$$\gamma(t) = \int_{-\infty}^{t} J(t-u) \frac{\partial \sigma(u)}{\partial u} \, du$$  \hspace{1cm} (2.32)

for creep, where \( J \) is the creep compliance, and\textsuperscript{10}

$$\sigma(t) = \int_{-\infty}^{t} G(t-u) \frac{\partial \gamma(u)}{\partial u} \, du$$  \hspace{1cm} (2.33)

for stress relaxation.
2.1.3 Time-temperature superposition

At different temperatures, polymeric materials have different characteristic relaxation times. Thus, at different temperatures, polymeric materials respond to the same deformation rate differently. A fast deformation at a high temperature is equivalent to a slower deformation at a lower temperature. Using time-temperature superposition principle\textsuperscript{2, 9-10, 25}, the dynamics of polymers could be shifted between different temperatures by a shifting factor $a_T$.

Time-temperature superposition principle could be used to expand the dynamic information of the material at a specific temperature. If dynamic information is collected at each of the different temperatures, a mastercurve at a specific temperature can be constructed by shifting all the dynamic data to a reference temperature. Figure 2.8 shows how this principle works for a polycarbonate melt.

![Figure 2.8 Demonstration of time-temperature superposition principle on a polycarbonate melt. SAOS measurements were performed at four different temperatures, and the mastercurve is constructed using one temperature as the reference temperature.](image-url)
The Williams-Landel-Ferry (WLF) equation\textsuperscript{25} is a widely used empirical equation to describe the time-temperature superposition principle. The format of the equation is as below

\[
\log a_T = \log \frac{\tau_T}{\tau_0} = -\frac{C_1 \cdot (T - T_0)}{C_2 + (T - T_0)}
\]  

(2.34)

where \(a_T\) is the shifting factor, and \(T_0\) is the reference temperature. \(\tau_T\) and \(\tau_0\) are relaxation times of the material at temperature \(T\) and \(T_0\) respectively. Specifically, if the reference temperature \(T_0\) is chosen to be the glass transition temperature \(T_g\), universally for most polymers, \(C_1\approx17.5\) and \(C_2\approx51.6\).

One important assumption for the success of time-temperature superposition is the assumption that all the relaxation modes in a polymer chain have the same temperature dependence\textsuperscript{2}. When this assumption does not hold, the breakdown of time-temperature superposition will be present.

2.2 Entangled polymers

In the previous section 2.1, the fundamental knowledge on polymer rheology has been introduced. In this dissertation, most focus will be placed on the behaviors of highly entangled polymer melts and solutions. In this section 2.2, unique features for highly entangled polymer melts and solutions will be reviewed and discussed. We will begin with classical rubber elasticity theory, which is used to describe crosslinked rubbers. We will then discuss the features of uncrosslinked, but entangled polymer melts and solutions.
2.2.1 Classical rubber elasticity theory

Rubber can be treated as a highly entangled network, with all the entanglement junctions crosslinked. The classical rubber elasticity theory\textsuperscript{2, 26}, which was developed decades ago, is used to describe the behaviors of rubbers.

For a given rubber network, as shown in Figure 2.9, let’s use the subscription $i$ to represent each string segment between entanglement junctions.

![Schematic show of a rubber network.](image)

Figure 2.9 Schematic show of a rubber network.

For each segment $i$, the conformational entropy is given by

$$ S_i = k_B \ln \Omega_i $$

(2.35)

where $k_B$ is the Boltzmann constant and $\Omega$ is the number of microstates. Assuming Gaussian distribution holds, we have

$$ \Omega_i \sim P(R_i) = e^{-\frac{3R_i^2}{2 \langle R^2 \rangle}} $$

(2.36)
where $R_i$ is the end-to-end distance of each segment, and $<R^2>$ is the mean-square end-to-end distance. Assuming the total number of string segments is $n$, therefore the total entropy is

$$S = \sum_{i=1}^{n} S_i = k_B \ln \Omega, \text{ where } \Omega = \prod_{i=1}^{n} \Omega_i.$$  \hspace{1cm} (2.37)

The Helmholtz free energy of the system is therefore

$$A = U - TS = U + \frac{3}{2} k_B T \sum_{i=1}^{n} \frac{R_i^2}{<R^2>}. \hspace{1cm} (2.38)$$

Consider a uniaxial extension, and assume stretching is along $z$ axis. When the deformation is affine (i.e., the microscopic and macroscopic deformation always have the same deformation ratio), we have the following end-to-end distance at each stretching ratio $\lambda$.

$$R_{iz} \rightarrow \lambda R_{iz}, R_{ix} \rightarrow \frac{1}{\sqrt{\lambda}} R_{ix}, \text{ and } R_{iy} \rightarrow \frac{1}{\sqrt{\lambda}} R_{iy}$$

where $R_{ix}$, $R_{iy}$ and $R_{iz}$ are the initial end-to-end distances at each direction. At each stretching ratio $\lambda$, we have

$$A(\lambda) = U + \frac{3k_B T}{2 <R^2>} \sum_{i=1}^{n} \left( R_{iz}^2 \lambda^2 + \frac{R_{ix}^2 + R_{iy}^2}{\lambda} \right). \hspace{1cm} (2.39)$$

since

$$\sum_{i=1}^{n} R_{ix}^2 = n \left( \frac{\sum_{i=1}^{n} R_{ix}^2}{n} / n \right) = n <R_{ix}^2> \hspace{1cm} (2.40)$$

$$\sum_{i=1}^{n} R_{iy}^2 = n \left( \frac{\sum_{i=1}^{n} R_{iy}^2}{n} / n \right) = n <R_{iy}^2> \hspace{1cm} (2.41)$$

$$\sum_{i=1}^{n} R_{iz}^2 = n \left( \frac{\sum_{i=1}^{n} R_{iz}^2}{n} / n \right) = n <R_{iz}^2> \hspace{1cm} (2.42)$$
\[ <R_{ix}^2> = <R_{iy}^2> = <R_{iz}^2> \]  
\[ (2.43) \]

\[ <R_{ix}^2> + <R_{iy}^2> + <R_{iz}^2> = <R^2>, \]  
\[ (2.44) \]

we have

\[ A(\lambda) = U + \frac{n k_B T}{2} (\lambda^2 + \frac{2}{\lambda}) \]  
\[ (2.45) \]

For an ideal rubber, the stretching does not change the internal energy. The retraction force \( F \) during a uniaxial extension is therefore

\[ F = \frac{\partial A}{\partial L} = \frac{\partial A}{\partial \lambda} \frac{\partial \lambda}{\partial L} = \frac{n}{L_0} k_B T (\lambda - \frac{1}{\lambda^2}) \]  
\[ (2.46) \]

Since \( z \) is the stretching direction, and \( \lambda = L/L_0 \), we have

\[ F = \frac{\partial A}{\partial L} = \frac{\partial A}{\partial \lambda} \frac{\partial \lambda}{\partial L} = \frac{n}{L_0} k_B T (\lambda - \frac{1}{\lambda^2}) \]  
\[ (2.47) \]

The engineering stress is therefore

\[ \sigma_{engr} = \frac{F}{A_0} = \frac{n}{A_0 L_0} k_B T (\lambda - \frac{1}{\lambda^2}) = \rho k_B T (\lambda - \frac{1}{\lambda^2}) = G(\lambda - \frac{1}{\lambda^2}) \]  
\[ (2.48) \]

where \( \rho \) is the number density of string segments. The above equation \( \sigma_{engr} = G_N^0 (\lambda - 1/\lambda^2) \) is called the neo-Hookean \(^2\) equation.

2.2.2 Edwards-Vilgis Model

Edwards and Vilgis tried to improve the rubber elasticity theory by considering the slip links between chains\(^{27-28}\), in addition to the crosslink junctions. In the Edwards-Vilgis model\(^{28-29}\), the engineering stress upon uniaxial extension is the summation of two contributions, namely a crosslink contribution (\( \sigma_c \)) and a slip link contribution (\( \sigma_s \)), and has the following form\(^{29}\):
\[
\sigma_{\text{enr}} = \sigma_c + \sigma_s, 
\]  

(2.49)

where

\[
\sigma_c = N_c k TD \left( \frac{1 - \alpha^2}{A^2} - \frac{\alpha^2}{A^2} \right),
\]  

(2.50)

\[
\sigma_s = N_s k TD \left\{ \frac{(1 - \alpha^2)(1 + \eta)}{A^2} \left[ \frac{(1 - \eta^2\lambda)^2}{B^2(\lambda + \eta)^2} + \alpha^2 \left( \frac{\lambda^2}{B} + \frac{2}{\lambda + \eta} \right) \right] + \frac{\lambda \eta}{B(\lambda + \eta)} - \frac{\alpha^2}{A} \right\},
\]  

(2.51)

and

\[
A = 1 - \alpha^2(\lambda + \frac{2}{\lambda}), \quad B = 1 + \eta \lambda^2, \quad \alpha = \frac{1}{\lambda_m}, \quad D = \lambda - \frac{1}{\lambda^2}.
\]  

(2.52-2.55)

In these equations, \(N_c\) and \(N_s\) are density of crosslinks and slip links, respectively. \(\lambda_m\) is the maximum attainable ratio during extension, and \(\eta\) is a dimensionless slip parameter. Edwards-Vilgis model will be used in CHAPTER IV and CHAPTER V of this dissertation.

2.2.3 Entangled polymeric materials

In this section 2.2.3, we will review the understanding of uncrosslinked, but highly entangled polymeric materials.

2.2.3.1 Historic backgound and the tube model

The effect of entanglements is of vital importance to understand the behavior of highly entangled polymeric materials. One most common example of the entanglement effect is the increase of viscosity as the function of molecular weight. The viscosity, \(\eta\),
first increases with molecular weight following a scaling law $\eta \sim M$. Once the molecular weight exceeds a critical value $M_c$, due to the effect of entanglement the scaling changes to $\eta \sim M^{3.4}$. This is schematically shown in Figure 2.10.

![Figure 2.10 Schematic show of $\eta$ vs. $M$ for polymeric materials.](image)

Over the past several decades, numerous efforts have been made to understand the physics of highly entangled polymer melts and solutions, especially by Green and Tobolsky\textsuperscript{30}, Yamamoto\textsuperscript{31} and Lodge\textsuperscript{32}, who extended the classical rubber elasticity theory to highly entangled polymer melts and solutions, by assuming the existence of a temporary network with constantly breaking and re-forming entanglement junctions.
During the past 30 years, significant efforts have been placed on the application of the tube model\textsuperscript{33-34}, which was first proposed based on P. G. de Gennes’s reptation idea\textsuperscript{35}, and then constructed by a series of publication of M. Doi and S. F. Edwards\textsuperscript{36-40}. In the tube model, a test chain is supposed to be confined in a tube formed by its surrounding chains, as illustrated in Figure 2.11. The movement of the test chain could only be realized by one-dimension reptation along the tube. A simple scaling analysis based on tube model could give a scaling behavior of viscosity and molecular weight as $\eta \sim M^3$. Later, new concepts such as contour length fluctuation (CLF), constrain release (CR) and convective constrain release (CCR) were introduced in order to improve the original model\textsuperscript{41-42}.

![Figure 2.11 A schematic illustration of the tube model.](image)

2.2.3.2 Recent developments on nonlinear rheology of entangled polymers

The improvement of tube model continues to very recently. More advanced versions of the tube model, such as Rolie-Poly model\textsuperscript{43} and GLaMM model\textsuperscript{44}, have become available. Despite of the success of tube model in the prediction of many linear and nonlinear viscoelastic properties, there is still debate on the foundation and basic
assumptions of the model. In the past decade, a new worldview has emerged\textsuperscript{15-16}, and it seems there are some missing components in the basic assumption of the tube model.

In the new worldview, a key concept to understand the nonlinear rheology of entangled polymeric material is yielding, which signifies a transformation from the initial elastic deformation to the irreversible deformation\textsuperscript{17-19,45-46}. This yielding behavior seems to be a leading characteristic. In the tube model, the experimentally observed stress overshoot is believed to be due to the chain over-orientation\textsuperscript{40}. In the new worldview, however, it is suggested that the shear stress\textsuperscript{15} (for shear deformation) or engineering stress\textsuperscript{46} (for extensional deformation) maximum signifies global yielding, at which the entanglement network suffers a massive structural breakdown through chain disentanglement. This yielding process is schematically shown in Figure 2.12.

![Figure 2.12 Schematic illustration of the yielding process.](image-url)
It has been suggested that this yielding behavior is due to the force imbalance between the growing elastic retraction force and the intermolecular gripping force (IGF)\textsuperscript{15-16}. Since the tube model is a single-chain mean-field theory, it is incapable to describe the IGF, which is caused by the topological uncrossability of entangled chains. The origin of IGF is shown in the following Figure 2.13.

![Figure 2.13](image)

Figure 2.13 The origin of the intermolecular gripping force (IGF): the uncrossability of entangled chains.

### 2.2.4 The yield-to-rupture transition in extensional deformation

It is recently found that when the applied Hencky rate is high, instead of showing a maximum, the engineering stress will monotonically grow, and the material will fail in a window-glass-like rupture manner\textsuperscript{21-22}.

Figure 2.14 shows the stress-strain curve of a SBR 1M solution\textsuperscript{22} (80 wt.\%, where the solvent is a SBR 20K melt) sample at different rates under room temperature. At low rates, i.e., no larger than a Hencky rate of 0.6s\textsuperscript{-1}, it is found that there is a maximum in the engineering stress. As discussed in the previous section 2.2.3.2, this engineering stress maximum signifies the global yielding, at which the entanglement network suffers massive structural breakdown. After the engineering stress maximum, the sample will eventual fail due to strain localization in a necking manner, as shown in Figure 2.15 (a).
When the applied Hencky rate is higher than 1s$^{-1}$, however, it is found that the engineering stress could grow monotonically, and a window-glass-like rupture is
observed. After the rupture, the sample can return to its original dimension. This is shown in Figure 2.15 (b).

Clearly, as the applied rate increases, there is a yield-to-rupture transition. The origin of this transition is interpreted as below.

All entanglement junctions in the entangled polymers do not have the same strength. Some are weaker, and are easier to disentangle upon external deformation, while some stronger junctions are more difficult to disentangle. A spectrum of entanglement state is shown in Figure 2.16.

![Figure 2.16 A schematic illustration of entanglement state. The red dots represent the strongest entanglement junctions, while the green ones represent the weakest. Reprint from ref 22 with permission.](image)

It seems at low rates, all the entanglement junctions can get lost eventually, thus a maximum is shown in the stress-strain curve. The sample will go through global yielding and fail in a necking-like strain localization manner. At high rates, it seems that some
strong entanglement junctions are capable of getting locked, and these locked junctions allow the monotonic growth of the engineering stress. When the stress level is too high, the sample will experience window-glass-like rupture possibly due to chain scission. In the following CHAPTER III, a systematic comparison will be made between shear and extensional deformation regarding this yield-to-rupture transition, and the mechanism of the yield-to-rupture transition will be discussed in more details.

2.3 Glass transition of polymers

Glass transition is an important phenomenon for amorphous polymers and semi-crystalline polymers. When glass transition occurs, many physical properties, especially mechanical properties, will dramatically change. The modulus and viscosity of the material will have a 3~4 orders of magnitude difference below and above the glass transition temperature ($T_g$). Other physical properties that change dramatically around $T_g$ include, but are not limited to thermal expansion coefficient ($\alpha$), heat capacity ($C_p$), refractive index ($n$) and specific volume ($v$).

Experimentally, one of the most widely used methods of demonstrating the glass transition and determining $T_g$ is by a differential scanning calorimetry (DSC) measurement. Figure 2.17 schematically shows the DSC curve as the temperature is scanned from below $T_g$ to above $T_g$ at a specific heating rate.
So far, the nature of glass transition is still under debate. There have been attempts to understand glass transition from a thermodynamic point of view\(^1\). In a first-order thermodynamic transition\(^1,49\), basic thermodynamic properties such as enthalpy \((H)\) and volume \((V)\) will change abruptly. An example of such transition is melting. In a second-order thermodynamic transition, the derivatives of \(H\) and \(V\) will change abruptly. The derivatives of \(H\) and \(V\) are heat capacity \((C_p)\) and thermal expansion coefficient \((\alpha)\) respectively, as defined below

\[
C_p = \left(\frac{\partial H}{\partial T}\right)_p \quad \text{and} \quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p .
\] (2.56)

Since heat capacity \((C_p)\) and thermal expansion coefficient \((\alpha)\) do change abruptly around \(T_g\), glass transition resembles a second-order thermodynamic transition, although detailed studies show that it is not a strict thermodynamic transition\(^1,47-48\).
Other attempts to understand the glass transition include free volume theory and kinetic theory. In the free volume theory\textsuperscript{1}, the “empty space” between polymer chains (free volume) will decrease as temperature is dropping, and will eventually reach a critical value when \( T_g \) is reached. William, Landel and Ferry suggested that universally the critical free volume fraction when glass transition occurs is 2.5%. In the kinetic theory\textsuperscript{48}, \( T_g \) is considered to be the temperature at which the segmental relaxation time is on the same order of magnitude as the experimental time scale. Kinetic description focuses on time-dependent phenomena and ascribes no causal or underlying role to thermodynamics.

In the glass transition regime, fragility\textsuperscript{47, 50-52} is the parameter used to characterize how quickly the dynamics of materials slow down upon cooling. Fragility is often defined as the slope of viscosity (\( \eta \)) or relaxation time (\( \tau \)) with temperature as \( T_g \) is approached. The mathematical form of fragility is shown as below:

\[
m = \left. \frac{\partial \log \tau}{\partial \left( \frac{T_g - T}{T} \right) \bigg|_{T=T_g} \right), \quad \text{or} \quad \left. \frac{\partial \log \eta}{\partial \left( \frac{T_g - T}{T} \right) \bigg|_{T=T_g} \right} \tag{2.57}
\]

where \( m \) is the fragility. Glass-forming materials with a high fragility are usually referred to as “fragile”, while those with a low fragility are usually referred to as “strong”\textsuperscript{51}.

In CHAPTER V, we will discuss the mechanical responses of polymer melts under unconventionally high rates. In order to achieve these conditions, temperatures of the test
must be closer to $T_g$ compared to conventional conditions. Cautions should be made to
distinguish the effect of glass transition and inter-segmental interaction on the mechanical
responses.
CHAPTER III

THE SIMILARITIES AND DIFFERENCES BETWEEN SHEAR AND EXTENSIONAL DEFORMATION

3.1 Introduction

In this chapter, we will extend our previous understanding concerning the nonlinear responses of entangled polymer solutions and melts to large external deformation in both simple shear and uniaxial extension. Many similarities have recently been identified for both step strain and startup continuous deformation, including elastic yielding, i.e., chain disentanglement after cessation of shear or extension, and emergence of a yield point during startup deformation that involves a deformation rate in excess of the dominant molecular relaxation rate. At a sufficiently high constant Hencky rate, uniaxial extension of an entangled melt is known to produce window-glass-like rupture. Yet, in the same rate range, the same entangled melt only yields in simple shear, and the resulting shear banding is clearly not a characteristic of rupture. Thus, we conclude that chain entanglements respond to simple shear in the manner of yielding whereas uniaxial extension is rather effective in causing some entanglements to lock up, making it impossible for the entanglement network to yield at high rates.
3.1.1 Background

As an important branch of polymer science and engineering, the subject of polymer rheology studies mechanical responses to well-defined forms of deformation and promises to be a useful guide for polymer processing\(^\text{14}\). Over 100 million tons of polymers undergo processing (e.g., extrusion and film blowing) every year worldwide that usually involves complicated and poorly defined deformations. The study of polymer processing behavior begins with rheology that typically deals with the two most commonly studied types of deformation: simple shear and uniaxial extension. Many commercial instruments have been designed to meet the need of rheology, i.e., to produce either shear or extensional deformation. The tradition in the field of polymer rheology had been for decades, until recently, to assume that homogeneous deformation would take place in these rheometers\(^9, 12-13\). This textbook assumption is both convenient and necessary for comparison with a constitutive description of polymer rheology. Recent experimental discoveries showed that the perception of homogeneous deformation, in either shear\(^1\text{7, 45, 53-55}\) or extension\(^1\text{9, 56-57}\), was incorrect for polymer solutions and melts that are well entangled.

3.1.2 Yielding: the commonality between shear and extensional deformation

Universally, entangled polymers yield on time scales much shorter than the reptation time when subjected to fast startup deformation\(^\text{15}\). The molecular origin of the macroscopic yielding is plausibly the chain disentanglement because of an imbalance\(^\text{15, 46}\), between the growing intrachain retraction force (due to chain deformation) and intermolecular gripping force (due to chain uncrossability). For well-entangled polymers,
the microscopic yielding (i.e., chain disentanglement) often leads to macroscopic strain localization. In startup continuous shear, we applied a particle-tracking velocimetric (PTV) method to discover shear banding beyond the stress overshoot. The state of shear banding can be rather stable, persisting for hundreds of strain units. For startup uniaxial extension, the strain localization causes specimen failure during stretching as many workers found out well before our work.

Our previous work has emphasized the commonality between shear and extension. First, there was the evidence that the stress overshoot during startup shear should be a yield point: The sheared sample can nearly undergo full elastic recovery before this point, and its ability to show elastic recovery sharply drops beyond the stress overshoot. This observation led to the understanding that startup uniaxial extension would also produce a transition from elastic deformation to irrecoverable deformation (flow) when the engineering stress \( \sigma_{\text{engr}} \) attains a maximum. The recognition of this commonality (i.e., yielding) has also clarified the confusion about the difference in the nonlinear responses of entangled melts to startup shear and extension. The transient shear viscosity \( \eta^+(t) \) at a finite rate is always lower than that obtained in the zero-rate limit \( \eta_0^+(t) \), whereas the transient elongational viscosity \( \eta_E^+(t) \) can deviate upward from the zero-rate elongational viscosity \( 3\eta_0^+(t) \). This difference has led experts to believe that entangled melts would really undergo strain hardening. It turns out that this difference has a great deal to do with yielding of the entanglement network. In the zero-rate limit, the transient viscosity can only increase linearly with time in both shear and extension. At high rates of deformation, stress can at best grow linearly with time in shear, whereas in uniaxial extension at a constant Hencky rate \( \dot{\varepsilon} \), the Cauchy tensile stress \( \sigma \) can grow...
exponentially with time before yielding takes place. Yielding leads to weaker stress increase than linear growth in simple shear, whereas in uniaxial extension the true extensional stress $\sigma$ could still increase much more strongly than linearly in time before yielding causes a sufficiently rapid decline of the tensile force$^{64}$.

The present chapter examines whether entangled melts would respond differently to shear vs. extension because of their kinematic difference. In particular, we note that an entangled melt has been known to undergo rubber-like rupture at sufficiently high Hencky rates of extension$^{31, 58-59}$. No parallel experiments have been performed on the same system to find out whether chain entanglements could actually avoid disentanglement in simple shear at the comparable rates.

3.2 Experimental

The material characteristics of the entangled polymer melt and the experimental methods will be discussed in this Section 3.2.

3.2.1 Materials

A nearly monodisperse styrene-butadiene random copolymer (SBR) was synthesized by anionic polymerization at Bridgestone Americas Center for Research and Technology via courtesy of Dr. Xiaorong Wang. Table 3.1 shows the molecular characteristics of this SBR melt.
Table 3.1 Molecular Characteristics of the SBR Melt in this Study

<table>
<thead>
<tr>
<th>T_g (°C)</th>
<th>M_w (kg/mol)</th>
<th>M_w/M_n</th>
<th>% Vinyl</th>
<th>% Styrene</th>
<th>% Butadiene</th>
</tr>
</thead>
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The linear viscoelastic properties of the SBR melt was first evaluated by performing small-amplitude oscillatory shear measurements on a Physica MCR 301 rotational rheometer with 8.8 mm diameter parallel plates. The master curve shown in Figure 3.1(a) was constructed from separate measurements at 25 and 60 °C, using the time-temperature superposition principle, with 25 °C being the reference temperature. The plateau modulus $G^0_N$ is found to be 0.53 MPa. The number of entanglements per chain $Z$ can be estimated as $Z = \frac{M_w}{M_c} = \frac{M_w}{(\rho RT/G^0_N)}$, which is about 37 for this SBR melt. The sample has a long terminal relaxation time $\tau$ of around 2500 s at 25 °C. The Rouse relaxation time $\tau_R$ of the sample can be estimated to be around 23 s.

The same SBR melt was also subjected to chemical crosslinking to provide a reference point. The curing agent for the crosslink reaction, dicumyl peroxide, was purchased from Sigma-Aldrich and used as received. Dicumyl peroxide has been proven to be an effective curing agent for the preparation of crosslinked rubbery materials. The mechanism of the crosslink reaction will be briefly discussed in Section 3.5 as an appendix of this chapter. The crosslinked SBR was prepared by first dissolving the SBR melt in toluene to achieve a uniform solution. Then 1 wt% of the crosslinker, dicumyl peroxide, was added into the solution. After reaching the uniform dispersion, the toluene is subsequently removed first in the hood and then vacuum oven for several days. The peroxide-containing SBR was then molded by the CARVER hydraulic press at 140 °C for
30 minutes to achieve the formation of a uniform thin film and the crosslink reaction simultaneously. The final rectangular sheet-like specimens were cut out from the thin film by a razor blade.
Figure 3.1 (a) Small amplitude oscillatory shear (SAOS) measurement of the SBR melt, revealing the elastic plateau modulus $G_{pl}$ and the terminal relaxation time $\tau$ as labeled. (b) SAOS measurement of the lightly-crosslinked SBR melt.

The linear viscoelastic properties of the crosslinked SBR was also evaluated by performing small-amplitude oscillatory shear measurements on a Physica MCR 301 rotational rheometer with 8.8 mm diameter parallel plates. The master curve shown in Fig. 3.1(b) was constructed from separate measurements at 25 and 70 °C, using the time-temperature superposition principle, with 25 °C being the reference temperature. The level of crosslinking is clearly rather low judging from the storage modulus $G'$ that is comparable to that of the SBR melt.
For the purpose of PTV observations, the SBR melt was first dissolved in toluene to achieve a uniform solution. Then around 600 ppm of silver-coated particles, averaged 10µm in size, were dispersed uniformly in the solution. The toluene is subsequently removed first in the hood and then vacuum oven for several days.

The specimens for the extensional and shear tests were prepared by pressing the SBR into a thin film between two Mylar sheets in a CARVER hydraulic press at 50 °C. After being removed from the Mylar, the final rectangular sheet-like specimens were cut out from the thin film by a razor blade. The typical dimension of the sample for the extensional tests was 20mm×4mm×0.5mm (SER) and 30mm×5mm×0.5mm (Instron), and that for simple shear tests was 20mm×20mm×0.8mm.

3.2.2 Apparatus

Uniaxial extension experiments were carried out using a first generation SER (Sentmanat extension rheometer) fixture mounted on an ARES rotational rheometer from TA Instruments. A constant Hencky strain rate could be easily exerted using this fixture by applying constant angular velocity to turn the two drums, on which the sample is wrapped around. We also employed an Instron Material Testing System (model 5543, maximum velocity: 1000 mm/min) to perform uniaxial extension tests, where the ends of specimen sample were first wrapped and fixed onto a metal bar with the help of the commercial adhesive (i.e. LOCTITE® 498), and then loaded onto the Instron. All the tests were performed at room temperature around 25 °C. Figure 3.2(a) and 3.2(b) show the schematic depiction of the SER and Instron extensional test fixtures.
A custom-built sliding plate rheometer (SPR) with PTV capability was employed to produce startup simple shear. In a typical startup simple shear experiment, with the bottom plate fixed, the movable upper plate is displaced by a step motor (Motion Parker Co, model number ZETA6104-57-83), where the resulting force is measured using a load cell (Omega dyne, Inc.). The step motor can be programmed to move suddenly at a prescribed velocity until reaching a given displacement. All the tests were performed at room temperature around 25 °C. The schematic depiction of the SPR is shown in Figure 3.2 (c), and more detail about the PTV setup has been described previously. To make sure there is no wall slip between the SBR melt and the plates, a piece of sandpaper (180 grit) was glued to both upper and bottom plates. Then a thin layer of commercial adhesive (i.e. LOCTITE® 498) was used to adhere the sample to the two plates. Similarly, the crosslinked SBR was adhered to the surface of the two plates by using LORD Chemlok® 250 adhesive in combination with Chemlok® 205 primer to prevent wall slip.
3.3 Results and discussions

In this section, the similarities and differences between simple shear and uniaxial extension will be discussed. In order to understand the extensional deformation better, a set of rate-switch experiments is also performed.

3.3.1 Rupture in extension and yielding in shear

As mentioned in the Introduction of this chapter, the responses of entangled melts to shear and extension are the same, i.e., characterized by the concept of yielding that can be phenomenologically identified by examining the degree of elastic recovery before and after the emergence of the stress maximum. Figure 3.3(a) shows how the engineering stress $\sigma_{\text{engr}}$ varies in terms of the stretching ratio $\lambda$ at eight different rates. At the first three low rates at 0.01, 0.03 and 0.06 s$^{-1}$, there appears a maximum in $\sigma_{\text{engr}}$. In our understanding, this overshoot signifies yielding of the entanglement network that occurs upon imbalance between the growing intrachain elastic retraction force and intermolecular gripping force, leading to chains mutually sliding past one another$^{15, 46}$. The nature of the response changes when the Hencky rate is increased to $\dot{\varepsilon} = 0.1$ s$^{-1}$: The relation between $\sigma_{\text{engr}}$ and $\lambda$ becomes monotonic until the point of specimen failure, reminiscent of the elasticity of a crosslinked rubber. The appearance of failure is rupture, like fracture of a window-glass or crosslinked rubber as shown in Figure 3.3(b) at 0.1, 0.3 and 0.8 s$^{-1}$. Previous studies have explored the rupture failure in some detail and concluded that most plausibly some entanglements are no longer able to escape by mutual chain sliding at such high rates$^{21-22, 57}$. Here we are interested in the question of
whether the same melt would also stop losing chain entanglements in simple shear at comparable shear rates.
Figure 3.3  (a) Engineering stress $\sigma_{\text{engr}}$ as a function of the degree of stretching ($\lambda - 1$) for eight different rates. Also shown is the neo-Hookean behavior given by $\sigma_{\text{engr}} = G_{\text{pl}}(\lambda - 1/\lambda^2)$, where $G_{\text{pl}}$ is given by the experimental value revealed in Figure 3.1.  (b) Respective photos of the two pieces after rupture at three rates, indicating sharp window-glass like crack surfaces.

If entanglements would also lock in during startup shear, the shear stress $\sigma_{12}$ should grow until a structural failure terminates the uniform deformation. Using a sliding plate (customer-built) shear rheometer, we measured the responses in the same rate range. Figure 3.4(a) shows the shear stress as a function of the elapsed strain $\gamma = \dot{\gamma} t$ for four different values of $\dot{\gamma}$. The data show a maximum even at the highest rates. Thus, the sample can avoid a monotonic buildup of shear stress. In other words, yielding still takes place at these high shear rates presumably because the chains can still escape entanglement through chain sliding.
Figure 3.4  (a) Stress as a function of the apparent shear rate for four different rates. (b) Particle-tracking velocimetric measurements of the deformation field before and after the stress overshoot.
Since our sliding plate device has the PTV capability, we further investigate the nature of the shear responses of entangled melts by examining the deformation field at different stages during a startup shear at a rate that produced sharp rupture in extension. At a shear rate of $\dot{\gamma} = 0.96\text{s}^{-1}$, our PTV observations reveals in Figure 3.4(b) that (i) the shear was first homogeneous not only at $\gamma = 0.8$ but all the way up to 6.0; (ii) then the shear banding develops over an extensive region in a period of seconds, showing no sign of window-glass-like rupture. The velocity profiles are consistent with the rheometric measurements in Fig. 3.4(a). In particular, the shear stress did not drop sharply upon the emergence of shear inhomogeneity. Actually, the local shear rate $\dot{\gamma}_h$ in the high-shear band is nowhere approaching the value expected from a material that has suffered rupture and reduced its molecular weight to the level of the entanglement molecular weight $M_e$:

Reading $\dot{\gamma}_h \sim 2.4\text{s}^{-1}$ from Fig. 3.4(b), we can estimate the viscosity $\eta_h$ in this band as $\eta_h \sim \sigma/\dot{\gamma}_h \approx 0.87/2.4 = 0.36\text{MPa.s}$. On the other hand, the viscosity of this SBR in the limit of full disentanglement, $\eta_e$, corresponding to the same SBR with $M_e$, can be crudely estimated from the zero-shear viscosity $\eta_0 \sim \eta^*(\omega\tau << 1) \approx 10^3\text{MPa.s}$ according to Fig. 3.1. Crudely, we have $\eta_e \sim \eta_0(M_e/M_w)^{3.4} = 4.7\text{ kPa.s}$. Thus, we find that $\eta_h/\eta_e \sim 77$. Based on this comparison, we conclude that the sample did not even fully disentangle, let alone undergoing chain scission to produce rupture.

3.3.2. Rupture of crosslinked SBR in both shear and extension

The possibility of chain disentanglement can be eliminated by crosslink of the SBR melt. Although some mutual chain sliding could still occur in presence of crosslinking, the crosslinked sample can only fail by rupture via chain scission. Fig.
3.5(a) compares the yielding and rupture behavior of the SBR melt against the response of the crosslinked SBR: In absence of crosslinking, the sample is much more stretchable because the number of chain entanglements can decrease during yielding\textsuperscript{22}. Many features of Fig. 3.5(a) are interesting to note. (i) The initial responses of the melt and crosslinked counterpart are the same, in agreement with the formula from the classical rubber elasticity theory: $\sigma_{\text{engr}} = G_p(\lambda - 1/\lambda^2)$. Therefore the crosslink density must be light. (ii) The crosslinking is ineffective at all the explored four rates in preventing initial loss of entanglements. (iii) The mechanical response is still dependent on the Hencky rate, implying that more chain entanglements are locked in at a higher rate, leading to a higher tensile force and a greater number of debonding events. (iv) The crosslinking does "soon" stop further yielding since the stretching ratio is only around 4 ~ 4.5 at the point of rupture, which is also the theoretical limit to straighten an equilibrium entanglement strand in a SBR melt\textsuperscript{22}. In absence of crosslinking, only a smaller fraction of entanglements survive so that the rupture involves the bond breakage of a more stretchable entangled network and can occur at a considerably higher stretching ratio in excess of 10, as explained previously\textsuperscript{22}.
Figure 3.5 (a) Engineering stress $\sigma_{\text{engr}}$ as a function of the degree of stretching ($\lambda - 1$) during uniaxial extension of the crosslinked SBR at four values of Hencky rate (filled symbols), as well as the curves of $\sigma_{\text{engr}}$ vs. ($\lambda - 1$) of the SBR melt (open symbols). (b) Shear stress vs. the applied strain during startup shear of the crosslinked SBR.
We also carried out rheometric shear measurement on a crosslinked SBR. Fig. 3.5(b) shows how the sample responded to a startup shear at $\dot{\gamma} = 1.1 \text{ s}^{-1}$. The comparison between Fig. 3.4(a) and Fig. 3.5(b) makes it clear that yielding leading to the stress decline is totally suppressed by crosslinking. Conversely, there is no sign of entanglement locking-in during startup shear of the SBR melt as shown in Fig. 3.4(a) that contrasts sharply with Fig. 3.5(b).

3.3.3 Rupture in extension by Instron

It is clear that at high enough Hencky rates sufficient entanglements freeze to cause window-glass like rupture in uniaxial extension of entangled melts. For the same range of rates, the entanglements can escape from locking-in during startup simple shear. One would speculate that the sharp contrast takes place because the kinematics are different between simple shear and uniaxial extension when the latter is carried out at a constant Hencky rate $\dot{\varepsilon}$. In simple shear, the degree of chain stretching could only grow linearly with time, whereas in uniaxial extension at constant $\dot{\varepsilon}$, the stretching takes place exponentially fast, as shown below.

Liquids have no memory of their past states and are constantly updated. Thus, to describe uniaxial extension of a liquid at a constant rate, the pulling velocity $V(t)/2$ on the two ends of a stretched specimen has to increase in keep with the increasing specimen length $L(t)$, so that the Hencky rate would be constant:

$$\dot{\varepsilon} = \frac{V(t)}{L(t)} = \text{constant.} \quad (3.1)$$
In other words, $V(t)$ will have to grow as fast as $L(t)$ if $\dot{\varepsilon}$ is to stay constant. Since $V = dL/dt$, integration of Eq (3.1) shows that the only way to maintain a constant Hencky rate is for $L$ to grow with time exponentially:

$$L(t)/L_0 = \lambda = \exp(\dot{\varepsilon}t). \quad (3.2)$$

In contrast, in shear, the rate is constant as long as the shearing surface maintains a constant speed:

$$\dot{\gamma} = V(y)/y, \quad (3.3)$$

so that the shear strain grows linearly with time as

$$\gamma = \dot{\gamma}t, \quad (3.4)$$

where $y$ is the distance of one layer of the sample from the stationary bottom surface. The shear rate would be the same and constant with respect to time for every value of $y$ only if $V(y)$ would be a linear function of $y$. It is worth noting that until recently one indeed assumed, as all textbooks have, $V(y)$ to be linearly proportional to $y$ in simple shear apparatuses at all times during startup shear of entangled polymer solutions and melts.

Extensive studies from our lab have convinced us of the following: Upon a startup deformation of either shear or extension, an entangled melt with long $\tau$ would only deform like a solid, not like a liquid, until the point of yielding, $t_y$, which could still be much shorter than $\tau$. Thus, as long as a polymer melt undergoes predominantly elastic deformation, its degree of stretching would grow exponentially with time during uniaxial extension at a constant Hencky rate, in sharp contrast to the simple shear. Thus, we cannot rule out that the exponential kinematics were the reason why the entanglements could tie up into "dead knots" to cause rupture under fast uniaxial extension.
The uniaxial extension does not have to involve the exponential kinematics. To compare the shear and extension deformation behavior of entangled melts on equal footing, we need to stretch the sample linearly in time. This means that the degree of the specimen's length should only grow linearly with time,

\[ \lambda - 1 = \frac{(V^* t)}{L_0} = \dot{\varepsilon}_0 t, \]  

(3.5)

where the symbol \( \dot{\varepsilon}_0 = \frac{V^*}{L_0} \) denotes the Hencky rate at the beginning of the extension, with \( V^*/2 \) being a constant velocity exerted at either end of the specimen. Under this condition, the tensile deformation depicted in Eq (3.5) resembles the shear deformation of Eq (3.4).

The condition of Eq (3.5) can be realized experimentally using an Instron tensile tester. Fig. 3.6(a) shows that the relationship between the engineering stress \( \sigma_{\text{engr}} \) and the degree of stretching, \( (\lambda - 1) \), involving six apparent Hencky rate \( \dot{\varepsilon}_0 \). Comparison with Fig. 3.3 shows that \( \sigma_{\text{engr}} \) no longer grows monotonically with time even at the highest \( \dot{\varepsilon}_0 = 1.6 \text{ s}^{-1} \). Here the smooth stress decline clearly arises from the fact that the Hencky rate \( \dot{\varepsilon} \) is dropping with increasing \( \lambda \):

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

(3.6)

where the last equality follows from Eq. (3.5). With decreasing Hencky rate, the point of force imbalance would be approached in an accelerated manner as intermolecular gripping force decreases with \( \dot{\varepsilon}(t) \). The ensuing chain disentanglement eventually results in ductile specimen failure at the three lowest rates. On the other hand, at the three higher rates, the specimen failure is brittle, i.e., exhibiting window-glass-like rupture.
We observe such rupture as shown in the photos in Fig. 3.6(b) despite the observed stress decline that indicates partial yielding of the entanglement network.

With $\varepsilon_0 = 0.8 \text{ s}^{-1}$ the specimen was stretched with the Instron up to $\lambda \sim 8$ when the instant stretching rate dropped to ca. 0.1 s$^{-1}$. Afterwards, the rate continued to drop until the point of rupture when the instant rate was a factor of 17 lower than the initial value, i.e., around $0.8/17=0.047$ s$^{-1}$. According to Fig. 3.3, even a startup extension at a rate of 0.06 s$^{-1}$ is too low to produce rupture. Thus, this rupture is rather remarkable. The phenomenon observed in Fig. 3.6(a) can be best understood as follows. Some entanglements become tied up upon a significant amount of stretching when the stretching rate was still high enough (i.e., before $\lambda \sim 8$). Apparently, many of these entanglements remain locked up as the stretching continued at an ever-decreasing rate. Before any chain disentanglement could occur, full chain extension in the surviving entanglement strands perhaps took place to build enough tension and cause chain scission, leading to the observed rupture.
Figure 3.6  (a) Engineering stress $\sigma_{\text{engr}}$ as a function of the degree of stretching ratio $(\lambda - 1)$ for six different apparent rate $\dot{\varepsilon}_0$.  (b) Respective photos of the two pieces after rupture at three rates, indicating sharp window-glass like crack surfaces.

3.3.4 Rate switching based on SER

Rate-switch experiments were performed in order to better understand the extensional behavior. The stretching condition realized by Instron is a rather unique way to produce rate switching: the rate decreases continuously. If we perform the rate switch
suddenly using the SER setup, we may expect different results, depending on when to switch. First, a switch from high rate to a rate as low as 0.06 s$^{-1}$ would not result in rupture because Fig. 3.3 shows that at 0.06 s$^{-1}$ the entanglements can escape, leading to yielding of the entanglement network. In other words, to have rupture in a rate-stepping-down experiment, the second (lower) rate needs to be high enough. This is confirmed in Fig. 3.7, where the data on the rate-switch from 0.8 to 0.01 and 0.03 s$^{-1}$ are presented. We need to choose the second rate to be 0.1 s$^{-1}$ or higher in order to explore the possibility of rupture after rate step-down. If the rate switching occurs before the sample has undergone substantial stretching then our experiment in Fig. 3.7 shows that rupture can still take place, as shown by the diamonds. The most interesting phenomenon emerges when the rate switching from 0.8 to 0.1 s$^{-1}$ was made after a great deal of stretching has been imposed on the sample at the high rate of 0.8 s$^{-1}$, e.g., switching at $\lambda = 7$. The decrease in the Hencky rate by a factor of 8 from the initial value of 0.8 s$^{-1}$ ensured that there was a sudden large drop in the intermolecular gripping force, leaving the substantial intra-chain elastic retraction unbalanced. All a sudden, the tightened entanglements get loose leading to force imbalance and mutual chain sliding. The system quickly underwent chain disentanglement to a point that the subsequent extension at 0.1 s$^{-1}$ could not cause the entanglements to tighten up again. In other words, due to the force imbalance, i.e., the significant elastic yielding, the state of chain entanglement may have been so significantly weakened that the new state could not respond to the rate switching to either 0.1 or 0.2 s$^{-1}$ effectively to freeze up. Consequently, the chain entanglements escaped to avoid chain scission, leading to the observed systematic decline in $\sigma_{\text{enr}}$ and yielding.
Figure 3.7 Rate-switching experiments from the first rate of $\dot{\varepsilon} = 0.8 \text{ s}^{-1}$ to a second rate of various values at different stages, showing the engineering stress $\sigma_{\text{engr}}$ as a function of the accumulated degree of stretching ($\lambda - 1$). When switched at $\lambda = 4$, the second rate of $0.1 \text{ s}^{-1}$ could still produce rupture in the end. When switched at $\lambda = 7$, even a higher second rate of $0.2 \text{ s}^{-1}$ could only result in yielding and necking.

Figure 3.8 Schematic sketching of the different impacts on chain entanglement between uniaxial extension and simples shear.
In summary, even when the extension is exerted to keep a linear growth of deformation with time, we still observed rupture, implying that entanglements can still tie up, contrary to the case of the shear deformation. It appears that the strongest entanglement formed by a pair of hairpins could become effectively tightened under uniaxial extension whereas the same entanglement in simple shear can dissolve. We can perhaps elucidate this difference in terms of the cartoons in Fig. 3.8. In other words, the projection of the shear force is rather different from that of the tensile force exerted on the entanglement strands, allowing chain mutual sliding in shear and entanglements to tighten in extension.

3.4 Conclusion

The present chapter made a first attempt to identify the true difference in the nonlinear responses of entangled polymer melts to simple shear and uniaxial extension. When the applied rate is below some critical value relative to the molecular relaxation rate, an entangled melt respond to startup of shear and extension in the same way that can be characterized by yielding due to chain disentanglement. When the applied deformation rate is sufficiently high, chain entanglements can tie up and become "dead knots" during startup uniaxial extension, perhaps due to the fact there are sufficient pairs of hairpins involving two strands displaced oppositely along the stretching direction. At high strains of such an extension, such entanglements can survive to allow full extension of the remaining entanglement strands, producing sufficient tension and subsequent chain scission. Shear deformation is different and displaces strands in opposite directions only if the strands are situated at different heights along the velocity gradient direction. As
consequence, the chain entanglements cannot be effectively tightened up. Thus, at the comparable rates, entanglements always escape because chain mutual sliding can always take place to free the entangled strands, leading to destruction of the entanglement network.

The different nonlinear responses of entangle melts to shear and extension allow such materials to undergo large deformation in complex geometries in ways that have just begun to be understood. The new understanding could potentially help improve molecular design of polymer compounds as well as construction of effective and efficient polymer processing equipment to avoid or overcome material failure or instability. On the other hand, molecular dynamics simulations are desirable in the near future because they could reveal whether and how chain entanglements freeze up in extension but not in shear. In other words, computer experiments should be carried out to either validate or modify the present picture concerning the response difference between shear and extension of entangled polymers.

3.5 Appendix

In this Section 3.5, the mechanism of the dicumyl peroxide crosslink reaction, which is used in this chapter, will be briefly introduced.\(^3,65-70\)

Basically, the crosslink is achieved through a free radical mechanism. Upon heating, the dicumyl peroxide will be decomposed to free radicals. The free radical will react with double bonds in the SBR melt, and created a new reaction site in the chain. When the reactive chain meets another chain, there are two possible ways of reaction: combination and disproportionation. Combination will result in the crosslink between chains, while disproportionation will only transfer the reactive site between chains thus
no crosslink is achieved. In other words, there is a competition between combination and disproportionation. The mechanism is demonstrated in Figure 3.9, where dicumyl peroxide is represented as ROOR.

Figure 3.9 The mechanism of dicumyl peroxide crosslink reaction. Reprint from ref 67 with permission.
CHAPTER IV

BREAKDOWN OF TIME-TEMPERATURE EQUIVALENCE IN STARTUP UNIAXIAL EXTENSION OF ENTANGLED POLYMER MELTS

4.1 Introduction

In this chapter, the breakdown of time-temperature equivalence in startup uniaxial extension of entangled polymer melts will be discussed. In rheological characterization of polymeric materials, the time-temperature superposition (TTS) principle allows us to acquire a wider spectrum of information on polymer dynamics. Although there are reports of the failure of TTS when both chain dynamics and local segmental dynamics are accessible at each of several temperatures, we have assumed that TTS would apply to describe the temperature dependence of transient responses of entangled melts to fast startup deformation. In this chapter we show that at the same effective rate (e.g., the same Rouse-Weissenberg number $W_iR$ equal to the product of the Hencky rate and the Rouse time) of uniaxial extension the nonlinear responses of several different polymer melts are different at different temperatures, pointing to an evident breakdown of the TTS. Specifically, we will show that for the same $W_iR$ well entangled polymer melts rupture at relatively low temperatures, yet still 20 to 30 degrees above the glass transition...
temperature $T_g$, but undergo necking-like failure at higher temperatures. Thus, at the same $Wi_R$, stress-strain curves are significantly different at different temperatures. Moreover, at the lower temperature, these polymer melts can reach an extreme level of extensibility at a critical $Wi_R$, which is completely unattainable at higher temperatures. These TTS violating phenomenon present a serious challenge to our existing theoretical understanding of nonlinear rheology of entangled polymeric liquids.

4.1.1 Historic background

Viscoelastic responses of polymeric materials to external deformation vary as a function of temperature and external deformation rate. Ordinarily, the principle of time-temperature equivalence (TTE) applies because the range of time scales probed in rheometric or dielectric measurements is typically not wide enough to access both chain and segmental level dynamics. In other words, it is always useful and valid to apply the time-temperature superposition (TTS)\textsuperscript{9,25} to characterize the terminal relaxation behavior such as the reptation dynamics in the case of entangled monodisperse polymers.

Breakdown of TTS occurs when rheometric\textsuperscript{74-85} or dielectric tests\textsuperscript{86-90} span over such a wide range of time scales that both chain and segmental dynamics are accessible and measured at each temperature. Such a breakdown show the limitation of most molecular theories\textsuperscript{40,91} including the popular tube theory because the currently available molecular models attribute the temperature dependence of chain dynamics to that of the segmental friction. It is often easier to demonstrate the lack of TTS in binary miscible polymer blends\textsuperscript{92} involving components of rather different glass transition temperatures. Here the failure to superimpose the small amplitude oscillatory measurements at different
temperatures arises usually from the fact that the chain dynamics of individual components in the blend still have different temperature dependence.\textsuperscript{92-93} In the literature, the examples of TTS breakdown often involve linear viscoelastic characterization. The TTS failure challenges the assumption that all chain modes have the same temperature dependence of their friction constant, which seems true at high $T$ but not necessarily correct when the experimental temperature is sufficiently close to $T_g$. The origin of the TTS failure is still under debate.\textsuperscript{94-96}

The principle of the TTS is routinely applied to study nonlinear rheological characteristics of entangled polymers\textsuperscript{10} because its breakdown has not been observed. Nonlinear steady-state properties usually do not disclose any failure of the TTS because the steady dynamics involve only one time scale, \textit{i.e.}, the reciprocal of the imposed rate. It is certainly unclear \textit{a priori} whether the TTE is always a reliable approach to extend our knowledge about nonlinear rheological behavior of polymers.

4.1.2 Recent developments

In recent years, the transient responses\textsuperscript{63, 97} of entangled polymers to startup fast deformation of both shear and extension have attracted a great deal of attention. In particular, yielding, \textit{i.e.}, a transformation from the initial elastic deformation to the irreversible deformation, seems to be a leading characteristic. Here "yielding" assumes a similar meaning as used in solid mechanics, treating the entangled melts as a transient solid capable of undergoing considerable elastic deformation before suffering flow. It was suggested\textsuperscript{15, 46} that the shear stress or engineering stress maximum signifies global yielding, at which the entanglement network suffers a massive structural breakdown.
through chain disentanglement. Such a claim is supported by the fact that elastic recovery is nearly complete when the entangled polymers are strained before the stress maximum. It is the yielding that leads to strain localization, i.e., initialization of non-uniform extension. In the past, the yielding characteristics have been studied at a given temperature.\textsuperscript{19, 22-23, 56}

The present chapter examines whether the transient responses of several monodisperse entangled melts to startup uniaxial extension would be the same at different temperatures above the glass transition temperature $T_g$. We found, to our surprise, that the TTE principle cannot be applied to depict the nonlinear responses in the following sense. At a lower temperature, the chain relaxation dynamics slow down by a specific amount that can be quantified with various linear viscoelastic characterizations such as small amplitude oscillatory shear and stress relaxation from small step strain. When the applied Hencky rate $\dot{\varepsilon}$ is lowered by the same amount to keep the Weissenberg number $Wi = \dot{\varepsilon} \tau$ fixed, we do not find the same transient response as observed at higher temperatures. At an intermediate Hencky rate, the "long-time" responses are also different when compared with those measured at higher temperatures at the same value of $Wi$. Specifically, the uniform extension persists to a much greater degree at the same $Wi$ when the experimental temperature is sufficiently low.

4.2 Experimental

This section describes the characteristics of the polymer melts used for the experiments in this chapter.
4.2.1 Materials and Sample Preparation

In this chapter, several nearly monodisperse polymer melts were used to determine the temperature dependence of nonlinear rheological behavior of entangled melts, including three styrene-butadiene random copolymer (SBR) with different molecular weights and microstructures, one 3,4-polyisoprene (PI) and one polystyrene (PS). The three SBR melts were synthesized by anionic polymerization at Bridgestone Americas Center for Research and Technology via courtesy of Dr. Xiaorong Wang. Their microstructures are indicated in Table 4.1. The PI melt was synthesized by Ntetsikas in Ioannina, Greece. The PS melt was synthesized by Dr. Hongde Xu at the University of Akron. The linear viscoelastic properties of these polymer melts were first evaluated by carrying out small-amplitude oscillatory shear (SAOS) measurements that generated the information in Table 4.2.

The specimens for the uniaxial extension tests were prepared by pressing the polymer melts into a thin film between two Mylar sheets in a CARVER hydraulic press for a sufficiently long time above their $T_g$. For PS, the sample was made by first dissolving it in toluene. The solution is then placed under the hood to evaporate enough solvent and then poured onto an alumina plate to be placed in the vacuum oven for several days at elevated temperature to remove the remaining solvent. After removal from the press, the final rectangular-shaped specimens were cut out from the thin sheet by a razor blade. The typical dimension of the sample was 18 mm×3 mm×0.4 mm.
Table 4.1 Microstructures of three SBR melts

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Table 4.2 Molecular Characteristics of Polymer Melts

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<th>Sample</th>
<th>$M_n$ (kg/mol)</th>
<th>$T_g$ (°C)</th>
<th>$M_w/M_n$</th>
<th>$G_N^0$ (MPa)</th>
<th>$M_e$ (kg/mol)</th>
<th>$Z=M_w/M_e$</th>
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<tr>
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<td>SBR325K</td>
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<td>0.76</td>
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<td>PI330K</td>
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<td>0.32</td>
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<td>PS1M</td>
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<td>100</td>
<td>1.02</td>
<td>0.22</td>
<td>16</td>
<td>64</td>
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4.2.2 Apparatus

An advanced rheometric expansion system (ARES)-LS rotational rheometer was used to carry out both SAOS and uniaxial extension experiments. The latter involves mounting a first generation SER fixture on the ARES-LS. A constant Hencky strain rate could be readily obtained using this fixture. A wide range of testing temperatures (-10~240 °C) is reached. The cooling is achieved by passing the input air through a dry ice
well instead of using a liquid nitrogen tank. Stress relaxation experiments were carried out using a Physica MCR 301 rotational rheometer (Anton Paar). The capillary extrusion measurements were done on a MONSANTO automatic capillary rheometer (Model 5619).

4.3 Experimental results

Experimental results will be discussed in this Section 4.3. The validity of TTS principle will be tested by a series of measurements.

4.3.1 Temperature dependence of chain dynamics from linear viscoelastic characterization

4.3.1.1 Small amplitude oscillatory shear

Small amplitude oscillatory shear (SAOS) measurements were carried out at different temperatures to determine the temperature dependence of linear viscoelasticity. The SAOS curves for the four melts at different reference temperatures are shown in Figure 4.1a to Figure 4.1d. The shaded area in each plot represents the range of the applied effective rates in this study. The terminal relaxation time $\tau$ at various temperatures can be evaluated from the SAOS curves as the inverse of the crossover frequency $\omega_c$ where $G'(\omega_c)=G''(\omega_c)$. The Rouse relaxation times, $\tau_R$, can be estimated from $\tau_R=(6M_w\eta_0/\pi^2\rho RT)/(M_c/M_w)^{2.4}$, according to Ref. 98. Table 4.3 lists both the reptation time $\tau$ and Rouse time $\tau_R$ at the various temperatures for these four melts, from which we can extract the WLF shifting factor $a_T = \tau(T)/\tau(T_{ref})$. Note that the values for Rouse time are under-estimated here because we used the last data point of $|\eta^*|$ as $\eta_0$. 

66
a) SAOS SBR 153K 30 °C

b) SAOS SBR 325K 30 °C
Figure 4.1 Small amplitude oscillatory shear measurements (SAOS) of the four polymer melts to produce the storage and loss moduli, $G'$ and $G''$, as a function of the frequency: (a) SBR153K, (b) SBR325K, (c) PI330K, and (d) PS1M. The full SAOS curves were
constructed from various temperatures as listed in Table 4, and involve the various reference temperatures respectively of 30 °C (SBR153K), 30 °C (SBR325K), 25 °C (PI330k), 120 °C (PS1M). The shade in each figure represents the range of the applied effective rates in this study.

4.3.1.2 Stress relaxation from small stepwise shear

Stress relaxation experiments were carried out in the linear response regime at different temperatures. Typical data were shown in Figures 4.2a and 4.2b for SBR153K and PI330K respectively. Here the stepwise shear was produced with a high rate corresponding to the Rouse-Weissenberg number $Wi_R = \dot{\gamma} \tau_R(T) = 5$ and 2.5 respectively, where $\dot{\gamma}$ is the applied shear rate, and $\tau_R(T)$ is the Rouse relaxation time at the measurement temperature $T$. The collapse of the three sets of stress relaxation data in Figures 4.2a-b confirms that the chain relaxation dynamics show the same temperature dependence as observed from the SAOS measurements. In other words, over three decades in time scales, the relaxation dynamics have the same temperature dependence.
Figure 4.2 Stress relaxation curves of (a) SBR153K at three different temperatures, with amplitude of 5% and 10% respectively and of (b) PI330K at four different temperatures.
with amplitude of 20%. The actual rates used produce the step shear for SBR153K are 0.038s\(^{-1}\) (20 °C), 0.385s\(^{-1}\) (30 °C) and 2.5s\(^{-1}\) (40 °C); the actual rates used for PI330K are 0.057s\(^{-1}\) (25 °C), 0.319s\(^{-1}\) (35 °C), 1.326 s\(^{-1}\) (45 °C) and 4.846s\(^{-1}\) (55 °C).

Table 4.3  Reptation and Rouse times of various melts at different temperatures

(a)  SBR153K

<table>
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<th>T (°C)</th>
<th>(\tau) (s)</th>
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(b) SBR325K

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<td>70</td>
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(c) PI330K

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

4.3.2.1 Yielding-to-rupture transition

At Weissenberg number $Wi = \dot{\varepsilon} \tau > 1$, the response to startup extension transitions from the initial elastic deformation to partially irrecoverable deformation on time scales shorter than the relaxation time $\tau$. This macroscopic yielding occurs, signified by the emergence of a maximum in the total tensile force or $\sigma_{\text{engr(max)}}$. Previous studies have shown that the peak position, given by $\sigma_{\text{engr(max)}}$ and $\varepsilon_{\text{max}}$, changes with the applied Hencky rate $\dot{\varepsilon}$. As $\dot{\varepsilon}$ increases beyond a critical value, the peak in $\sigma_{\text{engr(max)}}$ disappears, and $\sigma_{\text{engr}}$ grows monotonically until rupture. Here we first examine how the characteristics of transient response differ at two temperatures. At a high temperature of
50 °C, as shown in Figure 4.3a, the engineering stress $\sigma_{\text{engr}}$ always shows a maximum even at a Rouse-Weissenberg number $Wi_R$ as high as 10. In contrast, at 20 °C, the same SBR153K can be stretched to display a monotonic increase of $\sigma_{\text{engr}}$ until the specimen rupture with mirror-smooth sharp interfaces. The yield-to-rupture transition at 20 °C, occurs at a value of $Wi_R$ as low as 4.3, as shown in Figure 4.3b. Thus, it appears that the temperature dependence of the nonlinear rheological responses differs from that of the linear viscoelastic behavior given in the preceding section 4.3.1.
Figure 4.3 Stress-strain curves of SBR153K at (a) 50 °C and (b) 20 °C in terms of the engineering stress $\sigma_{\text{engr}}$ and the stretching ratio $\lambda$. Note that at 20 °C, the yield-to-rupture transition is clearly seen, while at 50 °C there is no rupture. The actual rates for SBR153K at 50 °C are: 1.0, 2.0, 6.0, 12 and 20 s$^{-1}$, respectively. The actual rates for SBR153K at 20 °C are: 0.01, 0.022, 0.033, 0.046 and 0.075 s$^{-1}$, respectively.
Figure 4.4 The critical Rouse-Weissenberg number \((W_i)_R\)\(_{\text{yield-rupture}}\) separating necking (initialized by shear yielding\(^{23}\)) regime and rupture regime for the four different melts. Note that as temperature decreases, the critical Rouse-Weissenberg number also decreases.
Figure 4.5 Stress-strain curves of (a) SBR153K, (b) SBR325K and (c) PI330K at different temperatures in terms of the engineering stress $\sigma_{\text{engr}}$ and the stretching ratio $\lambda$, showing the shape changes as the temperature varies. Note that at low temperatures, the engineering stress grows monotonically. The actual Hencky strain rates are: SBR153K: 20 °C, 0.046 s$^{-1}$; 30 °C, 0.47 s$^{-1}$; 50 °C, 12.0 s$^{-1}$. SBR325K: 0 °C, 0.081 s$^{-1}$; 20 °C, 2.24 s$^{-1}$; 30 °C, 8.0 s$^{-1}$. PI330K: 25 °C, 0.072 s$^{-1}$; 38 °C, 0.59 s$^{-1}$; 55 °C, 6.0 s$^{-1}$. 
To examine whether this loss of time-temperature equivalence is universal or not, we carried out similar startup extension experiments in the same range of $\text{Wi}_R$ for the other three polymer melts of SBR325K, PI and PS respectively. We denote the onset value of $\text{Wi}_R$ for rupture by $\text{Wi}_{R(yield-rupture)}$ and summarize our results based on four different melts as shown in Figure 4.4. It is evident from Figure 4.4 that $\text{Wi}_{R(yield-rupture)}$ depends on temperature for a given polymer, decreasing as the temperature is lowered. Moreover, the different polymers show different temperature dependence of $\text{Wi}_{R(yield-rupture)}$ and different values for $\text{Wi}_{R(yield-rupture)}$.

A more transparent way to demonstrate the failure of the time-temperature equivalence is to plot the transient responses at the same value of $\text{Wi}_R$ that involve several temperatures. Specifically, Figure 4.5a-c show the engineering stress $\sigma_{\text{engr}}$ as a function of the stretching ratio $\lambda$, respectively for SBR153K at $\text{Wi}_R = 6$, SBR325K at $\text{Wi}_R = 4.5$ and PI330K at $\text{Wi}_R = 3.1$. Since $\lambda = \exp(\dot{\varepsilon} t) = \exp[(\dot{\varepsilon} a_T)(t/a_T)]$, the condition of a constant $\text{Wi}_R$ amounts to setting $\dot{\varepsilon} a_T = \text{constant}$ so that the data in Figure 4.5a-c can be regarded as $\sigma_{\text{engr}}$ versus $t/a_T$ or $t/\tau_R$, which was used as the X axis in Figures 4.2a-4.2b. According to the conventional wisdom, the time-dependent rheological response of polymer melts, i.e., a plot of the transient stress $\sigma$ versus normalized time, should be quantitatively identical. Instead of overlapping, qualitative differences emerge in Figure 4.5a-c. All three samples show rupture at the lowest temperature, yielding and (unstable) neck at the highest temperature. In the case of rupture, the engineering stress grows monotonically. On the other hand, non-uniform extension can occur well after the maximum in $\sigma_{\text{engr}}$ and is initialized by shear yielding. A recent particle-tracking velocimetric characterization of the uniaxial extension of similar melts indicates that
4.3.2.2 Discrepancy in the yielding regime

A recent study has discussed\textsuperscript{23} different modes of failure during startup continuous uniaxial extension of well-entangled polymer melts at temperatures relatively high above the glass transition temperature $T_g$. At such "normal" temperatures, \textit{i.e.}, high enough temperatures, (a) SBR melts break up rupture-like (termed tensile decohesion\textsuperscript{23}) at rates around and just above Weissenberg number $Wi = 1$. (b) Shear yielding initializes unstable necking at higher values of $Wi$. (c) Eventually, typically for the Rouse-Weissenberg number $Wi_R \sim 10$, the engineering stress rises monotonically with the stretching ratio until the extremely sharp rupture with mirror smooth interfaces\textsuperscript{21-22}.

![Stress-strain curves of SBR153K](image)

Figure 4.6 Stress-strain curves of SBR153K in terms of the engineering stress $\sigma_{\text{engr}}$ and the stretching ratio $\lambda$, at different temperatures around $Wi_R = 1$, showing the increased stretchability at lowest temperature.
In regime (b), we explore any temperature dependence of the yielding behavior at a fixed $Wi$. We found notable differences as shown in Figure 4.6, which indicates the uniform extension terminates at different degrees of stretching. Throughout the paper we only present data that involve uniform uniaxial extension. Apparently, as the experimental temperature decreases the SBR melt can extend more after the global yield point at the maximum of the engineering stress before failure. The fact that these curves in Figure 4.6 do not overlap is another manifestation of the breakdown of the time-temperature equivalence.
Figure 4.7  (a) Stress-strain curves of SBR325K sample at 0 °C with the Rouse-Weissenberg number ranging from 0.11 to 11.2. At $Wi_R = 2.24$, the highest stretchability is achieved and the limiting stretching ratio is $\lambda^* = 52$.  (b) the same data plotted in terms of transient viscosity vs. time.  The photo in the inset shows the recovered specimen from the extreme extension at $Wi_R = 2.24$.  The linear responses data are taken from the SAOS measurements according to $\eta^*_E(t) |_{t=1/\omega}=3|\eta^*(1/\omega)|$.  

4.3.2.3 Limiting stretchability at low temperatures

As we explore the borderline between regime (b) and regime (c), a more remarkable characteristic shows up at a sufficiently low temperature.  Figure 4.7a represents the full spectrum of the rheological responses at different Hencky rates and 0 °C. The behavior ranges from the tensile decohesion at the lowest $Wi_R = 0.11$ to shear-yielding initiated (unstable) necking at intermediate rates and rupture for $Wi_R$ higher than 2.2. It is remarkable to observe the uniform extension at $Wi_R = 2.2$ up to $\lambda^* = 52$ when it
undergoes brittle rupture. At this borderline, \( i.e., \) \( Wi_R = 2.2 \) at 0°C, the engineering stress hardly decreases until rupture so that the Cauchy stress reaches a striking level close to 50 MPa. It is indeed striking that there is little sign of flow at the termination of extension (although significant yielding has occurred), evidenced by the fact that the specimen ends up breaking up like a window glass and has the capability to recover as shown in the photo in the inset of Figure 4.7b. Another way to show that the extension at these rates does not produce a fully developed flow state is to replot the data in Figure 4.7b in terms of the transient viscosity \( \eta_e^t \) as a function of time relative to the zero-rate envelope. The data show "strain hardening" and no sign of leveling-off at the end of uniform extension for \( Wi_R > 1 \).

The extraordinarily high stretchability at the low temperature is worth exploring. Thus, we examined the other three melts to identify the maximum extension before rupture. These melts has a wide range of entanglement level, as indicated in Table 4.2. In other words, the number of entanglements per chain \( Z = M_w/M_e \) increases from 37 to 152. It appears that the limiting stretching ratio \( \lambda^* \) depends explicitly on \( Z \). In particular, Figure 4.8 shows that it scales with \( Z^{1/2} \).
Figure 4.8  The limiting stretching ratio $\lambda^*$ for the four different polymer melts, plotted against the number of entanglements per chain, exhibiting a scaling relation: $\lambda^* \sim Z^{1/2}$. The experimental conditions are: SBR153K: 0.001 s$^{-1}$ at 10 °C; SBR250K: 0.004 s$^{-1}$ at -10 °C; SBR325K: 0.041 s$^{-1}$ at 0 °C; PS1M: 0.001 s$^{-1}$ at 120 °C. At $\lambda^*$, we may perceive the entanglement has deteriorated to the point of losing its last entanglement points as shown by the cartoon.
Figure 4.9 Stress-strain curves of SBR153K at three different temperatures. Note at similar effective rate, at 10 °C and 20 °C, the limiting stretching ratio $\lambda^* = 26$ is approached. At the higher temperature of 40 °C, yielding and necking are present and sample fails at a much smaller stretching ratio. Also plotted is the Edward-Vilgis model based on a plateau modulus of $G^0/N$, corresponding to entanglement network where the entanglement strand is the whole chain. This particular curve involves half of the strands being "permanent" and the other half sliding in a slilink environment. As an alternative, a Gaussian chain network with the same plateau modulus describes the stress vs. strain curve without diverging stress.

At higher temperatures, e.g., 50 °C above $T_g$, the stretching ratio is significantly lower before failure, as shown in Figure 4.9 for SBR153K at three different temperatures under similar effective rates. For this SBR153K, with its $T_g$ being -10 °C and $Z=37$, at 10 °C and 20 °C, the sample undergoes uniform extension up to $\lambda^* = 26$, before its brittle rupture. However, under a similar effective rate at 40 °C, severe strain localization
(unstable necking) takes place, making it impossible to show the same limiting stretchability observed at the lower temperatures.

4.3.3 Recovery of time-temperature equivalence at low rates and in steady shear

Finally, we examine the low-rate behavior in the full temperature range. When the applied Hencky extensional strain rate is lower, i.e., for $Wi_R < Wi_R(\text{yield-rupture})$, the stress vs. strain curves at different temperatures do approximately overlap. Figure 4.10a shows such "normal" behavior in the case of the polyisoprene melt, involving $Wi_R = 0.53$ at the same three temperatures as those involved in Figure 4.5c. Thus, at sufficiently low rates, the time-temperature equivalence follows, for all of these melts, with Figure 4.10b being another example.

The validity of the time-temperature superposition principle is also well known in the characterization of the steady state shear flow behavior of entangled polymers. Our pressure-controlled capillary rheometric data on the same PI330K confirm in Figure 4.11 that there is good overlapping when the stress vs. rate plots are normalized by plotting the measured $Wi_R = \dot{\gamma}_w \tau_R$ at the two different temperatures as a function of the applied pressure gradient $P/L$, where $P$ is the applied pressure and $L$ is the length of the die. Here $\dot{\gamma}_w$ is the shear rate at the wall, and the shear stress $\sigma_w$ at the capillary wall is given by $\sigma_w = (P/L)(D/4)$, where $D$ is the diameter of the die. In this study we use a die with $D=1$ mm and $L/D = 15$. 

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Figure 4.10 Stress-strain curves of (a) PI330K and (b) PS1M at the different temperatures at a fixed small value of $W_R$ (< 1). Here good overlapping is achieved for the curves from the different temperatures.
4.4 Discussions

The experimental observations in the preceding Section 4.3 demand explanations. In fact, they challenge the current theoretical understanding of nonlinear polymer rheology based on existing molecular theories. Below we discuss the two key findings.

4.4.1 Failure of the time-temperature superposition in transient responses

It is important to note that there is time-temperature equivalence (TTE) (i) for linear viscoelastic characteristics as shown in Figure 4.2, (ii) at sufficiently low rates as shown in Figure 4.10, and (iii) in steady shear as shown in Figure 4.11. However, the
same temperature dependence is no longer valid in the characterization of the transient responses to startup uniaxial extension at sufficiently high $Wi_R$, as shown in Figure 4.5a to 4.5c as well as Figure 4.4. Here the effective Hencky rate, i.e., $Wi_R = \gamma \tau_R(T)$, was applied according to the temperature dependence of the Rouse relation time $\tau_R(T)$ tabulated in Table 4.3. Oddly enough, as shown in Figure 4.5a to 4.5c, at the same $Wi_R$, these melts show such different mechanical responses, switching from rupture breakup at a low temperature to yielding at a high temperature. Consequently, the critical Rouse-Weissenberg number for the yielding-to-rupture transition, $(Wi_R)_{yield-rupture}$, is found to depend on temperature as shown in Figure 4.4.

This breakdown of the TTE evidently presents a challenge to the available theoretical treatments including the tube model. The modern literature has clearly recognized that the terminal chain dynamics for some polymers could be different from the segmental dynamics because the relaxation dynamics on the largest scales temporally and spatially average out the segmental-scale heterogeneities.\(^{90,94,101}\) It is important to note that our experiments did not involve rates as high as the segmental relaxation rates of these melts, as clearly indicated by the shaded regions in Fig. 4.1a-d. On the other hand, we noted that the $T/T_g$ ratios probed in this study for our four melts (SBR153K: 1.08~1.23; SBR325K: 1.15~1.28; PI330K: 1.14~1.30; PS1M: 1.05~1.16) are comparable to those in the previous reports\(^{75-76,83}\) of the breakdown of the TTS. Therefore, we cannot rule out the possibility that this failure of the TTE may have the same origin as that used to explain the previously reported violation of the TTS.\(^{74-90}\) In passing, we note that in our picture\(^{15}\) the yielding of the entanglement network via chain mutual sliding (i.e., disentanglement) occurs because of a force imbalance between the growing elastic
retraction force and the intermolecular gripping force.\textsuperscript{16} The present data show that we can no longer describe such force imbalance and corresponding yielding using the TTE principle for high rates at relatively low temperatures.

Since the apparent breakdown of the TTE is observed for four different polymer melts as indicated in Figure 4.4, the behavior might be universal. It is certainly more readily observable than the breakdown of TTS identified in a few polymers in their linear viscoelastic characterization. Currently, there is no theory in sight to provide an adequate account of such nonlinear extensional responses to fast startup uniaxial extension. The tube model\textsuperscript{40} already has difficulty in anticipating the emergence of the rupture regime, let alone explaining why this yielding-to-rupture transition does not follow the principle of TTE.

On the other hand, it is interesting to note that in steady-shear there is no obvious failure of the time-temperature equivalence as indicated in Figure 4.11 over the same rate range. We do not know whether steady extensional rheology would follow the WLF temperature dependence because the uniaxial extension always results in strain localization well before the point of steady flow.\textsuperscript{23} Moreover, there may exist a basic difference in the responses of entangled polymer melts to simple shear and uniaxial extension.\textsuperscript{24} It cannot be ruled out that the time-dependent molecular responses to startup shear obey the principle of time-temperature superposition, contrary to the present case of startup extension. This remains to be investigated.
4.4.2 Extreme extensibility at low temperatures

In the equilibrium network, the entanglement strand is straightened under affine
deformation for a stretching ratio of \( \lambda_{eq} = \frac{N_c l_K}{l_{ent}} = \frac{l_{ent}}{l_K} = \sqrt{N_c} \), where \( l_{ent} \) is the
equilibrium entanglement spacing, \( N_c \) is the average number of Kuhn segments within
one entanglement strand, and \( l_K \) is the Kuhn length. As the entanglements diminish
progressively\(^{22} \) until there is only one entanglement per chain, the entanglement strand is
as long as the whole chain. The condition to straighten this last entanglement strand
involves a stretching ratio of \( \lambda_{\text{max}} = \sqrt{N} = \sqrt{ZN_c} = \lambda_{eq}^* \sqrt{Z} \), where \( Z = N/N_c \) is the number
of entanglements per chain. With \( Z = 152 \) for the SBR325K and 37 for the SBR153K,
and \( \lambda_{eq}^* = 4.2 \) based on the information given in Ref.\(^{102} \), \( \lambda_{\text{max}} = 4.2 \times \sqrt{152} = 52 \) for
SBR325K and \( \lambda_{\text{max}} = 4.2 \times \sqrt{37} = 26 \) for SBR153K match the limiting \( \lambda^* \) respectively
observed from the experiment. Actually, Figure 4.8 shows that for all the four melts of
different chain length \( N \), \( \lambda^* \) increases with \( Z \) in a way consistent with the maximum
stretchability limit.

The elastic-like rupture at the end of extension of \( \lambda^* = 52 \), shown in Figure 4.7a-b
for SBR325K and \( \lambda^* = 26 \) for SBR153K as shown in Figure 4.9, indicates that an
entanglement network persisted up to the point of breaking. We applied the Edward-
Vilgis model\(^{28} \) to provide a reference point. The fact that the data were below the EV
curve for \( \lambda > 15 \sim 17 \) can be consistent with one of the following two possible scenarios
at the point of breaking. (a) There is a negligible fraction of chains that forms the largely
diminished entanglement network whose plateau modulus is much lower than that
Corresponding to entanglement per chain. Here the observed stress arises from the fact
that these few straightened strands in the limit of $\lambda^*$ contributes a diverging amount of force. (b) There are as many strands in the entanglement network as there are chains. At the limit of $\lambda^*$, although the Gaussian chains become straightened, there needs not a divergently large force produced within the straightened strand.

It appears that this extreme level of uniform extension to the point of one entanglement point per chain only occurs at a low enough temperature. Consequently, like the violation of the TTE during transient response to startup extension, this behavior was not discovered in our previous comprehensive study of the various failure modes of the same entangled SBR melts, which was carried out at room temperature, *i.e.*, a "high" temperature for these polymers.\textsuperscript{23}

We speculate that this extreme extensibility is related to the change of the relative importance between the elastic retraction and the intermolecular friction beyond the point of force imbalance.\textsuperscript{15, 46} As the temperature is lowered, a given degree of chain deformation still amounts to the same level of the elastic retraction force, but the interchain friction clearly grows. As the intermolecular friction interactions increase with lowering temperature, it is possible to reach a point where the yielding of the entanglement network no longer results in any strain localization. In other words, when the mechanical responses of the elastic and viscous states are not sufficiently different, the load transfer between the two states may take place uniformly.

### 4.4.3 Achieving isothermal condition

Our report of the breakdown of the TTE would be invalid if there is significant temperature increase when extending the melts at different temperatures. Although a
temperature-controlled oven was used in all tests, it is important to recognize that for a given equivalent rate, \( i.e. \), a fixed \( Wi_R \), at a higher temperature the applied Hencky rate is higher. Can the generated heat due to viscous dissipation during extension be taken away sufficiently fast, especially for high temperature tests? Would a slightly higher sample temperature (than the prescribed temperature) cause the observed different responses in Figure 4.5? In this Section 4.4.3, we attempt to accomplish a number of tasks, all aimed to determine whether it is adequate to treat our experimental condition as isothermal at the various preset temperatures and whether the sample's temperature remains essentially the same during the startup uniaxial extension despite the possibility of some heat generation by the viscous dissipation. Based on our analysis and evaluation presented here, we conclude that there is negligible correction to be made to such results as shown in Figure 4.5a-c. It appears that the observed breakdown of the TTE is genuine.

4.4.3.1 Dissipation and heat generation

It is necessary to estimate how much heat may be generated due to the viscous dissipation. Below, we will use SBR153K sample as an example to evaluate this effect. From Figure 4.5a, we found that at \( Wi_R=6.0 \), up to the stretching ratio of \( \lambda=6.5 \), stress-strain curves at different temperatures match exactly. We first calculate how much heat generation is possible up to \( \lambda=6.5 \) by performing a loading-unloading cycle\textsuperscript{103} as shown in Figure 4.12. The area in the hysteresis loop is the energy loss that amounts to heat generation. The resulting temperature increase \( \Delta T \) in the sample can be estimated by the formula

\[
\Delta T = \frac{\int_1^\lambda (\sigma_{\text{enr}} - \sigma'_{\text{enr}}) d\lambda}{\rho c_{sp}}.
\]

With \( \rho=920 \text{kg/m}^3 \) and \( c_{sp}=1890 \text{ J/kg·K} \),\textsuperscript{104} we have
$\Delta T = T - T_a = 1.4 \, ^\circ\text{C}$. Thus, since it takes 4 s for the sample to stretch to $\lambda = 6.5$ at $W_{R} = 6$ for SBR153K at 30 °C, our estimate of the temperature rise is given by $\Delta T(t) = At$, with $A = 1.4/4 \, ^\circ\text{C/s}$.

Figure 4.12 The hysteresis loop of SBR153K under 30 °C. The sample is stretched to $\lambda = 6.5$ at an effective rate of $W_{R} = 6.0$, and then returned back to the undeformed state at the same rate.
Figure 4.13 Stress-strain curves SBR153K at 20 °C and $W_{iR} = 6.0$ and 30 °C. Three experiments were made at 30 °C, two specimens of the same dimensions as that used to collect the data at 20 °C and extended at $W_{iR} = 6.0$ and 6.6, respectively; the third test (diamonds) involved a much smaller specimen so that the oven air convection is sufficiently effective to prevent any temperature rise in the specimen during extension.

4.4.3.2 Deviation from isothermal condition

We can estimate how convective cooling in the oven may keep the sample's temperature close to the preset value of 30 °C. For a sheet like sample of thickness $H$, the cooling due to air circulation causes the sample's temperature to decrease in the sense that the heat loss per unit volume due to the air cooling is given by

$$\rho c_v \frac{dT}{dt} = -\frac{h \Delta T}{H}.$$ 

Thus, the net temperature change is given by

$$\frac{dT}{dt} = A - \frac{hA_t}{\rho c_v H}. $$

Integrating over 4 s, we have

$$\delta T = (A_t - \frac{hA_t^2}{2\rho c_v H}) \bigg|_{t=0}^{t=4}. $$

Inserting $H = 0.3$ mm, and $h = 200$ W/(m²·K) for forced air convection, we find $\delta T = 0.3$ °C. We conclude that there can be a small deviation
from the isothermal condition, i.e., a slight temperature rise in the sample from 30 to 30.3 °C.

4.4.3.3 Correction to the Hencky rate

From the TTS shifting factor tabulated in Table 4.3, we found this 0.3 °C change can cause the relaxation time shift to a smaller value by a factor of 1.07. Thus, if we apply a rate corresponding to $Wi_R = 6.6$ at 30 °C, we should have the correct equivalent rate to compare with the data at 20 °C with $Wi_R = 6.0$. Figure 4.13 shows such a comparison.

This estimated correction of the oven efficiency can be further evaluated by examining a much smaller specimen, for which the air convection can ensure isothermal condition. Reducing the specimen thickness from 0.3 to 0.2 mm, the rate of heat removal by air cooling in the oven is higher than the rate of heat generation due to the viscous dissipation. Figure 4.13 indicates that (a) there is an effect although not enough to account for the observed difference in Figure 4.5a and (b) the estimated correction to $Wi_R = 6.6$ is consistent with the data from the thin specimen at $Wi_R = 6.0$ that are collected at 30 °C.

4.5 Summary

In conclusion, the peculiar responses of entangled polymer melts to start-up uniaxial extension at various temperatures have been characterized. Based on the five well-entangled polymer melts, we find that brittle rupture occurs at a smaller Rouse-Weissenberg number $Wi_R$ when the experimental temperature is sufficiently low, but still
considerably above the glass transition temperature $T_g$. Specifically, the critical effective Hencky rate (e.g., $W_{iR}$) for the yielding-to-rupture transition shifts with the temperature. In other words, the temperature dependence of the transient nonlinear responses to startup extension differs from that of the linear viscoelasticity. The previous demonstration of the breakdown of the time-temperature equivalence (TTE)\textsuperscript{74-85} requires a system of sufficiently low entanglement so that the segmental dynamics are not too far separate from the chain dynamics. Thus, the present study is the first to reveal the breakdown of TTE in well entangled polymers without involving time scales comparable to the segmental dynamics. This phenomenon presents a significant challenge to any theoretical description of the nonlinear rheology of entangled polymers and underscores the need to work out additional detail in our molecular picture\textsuperscript{15, 46} of chain disentanglement.

At the lower temperatures than previously explored,\textsuperscript{21-23} we also found that the entangled melt can undergo uniform uniaxial extension until there is only one entanglement strand per chain, with the specimen ending up in rupture. This is remarkable because the system breaks up like a window glass at the end of homogeneous extension instead of transforming into a flow state. Thus, the striking extreme extensibility demonstrates the resilience of the entanglement network and the dominant role of the networking. The phenomenon also suggests a missing ingredient in the current theoretical framework: the relative importance of the entropic elasticity to the intermolecular frictional interactions diminishes when lowering the temperature as the system transitions toward a flow state.
CHAPTER V

EXPLORING RHEOLOGY OF ENTANGLED POLYMER MELTS AND SOLUTIONS AT FAST RATES: THE EMERGENCE AND IMPORTANCE OF THE INTER-SEGMENTAL CONTRIBUTIONS TO THE MECHANICAL STRESS

This chapter elucidates the sources of mechanical stress of polymer melts and solutions upon fast external deformation, with the range of applied rates close to the second crossover of storage modulus $G'$ and loss modulus $G''$ in the small amplitude oscillatory shear (SAOS) measurements. Under these “unconventionally” high Hencky rates, it is found that for various polymer melts (PS, PMMA, SBR, PC) and solutions, the stress has two sources. The first one is an elastic component, which comes from the network structure of entangled polymer chains, and could be described by classical rubber elasticity theory. The second source of stress comes from the inter-segment interaction, which gives large elastic modulus at small strains and then transits into a viscous component. This transition is found to take a time much longer than typical $\alpha$-relaxation time, and the magnitude of the viscous component has been estimated and is found to match quantitatively with the dynamic viscosity determined from SAOS measurements. Study of Rouse melt confirms the existence of the inter-segmental interactions when the entanglement network is absent.
5.1 Introduction

Since the beginning of polymer science, extensive efforts have investigated microscopic origins of the mechanical stress arising from large deformation of entangled polymers well above the glass transition temperature $T_g$. The classical rubber elasticity theory\textsuperscript{9, 26, 106-110} identified the entropic origin of the stress associated with affine deformation of crosslinked polymers and provided a key ingredient for the tube model\textsuperscript{33-34, 36-40} that evaluates the mechanical stress in terms of intrachain retraction forces. On time scales much shorter than the Rouse relaxation time $\tau_R$, the tube model expects startup deformation to strain an entangled polymer melt or solution in an affine manner, producing a stress-strain curve consistent with the description of the rubber elasticity theory. On the experimental side, the initial response was indeed found to be elastic, as if a rubbery network with the elastic plateau modulus $G_N^0$ was undergoing affine deformation.\textsuperscript{63, 97} But the elastic deformation typically persists for only a time shorter than the reptation time $\tau$ at a deformation rate higher than $1/\tau$ (i.e., $Wi > 1$). In polymer dynamics the central question to deal with is when the affine elastic deformation ceases and flow begins upon startup deformation with Weissenberg number $Wi > 1$. Phenomenologically, the emergence of stress overshoot signifies this transition from elastic deformation to flow (irrecoverable deformation), that we termed "yielding"\textsuperscript{15-16}, generalizing its meaning in solid mechanics that refers a transformation from elastic to plastic deformation. In uniaxial extension, the stress overshoot refers to the non-monotonic change of the engineering stress $\sigma_{engr}$ against the tensile strain$^{19}$.

As the applied rate increases well beyond the reciprocal Rouse relaxation time $\tau_R$, i.e., for the Rouse-Weissenberg number $Wi_R$ much higher than unity (or $Wi >> \tau/\tau_R$), the
kinematic difference between shear and extension leads to very different responses in entangled polymers of linear chains\textsuperscript{24, 64}. Upon startup shear, the stress overshoot still shows up due to chain disentanglement, after the initial Hooke-like elastic deformation. However, $\sigma_{\text{engr}}$ can grow monotonically until glass-like rupture in startup uniaxial extension for $W_{iR} \sim 10$ or higher\textsuperscript{20-23}. Clearly, an entangled melt of linear chain behaves like a crosslinked rubber in such fast extension.

Previous studies have rarely probed the rheological response of entangled polymer melts at even higher rates. This is partially due to the fact that at normal experimental conditions, applied Hencky rates cannot reach values high enough. Therefore, we have no knowledge on whether it is always a good approximation to express the initial stress response in terms of intrachain entropic forces. In this chapter we report the observation of what appears to be inter-segmental response at small strains for startup extension. In addition to the contribution from entangled network, the inter-segmental contribution gives a large elastic modulus at small strains, and then quickly transits into a viscous flow. Such a phenomenon implies that the available theoretical description of polymer dynamics needs to be substantially revised. Especially, the tube model, as a single-chain mean-field theory, is incapable to describe such phenomenon\textsuperscript{33-34, 36-40}. It remains a theoretical challenge to explain the molecular origin of this dominant inter-segmental stress.
5.2 Experimental Section

5.2.1 Materials

This chapter studies the stretching behaviors of several different polymer melts and solutions at high Hencky rates. The PS1M, PS880K, PS163K, PS10K and PS4K were synthesized by Dr. Hongde Xu from the University of Akron. The PC63K is Lexan TM 141 111 obtained from Sabic (GE Plastic). The SBR161K was synthesized by Dr. Xiaorong Wang at Bridgestone Americas Center for Research and Technology. The PMMA125K is a Plaskolite brand with the item number CA-86. We also studied the mechanical responses of a slightly crosslinked SBR205K in this chapter. The SBR205K is also synthesized by Dr. Xiaorong Wang at Bridgestone. The chemical and mechanical properties of the materials are described in Table 5.1.
Table 5.1 Chemical and mechanical properties of the materials in this study

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_w$ (kg/mol)</th>
<th>$M_e$ (kg/mol)</th>
<th>PDI</th>
<th>$\tau$ (s)</th>
<th>temp ($^\circ$C)</th>
<th>$T_g$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1M</td>
<td>1028</td>
<td>13</td>
<td>1.02</td>
<td>122000</td>
<td>130</td>
<td>103</td>
</tr>
<tr>
<td>PS880K</td>
<td>880</td>
<td>13</td>
<td>1.02</td>
<td>25000</td>
<td>130</td>
<td>104</td>
</tr>
<tr>
<td>PS163K</td>
<td>163</td>
<td>13</td>
<td>1.01</td>
<td>166</td>
<td>130</td>
<td>101</td>
</tr>
<tr>
<td>PS10K</td>
<td>10</td>
<td>NA</td>
<td>1.01</td>
<td>NA</td>
<td>NA</td>
<td>94</td>
</tr>
<tr>
<td>PS4K</td>
<td>4</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>PC63K</td>
<td>63</td>
<td>1.3</td>
<td>1.58</td>
<td>3560</td>
<td>155</td>
<td>149</td>
</tr>
<tr>
<td>SBR161K</td>
<td>161</td>
<td>4.3</td>
<td>1.05</td>
<td>13200</td>
<td>20</td>
<td>-10</td>
</tr>
<tr>
<td>SBR205K</td>
<td>205</td>
<td>3.2</td>
<td>1.15</td>
<td>75</td>
<td>RT</td>
<td>-35</td>
</tr>
<tr>
<td>PMMA125K</td>
<td>125</td>
<td>13</td>
<td>1.41</td>
<td>2250</td>
<td>135</td>
<td>113</td>
</tr>
</tbody>
</table>

Table 5.1 lists the terminal relaxation time $\tau$ for each sample that is evaluated from small amplitude oscillatory shear (SAOS) measurements of the storage and loss moduli $G'$ and $G''$ as a function of frequency. The SAOS were carried out with an Advanced Rheometric Expansion System (ARES) rotational rheometer and is shown in Figure 5.1 for PC63K at 155$^\circ$C and PS1M at 120 $^\circ$C as examples. The shaded regime in each plot represents the range of effective rates applied in this study. The molecular weight and PDI were found using GPC, where SEC was done using a Wyatt Dawn Eos multiangle laser light (MALLS) detector in conjunction with Waters Model 2414 differential refractometer concentration detector. This was coupled with Wyatt Astra V 4.73.04 software and three Waters HR styrogel columns using THF at 35 $^\circ$C flowing at 1
mL/min. Glass transition temperatures were found using a TA Instruments Q2000 DSC ramping at 10 °C/min to well above $T_g$ followed by cooling at the same rate.

5.2.2 Sample Preparation and Apparatus

The stretching of the polymer samples were carried out at different temperatures above their glass transition temperatures using a first generation SER fixture mounted on the ARES-LS rotational rheometer equipped with a Rheometric Scientific Oven accurate to 0.1 °C. In order to prepare uniform specimens to use on the SER fixture, the PS, SBR, PC and PMMA were compression molded using a CARVER press, allowing sheets with thickness of 0.5 mm (for PC it is ~0.1 mm) to be made. Dimensions of 20 mm × 2 mm × 0.5 (0.1) mm were then cut from the large sheets. For PS solutions, the sample was made by first dissolving the mixture of long-chain melt and oligomer in toluene. The solution is then placed under the hood to evaporate enough solvent and then poured onto an alumina plate to be placed in the vacuum oven for several days at elevated temperature to remove the remaining solvent. The sample was then compression molded following the same procedure as for above-mentioned melts. After removal from the press, the final rectangular-shaped specimens with dimensions of 20 mm×2 mm×0.5 mm were cut out from the large sheet. The ends of the specimens were adhered to the SER fixture using commercially available LOCTITE 486® glue. After the LOCTITE® glue dried, the temperature of the oven was increased (or decreased, in the case of SBR161K) to the desired temperature, and the sample was allowed to equilibrate for at least 5 min. Subsequently, the samples were extended under prescribed conditions.
The crosslink of SBR205K is achieved by similar steps that were used to prepare the crosslinked SBR in CHAPTER III of this dissertation\textsuperscript{24}. The curing agent for the crosslink reaction, dicumyl peroxide, was purchased from Sigma-Aldrich and used as received. The SBR205K was first dissolved in toluene to achieve a uniform solution. 1wt\% of the crosslinker, dicumyl peroxide, was then added into the solution. After reaching the uniform dispersion, the toluene is subsequently removed first in the hood and then vacuum oven for several days. The peroxide-containing SBR was then molded by the CARVER hydraulic press at approximately 160 °C for 10 minutes to achieve the formation of a uniform thin film and the crosslink reaction simultaneously. The final rectangular sheet-like specimens were cut out from the thin film by a razor blade.

The transient stress-strain curves of SAOS were recorded on an ARES-G2 rotational rheometer from TA Instruments, coupled with 8mm parallel plates. Dynamic mechanical analysis (DMA) measurements for PS1M were carried out using a Q800 Dynamic Mechanical Analyzer from TA Instruments. The temperature was ramped from 95 °C to 150 °C, with the interval of 5°C. At each of the prescribed temperature, the sample was allowed to equilibrate for enough time before the extensional oscillation started. At each temperature, the oscillation with the discrete frequencies of 0.1Hz, 1Hz and 10Hz were performed respectively.
Figure 5.1 Small amplitude oscillatory shear (SAOS) of PC63K (a) and PS1M (b). The full SAOS curves were constructed from measurements at different temperatures and using 155 °C as reference temperature for PC63K and 120 °C for PS1M, respectively. Shaded regimes indicate the ranges of applied Hencky rates in this study.
5.3 Results

We have carried out stretching for the different materials close to their glass transition temperatures. Figure 5.2 a-d show typical stress-strain curves for PS1M and PC63K as examples. Also shown are the neo-Hookean curves for these polymers, based on the classical rubber elasticity theory and calculated from $\sigma_{\text{engr.}} = G_N^0(\lambda - 1/\lambda^2)$, where $G_N^0$ is the rubbery plateau modulus determined from SAOS measurements, chosen as the value of $G'$ when the $\tan(\delta) = G''/G'$ shows a minimum. In the range of applied effective rates shown by the shaded regimes in Figure 5.1, there are several striking observations, which are not found in the previous studies of uniaxial extension of entangled polymer melts at higher temperatures\textsuperscript{20-23}. Upon external deformation, there is an instant increase of the stress, and the stress level could be much higher than the value calculated from the rubber elasticity theory. The sharp rise in stress is followed by a leveling off or a decline (e.g., at 10 s\textsuperscript{-1} for PS at 120°C) to indicate a yield-like transition. This yielding is clearly not related to the properties of the entanglement network because it occurs at only a few percent of strain, at which time the network has hardly deformed. The stress continues to grow after this apparent yielding, before the sample shows fracture-like ruptures and retracts almost to the original dimensions. At higher temperatures, such as 150 °C for PS1M (Figure 5.2e), the shaded regime in Figure 5.1 is difficult to reach, and such “abnormal” behaviors were not observed.
5.4 Discussions

Detailed analysis of the stress-strain curves in the previous section reveals the existence of inter-segmental interactions in addition to the entanglement network. In this Section 5.4, we will discuss the leading features revealed from the stress-strain behaviors.

5.4.1 The Yielding Stress

From the data in Figure 5.2a-d, it seems there is a yielding stress $\sigma_Y$ at very small strain for each of the stress-strain curves. Literature data$^{111-113}$ has shown for amorphous polymers near the glass transition regime, the stress-strain curve will show a yielding phenomenon, just as the case for polymer glasses. In those cases, the mechanical stress is
decomposed to a rubbery contribution and a glass contribution\textsuperscript{111-115}. We examined and re-plotted those literature data, and found in their case the yielding stress $\sigma_Y$ has a logarithmic dependence on rate, as shown in Figure 5.3a. This logarithmic dependence confirms that the yielding behaviors are dominant by glass contributions, since it has been known for decades that such dependence exists for polymer glasses\textsuperscript{116}. We also examined the yielding stress vs. rate from the stress-strain curves in Figure 5.2a, and compared them with literature data.
Figure 5.3 (a) The yielding stress vs. Hencky rate, for literature data at 100°C and 105°C (re-plotted with permission from ref 112) and experimental results from this study for PS1M at 120°C; (b) The yielding stress for PS1M at 120°C and corresponding G”.

Apparently, in the temperature and rate range of this study, the yielding stress does not have a logarithmic dependence on applied rates. Rather, a more detailed analysis shows that the yielding stress $\sigma_Y$ seems to be determined by the value of $3G''$ from SAOS at corresponding angular frequencies. This numerical fit will be discussed in more details in the following sections. We can draw a conclusion from Figure 5.3 that the yielding behavior observed in this study has a different nature from that recorded in the literature. In other words, the observed yielding in this study has nothing to do with glassy dynamics.
5.4.2 The Large Initial Modulus

A more detailed analysis of the stretching data reveals that at each of the temperature close to $T_g$, the initial modulus $G_{\text{initial}}$ will increase to a saturated value, which stays far above $G_N^0$ and the corresponding $G'$ from SAOS at the same $Wi$ ($De$). Here, the $G_{\text{initial}}$ from stretching tests was calculated from the initial Young’s modulus $E_{\text{initial}}$ using the relationship $G_{\text{initial}}=E_{\text{initial}}/3$. We performed shear tests at $120^\circ$C for PS1M and confirmed the validity of the above relation. In sharp contrast, we found at higher temperatures (e.g., $150^\circ$C for PS1M or $170^\circ$C for PC63K), the initial modulus doesn’t have the trend to rise. These analyses were shown in Figure 5.4, taking PS1M and PC63K as examples. The striking observation that at temperatures close to $T_g$ the saturated moduli will be much higher than the corresponding $G'$ from SAOS at the same $Wi$ ($De$) is quite unexpected, since any stress-strain behavior is supposed to obey linear viscoelasticity at such small strains$^{9-10}$.
Figure 5.4  An analysis of the data in Figure 5.2, showing $G_{\text{initial}}$ vs. $Wi$ ($De$) at each temperature. (a) PS1M; (b) PC63K.

To make sure the observation that the saturated $G_{\text{initial}}$ is much higher than $G'$ from SAOS is genuine, we conducted dynamic mechanical analysis (DMA) tests. DMA data confirms that $G'$ from SAOS and $E'/3$ from DMA measurements are identical. The DMA data for PS1M, together with the saturated $G_{\text{initial}}$ from various long-chain PS melts, were included in Figure 5.5. Since the entanglement molecular weight $M_e$ for PS is $\sim$13kg/mol$^{102}$, all the PS included in Figure 5.5 are well entangled. It seems for highly entangled melts, the saturated $G_{\text{initial}}$ from different molecular weights share the same value at each of the temperature close to $T_g$. In other words, it seems for well entangled polymer melts, the saturated $G_{\text{initial}}$ does not have much molecular weight dependence.
Figure 5.5 The saturated $G_{\text{initial}}$ of different entangled PS melts vs. normalized temperature. Also shown are the $G'$ from SAOS and $E'/3$ from DMA for PS1M. $G'$ from SAOS is from the range of angular frequencies corresponding to the shaded area in Figure 5.1b.

To understand why the saturated initial modulus is higher than corresponding $G'$ from SAOS when temperature is approaching $T_g$, we performed SAOS at specific frequencies under different temperatures, and recorded the transient stress-strain curves. Typical data are shown below in Figure 5.6.
(a) PS 1M 150 °C
ω=3 rad/s, strain=1%

(b) PS 150 °C
ω=0.3 rad/s, strain=1%
Figure 5.6 The transient stress-strain curves of PS1M during SAOS at specific frequencies. The testing conditions are included in each plot. The data recorded contain 20 cycles for (a) and (c), and 10 cycles for (b).

From Figure 5.6, we found at 120 °C, the initial modulus is substantially larger than the modulus of later cycles. This large initial modulus disappears as the oscillation continues, and the value of the modulus at $\gamma=0$ drops back to $G'$ from SAOS. At 150 °C however, the initial modulus and the modulus later on are almost identical. The initial modulus measured here is consistent with the initial modulus of the stress-strain curves reported in Figure 5.2. A comparison between the $G_{\text{initial}}$ from the transient SAOS stress-strain behaviors and the $G_{\text{initial}}$ from startup stretching has been included in Figure 5.4a.

We noticed that this large initial modulus is only available at the beginning of external deformation. To confirm this, we performed continuous stretching immediately after several cycles of small amplitude oscillation. We found if a startup deformation is
followed by several cycles of oscillation, the “abnormally” large modulus will not be observed, as shown in Figure 5.7.

Figure 5.7  Stress-strain curves of startup deformations of PS1M at 120°C followed by several cycles of SAOS. The switch from SAOS to continuous stretching is conducted at \( \gamma = 0 \) after 3 cycles, and the rate of the continuous stretching is the same rate as the rate of SAOS at the switching moment.
Since the large initial modulus only persists to a few percent of strain when the entangled network has hardly deformed, clearly, it is not related to the properties of the entanglement network. We speculate the origin is from inter-segmental interaction. Upon external deformation with rates high enough, segmental level interchain interactions produce a significant amount of mechanical stress. Because the inter-segmental process leading to the sudden buildup of stress plausibly involve length scales within the entanglement spacing, polydispersity of the molecular weight distribution should not play any role, and there is no molecular weight dependence (as shown in Figure 5.5). A yield-like behavior quickly occurs and such interactions will transit into a flow state, which is the topic of the following sections.

5.4.3 The Yielding Time

In order to understand the nature of the yielding process at very small strains, we compared the yielding time $t_y$ from stress-strain curves in Figure 5.2, and compared them explicitly with $\alpha$-relaxation time from literature, and the comparison is shown in Figure 5.8. The $\alpha$-relaxation time is the characteristic time for the local segmental relaxation process known to associate with glass transition$^{89}$, and mostly determined by measurements from dielectric relaxation spectrum (DRS)$^{86-90}$. 
Figure 5.8  (a) Yielding time at different temperatures and rates for PS1M in this study, and (b) the $\alpha$-relaxation time of a PS melt, re-plotted using data from ref 89 with permission. Dashed lines in (a) represent the values of $\tau_\alpha$ reading from (b), at 110°C and 120°C respectively.
There are several important features revealed in Figure 5.8. First, the yielding time here is significantly larger than $\alpha$-relaxation time recorded in existed literature. This confirms again that the dynamics governing the yielding behavior is not the same as that governing the yielding process in glass dynamics. Second, the yielding time and $\alpha$-relaxation time seem to get close when $T_g$ is approaching. It cannot be ruled out that when $T_g$ is further approached, $\alpha$-relaxation process could be the governing factor to determine the yielding behavior.

5.4.4 The Dissipative Flow at Large Strains

From Figure 5.2, we found that at longer time, the stress continue to grow after the apparent yielding at small strains. Considering the fact that the stress keeps growing above the rubber elasticity level, it is reasonable to suggest that there must be a contribution other than the entangled network. Therefore, we can write the total true stress in the form of $\sigma_{true}=\sigma_c+\sigma'$, where $\sigma_c$ is the stress coming from the entangled network, and $\sigma'$ is the extra contribution. In order to study the nature of $\sigma'$ quantitatively, we used Edward-Vilgis model\textsuperscript{28-29, 100}, which is considered to be one of the most successful network models, to represent the contribution from the entangled network, and we can therefore write $\sigma_{true}=\sigma_{E-V}+\sigma'$, where $\sigma_{E-V}$ is the stress originated from the entangled network based on Edwards-Vilgis model calculation. Based on such representation, and with the help of the programming and fitting functionality of MATLAB\textsuperscript{®117-119}, we actually found $\sigma'$ could reach a steady state, as shown in Figure 5.9 using the data for PS1M at 120 °C as an example. The details of how we determined $\sigma'$ using MATLAB\textsuperscript{®} will be introduced in Section 5.6 of this chapter as an appendix. We
further found that the value of the steady-state stress of $\sigma'$ could be represented by an apparent viscosity $\eta_a$, assuming $\sigma' = \eta_a \dot{\varepsilon}$. If we read the magnitude of $\eta_a(\dot{\varepsilon})$ and compare it with the extensional dynamic viscosity $3\eta'(\omega)$ as a function of frequency from the SAOS measurements, we find that there exists a modified Cox-Merz rule

$$\eta_a(\dot{\varepsilon}) = 3\eta'(\omega)\bigg|_{\dot{\varepsilon} = \omega},$$

as shown in Figure 5.10a. Here we summarize similar data from similar startup extensional deformation experiments on other polymer melts including polydisperse PC and PMMA, a monodisperse SBR and a second monodisperse PS of lower molecular weight, as well as two PS-based polymer solutions. The observed correlations between $\eta_a(\dot{\varepsilon})$ and $3\eta'(\omega)$ for these different melts point to the universality of the phenomenon. Again, since the inter-segmental process plausibly involve length scales within the entanglement spacing, polydispersity of the molecular weight distribution does not affect the correlation, and there is no molecular weight dependence.

We further noticed that $\eta_a$ follows a WLF type superposition\textsuperscript{25}, which is demonstrated in Figure 5.10b. Also, we found the steady-state value of $\sigma'$ actually determines the yielding stress of stress-strain curves in Figure 5.2. This explains the match between yielding stress $\sigma_Y$ and $3G''$ in Figure 5.3b.
Figure 5.9  The plot of viscous stress $\sigma'$ as the function of stretching ratio, using the data of PS1M at 120 °C as an example. The determination of $\sigma'$ is described in the text.
Figure 5.10 (a) The plot of apparent viscosity $\eta_a$, as well as the dynamic viscosity $\eta'$ from SAOS, for various polymer melts and solutions; (b) the apparent viscosity and dynamic viscosity of PS1M, showing the WLF type superposition. Here, for $\eta'$ and $\eta_a$ measurement, $De(Wi)=1.6\times10^6$ at 120 °C and 130 °C; $De(Wi)=1.0\times10^6$ at 110 °C.

Since $\eta_a$ and $3\eta'$ has the same value, and $\eta'$ is known to represent the dissipative component of viscoelasticity\(^{9-10}\), the data in Figure 5.10 suggests that $\sigma'$ has a dissipative nature. To confirm this, we performed the loading-unloading cycle\(^{103}\) measurements. We stretched the sample at a prescribed rate, and then forced it to return under the same rate. We then compared the percentage of the dissipative energy from the hysteresis loop with the ratio of the integral area of $\sigma'$ to that of the total stress $\sigma_{\text{true}}$. As an example, Figure 5.11a shows the loading-unloading cycle of a PS880-10K 80% solution at 120°C under 0.1s\(^{-1}\) till the Hencky strain of 0.6 (i.e., $\lambda_1=0.82$). The shaded area in the hysteresis loop represents the dissipative energy. We found the ratio of dissipative energy is 73%, out of
the total energy input. When we re-plot the stress curve of PS880-10K 80% at 120°C under 0.1s\(^{-1}\), till the same Hencky strain of 0.6 as in Figure 5.11a, we found the ratio of the shaded area in Figure 5.11b, which is the total energy input subtracting the elastic energy, is 76%. The agreement of the two ratios suggests that they have the same nature. In other words, the shaded area in Figure 5.11b, which represents the mechanical stress in excess of neo-Hookean, has a dissipative nature.
As discussed in the preceding paragraphs, the origin of $\eta_a$ is plausibly intermolecular. Since no molecular models are available to account for any intermolecular contributions to the mechanical stress, it is difficult to offer a perfect intelligent account for the nature of this extra stress. However, it is still possible to do a semi-quantitative estimation of how and when this viscous contribution will become obvious. As we know, polymer melts have a whole spectrum of relaxation times, and some are apparently more importantly pertinent than others. When materials are probed on long time scales, i.e., low rates, i.e., $Wi \sim 1$ or $Wi > 1$ (but nothing excessive) the fast processes die out quickly, i.e., the small length scale dynamics quickly turns viscous, dictated by the “local viscosity $\eta_1$”, i.e., viscous process associate with chain segments.
The viscous contribution is given by $\sigma_v = \eta_1 \dot{\varepsilon} = Wi(\eta_1/\eta_0) G_N^0 \ll G_N^0$ because $(\eta_1/\eta_0) \ll 1$, where $\eta_0$ is the zero-shear viscosity of the material. For such a contribution to be significant, we need a rate corresponding to $Wi = \tau/\tau_c$ so that $\sigma_v = (\eta_1/\eta_0)(\tau/\tau_c) G_N^0 \sim G_N^0$, assuming $\tau/\tau_c = \eta_0/\eta_1$. Looking back at the shaded areas in Figure 5.1, we found our analysis predicts the experimental facts very well, since the condition $Wi = \tau/\tau_c$ indeed represents the second crossover in SAOS.

5.4.5 Rouse Melts: the Situation without Entangled Network

For entangled polymer melts, we have shown that the mechanical stress is the summation of the entanglement network contribution and the inter-segmental contribution. If this is true, we should expect this inter-segmental contribution to be present even without the existence of a highly entangled network. To better understanding the nature of the stress without network, we performed measurements on a Rouse melt PS10K, with the molecular weight lower than the entanglement molecular weight $M_e \sim 13$kg/mol. We found even for this Rouse melt, at temperatures sufficiently close to $T_g$, a large initial modulus will be observed. From Figure 5.12b, we noticed the $G_{\text{initial}}$ for PS10K is substantially lower than that of the highly entangled PS melts, at each of the normalized temperature. Therefore, although the inter-segmental process leading to the sudden buildup of stress plausibly involve length scales within the entanglement spacing, it seems the magnitude of $G_{\text{initial}}$ does depend on whether the material is sufficiently entangled. In other words, the existence of entanglement junctions may lead to stronger inter-segmental interactions.
Figure 5.12  (a) The stress-strain curves of PS10K at 110 °C at three different rates, and (b) the $G_{\text{initial}}$ as the function of temperature, with the Rouse melt PS10K plotted together with long-chain entangled PS melts in this study.
We also performed the loading-unloading tests, and such measurement confirms that the stress from the Rouse melt is of a dissipative nature, analogue to $\sigma'$ from highly entangled melts or solutions, since the dissipative energy ratio is almost 100% here.

Figure 5.13 The loading-unloading test for PS10K. The dissipative energy has a percentage of almost 100%.

5.4.6 Existence of the Inter-segmental Interactions in Crosslinked Polymer

As discussed in the preceding paragraphs, the inter-segmental process leading to the sudden buildup of stress plausibly involve length scales within the entanglement spacing. We have shown that once the material is well entangled, the behaviors do not have any dependence on molecular weight or molecular weight distributions, although
the existence of entanglement junctions may play certain roles. If our understanding is correct, the inter-segmental contributions should appear in the mechanical responses of slightly crosslinked materials as well. To prove this, we did measurement for a crosslinked SBR205K and performed analysis.

![Figure 5.14](image)

Figure 5.14  Small amplitude oscillatory shear (SAOS) for crosslinked SBR205K at 0°C. The full SAOS curve was constructed from measurements at 0°C, 20°C and 40°C, and using 0°C as the reference temperature.

We also performed uniaxial stretching of the crosslinked SBR205K, and presented the stress-strain curves in Figure 5.15. The Hencky rates we applied correspond to the
shaded area in Figure 5.14, which is SAOS measurement of the crosslinked SBR205K at 0°C.

Figure 5.15 Stress-strain curves of the crosslinked SBR205K at 0 °C at three different rates.

From Figure 5.15, we found the stress-strain behavior of the crosslinked SBR is very similar to that of the uncrosslinked melts: the stress has a quick rise, and then experience a yield like levelling-off. The stress keeps growing beyond the rubber elasticity predictions, which is calculated using neo-Hookean equation $\sigma_{\text{engr}} = G_N^0(\lambda - 1/\lambda^2)$, taking $G_N^0 = 3.7$ MPa, as shown in Figure 5.14.
We also analyzed the viscous stress as we did for uncrosslinked melts in Section 5.4.4 (instead of using Edwards-Vilgis model, here we simply used neo-Hookean equation to represent the elastic stress from network), and again we found that the magnitude of the viscous stress $\sigma'$ is determined by the dissipative component from SAOS measurement. Figure 5.16 shows the apparent viscosity $\eta_a$ and the value of $3\eta'$ from SAOS. It seems the modified Cox-Merz relationship works not only for uncrosslinked melts, but also for crosslinked materials.

![Figure 5.16 Apparent viscosity $\eta_a$ and $3\eta'$ for the crosslinked SBR205K. The modified Cox-Merz relationship is proven to be valid.](image_url)
In summary, it seems the inter-segmental contribution does not only exist in polymer melts, but also in crosslinked rubbery material. The leading features present in previous sub-sections for polymer melts can be found in crosslinked SBR205K as well. This proves that the inter-segmental process leading to the sudden buildup of stress indeed involves length scales much shorter than the entanglement spacing, so it is available in crosslinked systems.

5.5 Summary

In conclusion, the exact sources of mechanical stress of polymer melts and solutions at high Hencky rates are largely missing in the literature. In this chapter, we made the first attempt to systematically study the mechanical stress of polymer melts to startup deformation under “unconventionally” high Hencky rates. It seems the inter-segment interactions play a very important role under high deformation rates. At small strains, there is a large elastic modulus, which could be orders of magnitude higher than $G_N^0$. This is quickly transited to a dissipative flow through a yielding-like behavior, and the transition takes a time longer than typical $\alpha$-relaxation time. After the yielding, the mechanical stress is the summation of an elastic stress and a viscous one. To understand the nature of the viscous component, an apparent viscosity is calculated after the subtraction of the elastic part from the total stress. It is found that the apparent viscosity, which represents the contribution of the viscous stress, matches the dynamic viscosity from SAOS measurements quantitatively. The dissipative nature of this viscous contribution is proven by the loading-unloading cycles. To further understand the inter-segmental contributions, we studied the stress-strain behaviors of a Rouse melt, where no
entanglement network existed. Indeed, even without the existence of the entanglement network, the effect of the inter-segmental contribution is clearly present, although more details about this contribution and its molecular origin are still under investigation. Moreover, we found even for slightly crosslinked rubbery material, this inter-segmental interaction makes a significant amount of contribution to the total mechanical stress. This proves that the inter-segmental process involves a length scale that is well below the entanglement spacing $M_w$ level.

All these observations point out to the deficiency of current rheological theories, dominated by the tube model-based single-chain mean-field approximation\textsuperscript{33-34, 36-40}. The importance of interchain interactions, whether at chain level or segmental level, must be addressed in the next-generation description of nonlinear rheology of entangled polymer melts.

5.6 Appendix

In this Appendix, the fitting of stress-strain curves and the determination of $\sigma'$ in Section 5.4.4 according to Edwards-Vilgis model using MATLAB\textsuperscript{®} will be introduced. MATLAB\textsuperscript{®} is a powerful programming language and numerical computing environment developed by The MathWorks, Inc.

First, codes for Edwards-Vilgis model are written, according to Equation 2.49-2.55. There are three independent parameters to be determined by fitting: the crosslinked ratio ($\frac{N_c}{N_c + N_s}$, see Section 2.2.2 of this dissertation), the maximum stretching ratio $\lambda_{\text{max}}$ and the apparent viscosity $\eta_a$. The codes are written as below, taking the case for PS1M stretching at 120°C under 0.1s\(^{-1}\) as an example:
function [f]=fff(para,x)

    eta=0.2;
    rate=0.1;
    GN0=0.2;

    alpha=1/para(2);
    A=1-alpha*alpha.*(x.*x+2./x);
    B=1+eta.*x.*x;
    D=2.*(x-1./x./x);

    sigmac=para(1)*GN0.*D.*(((1-alpha*alpha)./A./A)-alpha*alpha./A);
    sigmas=(1-para(1))*GN0.*D.*((1-alpha*alpha)*(1+eta)./A./A.*((1-eta*eta.*x).*x.*x.*A./B./B/(x+eta)./(x+eta)+alpha*alpha.*(x.*x./B+2./(x+eta))) + eta.*x./B./(eta+x)-alpha*alpha./A);

    stresse=sigmac+sigmas;
    stressv=para(3)*rate./x;
    f=stresse+stressv;
end

In the codes above, “x” and “y” are $\lambda$ and $\sigma_{\text{engr}}$, respectively, input from the experimental data. “para(1)”, “para(2)” and “para(3)” are the three independent parameters to be determined, and they are crosslink ratio, maximum stretching ratio $\lambda_{\text{max}}$ and apparent viscosity $\eta$, respectively. “rate” is the applied Hencky rate, and “GN0” is the plateau modulus of the material. “eta”, “alpha”, “sigmac” and “sigmas” are $\eta$, $\alpha$, $\sigma_c$ and $\sigma_s$ respectively, as introduced in Section 2.2.2 of this dissertation. “A”, “B” and “D” also have the same meanings as in Section 2.2.2. “stresse” is the elastic network component of the stress, and “stressv” is the viscous component, $\sigma'$. “f” is the total engineering stress.

Then, we can write the codes to do the fitting and determine the three parameters:

para0=[1 14 0];
for i=1:100
    para=lsqcurvefit('fff',para0,x,y,[0 1 0],[1 100 10]);
    para0=para;
end

Upon running the above codes, the three parameters could be determined. Once the
three parameters $\frac{N_c}{N_c + N_s}$, $\lambda_{\text{max}}$ and $\eta_a$ are determined, we can calculate the stress-strain
curves based on Equation 2.49-2.55. Figure 5.17 shows the stress-strain curve from
fitting and the experimental stress-strain curve, and they have excellent match. We can
also calculate $\sigma'$, and make plots such as Figure 5.9.

![Figure 5.17 Stress-strain curves for PS1M stretching at 120 °C under a Hencky rate of
0.1s$^{-1}$, from experimental stretching and Edwards-Vilgis model fitting, respectively.](image-url)
CHAPTER VI

SUMMARY

Polymers, as viscoelastic materials, show a rich variety of nonlinear rheological phenomena. In practical applications and processing, it is crucial to understand the nonlinear rheological behaviors.

In this dissertation, various nonlinear phenomena of entangled polymer melts during startup deformation have been studied for the first time. It is found that, as the applied rate increases well beyond the reciprocal Rouse relaxation time $\tau_R$, i.e., for the Rouse-Weissenberg number $Wi_R$ much higher than unity, the kinematic difference between shear and extension leads to very different responses in entangled polymers of linear chains. During startup shear, polymer chains can always disentangle to yield. Upon fast startup extensional deformation, however, entanglements can get locked up to act like crosslinks so that yielding does not prevail and non-Gaussian stretching could take place.

The yield-to-rupture transition has been systematically studied as the function of temperature. It is found that the transient rheological responses under different temperatures do not obey time-temperature equivalence principle. At the same effective rate according to the temperature dependence of the low frequency (terminal) dynamics, yielding is seen at higher temperatures but rupture is observed at lower temperatures.
Apparently, the dynamics dictating chain entanglement and disentanglement follow different temperature dependence from that characteristic of the terminal relaxation.

Rheological responses at unconventionally high rates have been studied by conducting experiments closer to glass transition temperature $T_g$. Below a threshold temperature and above a critical effective rate, upon startup deformation transient inter-segmental interactions produce an initial elastic response with stiffness that is orders of magnitude higher than the rubber plateau modulus $G_N^0$ and a frictional contribution to the mechanical stress beyond the point of yielding that takes place at a few percent of strain after the inception of deformation.

The nonlinear phenomena studied in this dissertation challenge the current theories of nonlinear rheology of entangled polymers and are expected to inspire new theoretical development. On the other hand, molecular dynamics (MD) computer simulations can be a valuable tool to elucidate the molecular origins of these new rheological characteristics, in particular to delineate how the transient elasticity arises from inter-segmental association. Future work should also examine how polymer blends and mixtures behave under similar rheological conditions.
BIBLIOGRAPHY


