THE EFFECTS OF MELT STRETCHING ON THE MECHANICAL
BEHAVIOR OF POLYMER GLASSES

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Gregory D. Zartman
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Entangled polymer glasses are commonplace, and understanding their response to external deformations is very important. Past descriptions of polymer glasses fail to explain the effects of melt stretching and aging on their mechanical behavior. Even in absence of melt stretching and aging, the physical properties of glasses remain a challenge to describe with the current framework.

In this dissertation, the effects of melt stretching on the mechanical properties of several common polymer glasses (polystyrene, poly(methyl methacrylate), poly(styrene acrylonitrile), and polycarbonate were investigated. Polymers were deformed systematically in the melt state followed by a rapid thermal quench, preserving the effects of melt stretching. The mechanical properties of the resulting glasses were then tested. Several interesting changes happened upon melt stretching. In the direction of melt stretching, brittle glasses became ductile. While perpendicular to melt stretching, polycarbonate becomes brittle. We have suggested that the origin of the change in failure behavior is a condensation or dilation of load bearing strands. Our experimental results were examined under our perception of a polymer glass as a double network made up of the inter-segmental van der Waals interactions and the entangled chain network. We also use our double network picture to shed new light on changes in mechanical behavior resulting from aging, and blending low and high molecular weight polymer.
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CHAPTER I

INTRODUCTION

Well entangled polymers are widely used in their amorphous glassy state for a variety of applications from windows to bottles to safety equipment. The unique physical properties of these materials, i.e., high modulus, toughness, and strength, below $T_g$ and ease of processing above $T_g$, lend themselves to a multiplicity of engineering applications. Despite the ubiquity of these materials, a unified theory on the effect of melt stretching above $T_g$, followed by rapid quenching into the glassy state, on the physical properties of the polymer glass is lacking.$^{1-4}$ Understanding what causes amorphous polymers to be brittle or ductile, and how melt deformation effects the ductility of polymer materials, is imperative to developing new products or processes that take advantage of these special properties.

The most popular way to look at the complex mechanical behavior, of both polymer melts and glasses, is to perform rheological measurements. Since billions of pounds of polymers are processed each year, the study of polymer deformation and flow in the melt state is among the most important subjects in polymer science and has been study in detail throughout the past century.$^{5-8}$ The physical properties of polymers in the glassy state are also of interest, since many polymer products are used below $T_g$, these properties have also been extensively studied in the past.$^{1-4,9-11}$ Studies have linked
macroscopic deformations of amorphous polymer glasses to microstructural yielding called crazing.\textsuperscript{4, 12-20}

This study’s primary focus is to investigate the effects of melt stretching on the physical properties of polymer glasses and how this can be used to help us develop a more detailed understanding of the mechanical behavior of polymer glasses. We were first intrigued by the long known phenomena that polystyrene can be made ductile upon melt stretching above $T_g$ followed by rapid thermal quenching into the glassy state.\textsuperscript{21-22} Despite the fact that this has been known for more than 50 years, there is no satisfactory theoretical explanation. Past researchers have attributed this change in ductility and strength to alignment of molecules.\textsuperscript{23-24} Others have used a reduction in strain softening as an explanation of how the material becomes ductile.\textsuperscript{25} While one group suspected that this brittle-ductile transition is unique to polystyrene and is caused by a rearrangement of the phenyl side groups.\textsuperscript{26}

The physical properties of entangled polymer melts are determined, for the most part, by the structure of their entanglement network.\textsuperscript{27-31} These entanglements arise due to the noncrossability of polymer chains formed by covalent bonds. Recent studies on the extensional rheology of polymer melts have provided experimental evidence for, and a molecular picture of, what happens to the entanglement network upon extension.\textsuperscript{32-33} These insights allow for the elucidation of the precise consequence of melt stretching on the polymer glass. In this dissertation, we have used this understanding to help develop a new double network picture of a polymer glass, that not only can explain the effects of melt stretching, but the affects of aging and blending as well.
This dissertation was organized into six chapters, starting with fundamentals of polymer rheology and ending with our newly developed double network picture of polymer glasses. In Chapter II, the basic background of polymer rheology is introduced. This includes the fundamentals of linear and nonlinear polymer rheology, an introduction to the molecular picture of entangled polymer liquids, and a detailed description of the behavior of entangled polymer melts in extension.

Chapter III presents a broad look at the past literature studies on polymer glasses. Including the glass transition, polymer glass failure behavior, past approaches to describing the mechanical behavior of polymer glasses, and some intriguing phenomena related to the physical properties of glasses that are difficult to explain with past descriptions of polymer glasses.

Chapter IV contains the melt stretching experiments. In this chapter we melt stretched the polymer glasses in a variety of different ways. First, PS was stretched at different temperatures (rates) to a fixed Hencky Strain. Next, PS, PMMA, and SAN were stretched at a single high rate to different Hencky Strains. Finally, a large sheet of polycarbonate was melt stretched so that the stretched sheet can be prepared to allow room-temperature uniaxial extension in the direction perpendicular to the direction of melt stretching.

Chapter V looks at how the melt stretching affected the mechanical behavior of polymer glasses. The change in response ranged from no change at a low degree of melt stretching, to a complete change in failure behavior, i.e. from brittle to ductile in the case of PS, PMMA, and SAN. Polycarbonate was also shown to be brittle upon sufficient melt stretching perpendicular to the direction of glassy state tensile testing.
Chapter VI develops the double network picture and describes how our melt stretching picture can explain the change ductility upon melt stretching. Polycarbonate was blended with a short chain component and mechanically extended at room temperature to elucidate the importance of the chain network. Commercial polycarbonate was also annealed below $T_g$ to demonstrate the effect of aging by comparing the mechanical behavior of the aged PC with the quenched PC. The double network picture was applied to all of these different sample treatments to explain the observed behaviors. Also contained in Chapter VI is a conclusion section highlighting the most important results of this study.
2.1 SHEAR RHEOLOGY

Rheological measurements of entangled polymers are often taken in two ways: simple shear or uniaxial extension. Understanding the basic concepts of rheology using simple shear is necessary, and perhaps easier, than using extension as an introduction. Hence, rheological concepts using simple shear will first be introduced followed by their analogous components in uniaxial extension.

Simple shear places the test sample of thickness $H$ between two plates and displaces one of the plates relative to the other. Figure 2.1 depicts a simple shear experiment where the top plate is moved relative to the bottom plate at a speed $V$. After some time $t$, the top plate has been displaced with respect to the bottom plate a distance $\Delta x = Vt$. This displacement deforms the sample of thickness $H$ by the same distance $\Delta x$ and allows us to define strain $\gamma$:

$$\gamma = \frac{\Delta x}{H},$$

as the amount the sample has been deformed with respect to the height of the sample. Also of interest is the how fast the sample is being sheared with respect to $H$ known as the shear rate $\dot{\gamma}$:

$$\dot{\gamma} = \frac{d\gamma}{dt} = \frac{V}{H}.$$

(2.1)

(2.2)
The amount of force $F$ required to cause deformation of the polymer sample is often of interest, however, the force is dependent on the size of the sample so it is more convenient to use stress $\sigma$:

$$\sigma = \frac{F}{A}. \quad (2.3)$$

This is simply the force acting on the area $A$ of the specimen and has units of N/m² which is known as the Pascal (Pa).

This most basic geometry for producing simple shear possesses a major problem in the fact that the sample is only able to undergo a finite amount of strain before problems begin to occur at the edges of the sample. This gives rise to instabilities in the sample and errors in the measurement of stress when the aspect ratio of the sample is not sufficiently large to neglect problems at these edges. In order to overcome these hardships a different way to examine simple shear is needed.

![Schematic of a sample undergoing simple shear](image)

**Figure 2.1** Schematic of a sample undergoing simple shear
Rotational rheometers use the same basic principles as simple shear between two plates but eliminate challenges related to the finite strain the sample is able to undergo. This type of setup where a disk of sample is placed between plates and torsion is used to displace the sample was first suggested by Mooney and Ewart\textsuperscript{35} and is now a standard way to measure rheological properties of materials. Figure 2.2 and 2.3 represent two basic types of rotational rheometer plate designs: parallel and cone and plate respectively. Simply using two parallel plates in torsion has the problem of creating more shear in the radial direction away from the center which undergoes zero shear. This problem can be solved by using a cone shaped plate which allows more uniform shear throughout the sample in the radial direction. Rheometers using these basic setups are often used to look at physical properties of polymer materials as is discussed in the following sections.

![Side view of a parallel plate rotational rheometer](image-url)

Figure 2.2 Side view of a parallel plate rotational rheometer
2.1.1 VISCIOUS LIQUID, ELASTIC SOLID, AND VISCOELASTICITY.

The difference between a liquid and a solid is that upon the application of an external force a liquid will flow indefinitely. Solids can only deform a finite amount without suffering structural failure due to the external conditions. There are two primary types of liquids: viscous liquids and viscoelastic liquids. They differ in the sense that upon application of an external disturbance the viscous liquid immediately undergoes flow as governed by Newton’s Law whereas viscoelastic liquids do not.

\[
\sigma = \eta \dot{\gamma}
\]  

(2.4)

Newton’s Law provides the definition of viscosity \(\eta\) for a liquid and the dimensions of viscosity being Pa* s from the definitions of stress and shear rate. Newton found that
many common liquids such as water and oil have a simple linear relationship between applied stress $\sigma$ and shear rate $\dot{\gamma}$. Viscoelastic liquids such as polymer melts, toothpaste, ketchup, and yogurt do not have a simple relationship between stress and shear rate.

In order to understand the behavior of viscoelastic materials one must first look at elastic solids. Elastic solids were first described by Hooke in the 17th century. What Hooke found was that at small strains there was a linear relationship between the applied stress $\sigma$ and the deformation $\gamma$ of the solid.

$$\sigma = G \gamma$$  \hspace{1cm} (2.5)

Hooke’s Law provides the definition of the elastic modulus $G$ and its dimensions as Pa since $\gamma$ is dimensionless. Upon application of an external stress the sample is instantaneously deformed by $\gamma$, however, unlike a liquid deformation, it does not continue indefinitely and the sample deformation stops at the prescribed strain.

Viscoelastic materials differ from both the Hooke’s Solid and the Newtonian liquid. Upon application of an external force viscoelastic materials first deform in a solid or elastic manner. After the initial elastic deformation the sample will begin to flow and behave more like a Newtonian fluid. The fact that initially the material possesses elastic behavior followed by viscous flow is what gives rise to the term viscoelastic. Also important when dealing with viscoelastic materials is the time scale in which the deformation takes place. Often when the material is examined on very short time scales the material behaves like an elastic solid, yet, when the material is examined on longer time scales it behaves in a liquid like manner. In order to quantify these time scales models are developed to find time scales intrinsic to viscoelastic materials.
2.1.2 POLYMER CHAIN ENTANGLEMENT

In order to predict properties such as viscosity for polymer solutions models such as the Zimm and Stokes – Einstein have been developed. These models do a good job predicting viscosities of polymer solutions in the dilute limit, when polymer chains are not interacting with each other. When chains are overlapping or in a polymer melt these models fail to make accurate predictions. The Rouse model works well for low molecular weight polymer melts and predicts that the viscosity is increased linearly with Molecular Weight ($M_w$). This is true up to some critical molecular weight ($M_c$), were the scaling of viscosity with $M_w$ changes from a power of 1 to a power of 3.4.

![Schematic plot of viscosity ($\eta$) as a function of $M_w$.](image)

Figure 2.4 Schematic plot of $\eta$ as a function of $M_w$.

This change in the behavior of the polymer melt with increasing $M_w$ tells us we can no longer use a simple picture of friction between chains, when chains become sufficiently
long. Also, the fact that polymer chains prefer to take on the shape of random Gaussian coils implies that a great deal of chain interpenetration must take place, and increasing the size of the chain increases the level of interpenetration. This interpenetration allows inter-chain interactions beyond that of simple frictional forces and allows temporary elasticity.\textsuperscript{29-31} This intertwining of polymer chains gives rise to the idea of chain entanglement. Chain entanglement is very elusive in terms of a mathematical description although entanglement can be seen a variety of experimental measurements. The following sections provide several examples of how chain entanglement is observed experimentally.

2.1.2.1 ELASTIC PLATEAU IN SMALL AMPLITUDE OSCILLATORY SHEAR

Small amplitude oscillatory shear (SAOS) is quite perhaps the most commonly used technique to probe the linear viscoelastic properties of polymer materials.\textsuperscript{5} In oscillatory shear the deformation is created by varying the motion of the top plate according to a sine wave:

\[ x(t) = x_0 \sin(\omega t) \]  \hspace{1cm} (2.6)

Here \( x_0 \) is the maximum amplitude of the oscillation and \( \omega \) is the oscillation frequency

\[ \omega = \frac{2\pi}{T} \]  \hspace{1cm} (2.7)

where \( T \) is the period or time to complete a full cycle. Differentiating with respect to time one finds the velocity as a function of time to be:

\[ V(t) = x_0 \omega \cos(\omega t) . \]  \hspace{1cm} (2.8)

The samples strain and strain rate can now be easily defined as
\[ \gamma(t) = \frac{x_0}{H} \sin(\omega t) \equiv \gamma_0 \sin(\omega t) . \quad (2.9) \]

\[ \dot{\gamma}(t) = \gamma_0 \omega \cos(\omega t) \equiv \dot{\gamma}_0 \cos(\omega t) . \quad (2.10) \]

Strain and frequency are two variables that can be varied in this type of experiment, although, most often strain remains constant while frequency is varied. In typical SAOS measurements of entangled polymers strains are typically between \( \gamma = 1\% -5\% \) and the frequency is swept between \( 10^{-3} \text{s}^{-1} \) and \( 100 \text{s}^{-1} \). Figure 2.5 shows a SAOS curve of SBR at room temperature. These types of rheological measurements are quite useful as will be shown in subsequent sections.

The most common way to demonstrate the existence of chain entanglement is with SAOS and the elastic plateau. Other than the elastic plateau, SAOS is also a good way to find the terminal relaxation time of the material \(^5,7\). Where \( G' \) and \( G'' \) cross is referred to as \( \omega_c \) and its inverse \( \tau \) is the terminal relaxation time. This relaxation time is an important material property that defines if the material is behaving as a solid or liquid. Below \( \omega_c \) or on experimental time scales greater than \( \tau \), the material behaves like a liquid. However, when probed at frequencies above \( \omega_c \) the material behaves like an elastic solid with a plateau modulus \( G_p \). This liquid and solid like behavior can be seen in detail in figure 2.5.
2.1.2.2 ELASTIC RECOVERY

One of the simplest ways to exhibit chain entanglement is to look at how a polymer melt or solution reacts to a sudden step strain. If we have a polymer sandwiched between two plates as shown in figure 2.1 and we apply a fixed velocity $V$ to the upper plate for some time $t$ we produce a deformation $\gamma = Vt/H$. If upon shear
cessation we allow that moveable plate to go free the sample will return towards its initial position as illustrated in figure 2.6.

![Diagram of movement](Image)

Figure 2.6 Illustration of a small step strain followed by the release of the moveable plate and subsequent elastic recoil of the sample.

The materials return towards its initial position after small step deformation implies that the sample is initially incapable of undergoing flow on time scales shorter than $\tau$, as described in section 2.1.3.1. This takes place because such a modest strain is incapable of producing irrecoverable strain in all polymer chains contained in the sample. The connectivity provided by entanglement allows chains that have been displaced little, to have an effect on displaced chains, and return them towards their equilibrium positions. The fact that chains cannot sort themselves out on very short time scales allowing recoverable deformation is a direct effect of chain entanglement.

Other evidence exists that there is chain entanglement, including: a plateau in creep compliance and a plateau in stress after a step shear, but these are beyond the scope of this dissertation. With an idea of entanglement and linear viscoelastic responses we can now look what commonly occurs when entangled polymers are deformed at rates higher than their reciprocal relaxation times for large strains.
2.1.3 WEISSENBERG NUMBER

When making a rheological measurement of a viscoelastic material it is important to know whether the material is responding based on its elastic properties or its viscous properties. This can be done by relating the rate of deformation $\dot{\gamma}$ and the relaxation time of the material $\tau$,

$$\dot{\gamma}\tau \equiv Wi.$$  \hspace{1cm} (2.11)

This product is unitless and is commonly referred to as the Weissenberg number \(^{37}\).

When $Wi << 1$ the material is behaving in a viscous manner with Newton’s Law governing the response of the material. On the other hand, when $Wi >> 1$ the material is behaving as a solid and Hooke’s Law describes the material response. In the Elastic regime deformation is often recoverable and in the viscous regime the material undergoes flow with little or no elastic recovery available. When $Wi \sim 1$ the material is in the viscoelastic regime where both the viscous and elastic properties of the material are important in determining the response of the material. Knowing the regime in which you are examining the materials rheological behavior allows better understanding of the materials response to either a fast deformation or flow.

2.1.4 NONLINEAR RHEOLOGY

Entangled polymers are often deformed in such a way that their stress is not simply proportional to strain or shear rate. This deviation from a simple linear relationship is referred to as nonlinear behavior. Since processing and end use often deform the material in the nonlinear regime, understanding mechanical responses here is very important.
2.1.4.1 SHEAR THINNING

When a well entangled polymer melt or solution is deformed at rates $\dot{\gamma} << 1/\tau$ the material obeys Newton’s Law and $\eta = \frac{\sigma}{\dot{\gamma}}$. On the other hand, when $\dot{\gamma} > 1/\tau$ Newton’s Law breaks down and stress and viscosity are not linearly related. In this regime the stress has a negative deviation from shear rate and so called shear thinning occurs.\(^5\)

2.1.4.2 STRESS OVERSHOOT

Upon application of a sudden startup shear as demonstrated by figure 2.7 and 2.8 the stress initially increases according to the materials Young’s modulus, after some deformation, breakdown of the solid like entanglement structure occurs. When strained further the material begins to undergo irrecoverable flow and the stress no longer simply increases with strain according to its modulus. The stress begins to level off, and in most cases decreases, followed by a stable flow condition where the stress remains constant. This initial increase followed by a drop in stress, as highlighted by figure 2.8, is referred to by us as the stress overshoot and the maximum is called the yield point.\(^{41-42}\)
Figure 2.7 Illustration of shear rate as a function of time for a start up shear.
Recent studies on startup shear and step strain have elucidated the meaning of the stress overshoot in terms of the state of the entanglement network. In the elastic regime $Wi \gg 1$, the chain network remains intact until the yield point. This is the reason for the terminology “yield point”, up to this point the network remains intact as shown by elastic recovery experiments. Beyond this point the sample yields and the material undergoes irrecoverable flow and, hence, the stress maximum is referred to as the yield point. The

Figure 2.8  A typical stress overshoot curve for startup shear of an entangled polymer melt.
strain at which this occurs is called the yield strain and the stress is called the yield stress.\textsuperscript{41-42} The yield stress and yield strain strongly depend on applied rate and are found to obey simple scaling behavior.\textsuperscript{41}

Since we now have an idea of linear and linear rheology of entangled polymers in simple shear we can use this knowledge to help introduce similar concepts in uniaxial extension.

2.2 UNIAXIAL EXTENSION

Beyond shear, uniaxial extension is another convenient method to probe the mechanical properties of entangled polymers. Extension is important in that it closely mimics several common industrial processes including fiber spinning, film blowing, and two roll milling. Extensional rheology is also convenient because it allows experiments to be performed with melts and glasses that would be impossible on a commercial shear device. In this work, we plan to explore physical properties of polymer glasses in extension in two different states. First, we will look at the behavior of the glass in its as received form. Second, we will pre-melt-stretch the polymer glass before examining its mechanical properties, and in this regard a thorough review of melt extensional rheology is needed.

Uniaxial extension deformation occurs as follows: a strip or cylinder of material, with a large aspect ratio in the tensile stretching direction of length $l_0$, is gripped at both ends of the samples, and a constant velocity $V$ is applied to one end of the sample as shown in figure 2.9.
At some time $t$ the sample has been extended a distance $\Delta l = Vt$ and the sample has a new length $l$. We can now define the extension ratio $\lambda$:

$$\lambda = \frac{l}{l_0} = \frac{l_0 + \Delta l}{l_0} = 1 + \frac{\Delta l}{l_0}. \quad (2.12)$$

It is often more convenient to use Cauchy Strain $e$

$$e = \frac{\Delta l}{l_0} = \lambda - 1 \quad (2.13)$$

This allows us to easily define the initial extension rate $\dot{e} = \frac{V}{l_0}$. Stress is defined as the force acting on the cross-sectional area of the sample, although unlike shear, the cross
section of the sample is constantly changing with increased strain. This means there are two different types of stress one can define: the engineering stress and the true stress.

The engineering stress $\sigma_{\text{eng}}$

$$\sigma_{\text{eng}} = \frac{F}{A_0}$$  \hfill (2.14)

relates the tensile force $F$ acting on the initial cross section area $A_0$. Where the true stress $\sigma$:

$$\sigma = \frac{F}{A(t)}$$  \hfill (2.15)

relates the force $F$ acting on the instantaneously changing cross sectional area. The cross sectional area decreases by a factor $\lambda$ when the sample is extended $\lambda$ due to conservation of volume. This gives a simple relationship between the true stress and engineering stress:

$$\sigma = \sigma_{\text{eng}} \lambda.$$  \hfill (2.16)

Often times researchers use engineering stress to define the deformation of solids and true stress is in the study of liquids.$^{2,5}$ However, as will become clear in a later section the use of engineering stress to characterize entangled polymers has its merits.

The major problem with uniaxial extension using an Instron type device is that extension rate continually decreases with increasing strain. For instance look at our sample in figure 2.9, initially

$$\dot{\epsilon}_0 = \frac{V}{l_0}.$$  \hfill (2.17)

However, after time $t$:
\[
\dot{\varepsilon} = \frac{V}{l} = \frac{V}{l_0 + \Delta l} < \frac{V}{l_0}.
\]  

(2.18)

When deforming solids like metals and crosslinked rubbers this change in extension rate is of little consequence. On the other hand, when deforming polymer liquids which have a strong dependence on rate of deformation, this change in rate is important and cannot be ignored.

### 2.2.1 CONSTANT RATE EXTENSION RHEOMETERS

To combat the change in rate with increased strain, different types of extension devices have been explored. Researchers first attempted to simply increase the crosshead velocity exponentially as the sample is extended, keeping the rate constant. Although some success was achieved with this approach, there were sever limitations on the range of applied strain and rate.\(^{43-44}\) To overcome several of these difficulties extension rheometers with fixed sample lengths were developed. The first of these was the Meissner rheometer and the wind-up rheometer.\(^{45-46}\) Even though these rheometers solved some of the problems associated with Instron type setups, they had problems of their own including sample slippage and non uniform deformation near the sample ends.\(^ {47}\)

The Sentmanat Extension Rheometer (SER) was a major step forward in the world of extensional rheometers.\(^ {48-49}\) The rheometer makes use of counter rotating cylinders, as seen in figure 2.10, to produce extension with a fixed sample length.
Figure 2.10 Schematic of the Sentmanat Extension Rheometer SER. As the drums rotate
the sample remains a fixed length.

The double drum can be fixed to commercial rotational rheometers making its use very
convenient and accurate. The centers of drums of diameter $D$ are separated by a distance
$l$, and rotated with an angular velocity $\Omega$. This produces a velocity $V = D\Omega$ and a
constant Hencky Rate $\dot{\varepsilon} = \frac{V}{l}$. Hencky strain or true strain is defined as a constant
incremental strain:
\[ d\varepsilon = \frac{dl}{l} \implies \]
\[ \int_0^\varepsilon d\varepsilon = \int_{l_0}^l \frac{dl}{l} \]
\[ \varepsilon = \ln \left( \frac{l}{l_0} \right) = \ln (\lambda) \implies \]
\[ \lambda = e^{\varepsilon} \]

This gives a simple relationship between the Hencky Strain and Extension Ratio. In this dissertation, all melt extension data will be presented in terms of Hencky Strain and Hencky Rate, and glass extension will be presented in Cauchy Strain and extension rate based on the velocity and initial sample length. With a clear idea of the apparatuses used to create uniaxial extension, we can now look at how the devices are used to probe the physical properties of entangled polymer melts.

2.2.2 LINEAR VISCOELASTIC RESPONSE IN EXTENSION

Analogous to simple shear, one can define both the linear and nonlinear regimes in uniaxial extension of entangled polymer melts. Redefining the Weissenberg number \( Wi = \dot{\varepsilon} \tau \), we now have a simple way to judge the relative speed of extensional deformation related to the terminal relaxation time of the sample. When the sample is extended at a rate \( \dot{\varepsilon} \ll 1/\tau \) the material is able to flow as described by Newton’s Law. Since the Hencky Rate is less than the inverse relaxation time, the chains are able to undergo molecular diffusion faster than the rate of deformation. This causes the sample to rearrange uniformly from its initial entanglement network through molecular diffusion.
On the other hand, a very fast $\dot{\varepsilon} \gg 1/\tau$ deformation of small strain allows the material to behave like a Hookean Solid. In this elastic regime the strain is nearly fully recoverable and the material behaves like a crosslinked rubber. In the past two examples the material behaves as either an elastic solid or a viscous liquid but away from these to regimes nonlinear behavior occurs.

2.3 NONLINEAR RESPONSE IN EXTENSION

In industrial processes such as fiber spinning and film blowing throughput is of high importance, and slow or small deformations are not the primary material responses to these processes. Therefore, it is important to look at the rheological properties in the large strain, high rate regime. Such deformations produce three distinct regimes in uniaxial extension, namely, the viscoelastic regime, elastic regime, and the rupture regime.

2.3.1 VISCOELASTIC REGIME AND THE ENGINEERING STRESS OVERSHOOT

When an entangled polymer melt is extended continuously at a rate $\dot{\varepsilon} \sim 1/\tau$ there is a competition between the thermal diffusion and stretching of the individual chains caused by the externally applied deformation. In this regime there is a distinct shape to the plot of $\sigma_{\text{eng}}$ and $\varepsilon$ in Figure 2.11. Notice the plot of true stress is monotonically increasing with no particular defining features. The true stress constantly increases with increasing strain due to the fact that its cross-section is continuously decreasing. This is the origin of true stress continuously increasing, even when the tensile force applied levels off or decreases (as long as the decrease in force is less than the decrease in cross...
sectional area). Until recently nearly all extensional rheology of entangled polymers was characterized using the true stress, but there are advantages to using engineering stress to analyze this type of mechanical response.32-33

![Diagram of true stress and engineering stress as a function of Hencky Strain](image)

Figure 2.11 Plot of true stress and engineering stress as a function of Hencky Strain for polystyrene at 150°C. $\dot{\varepsilon} = 0.2$ and $\tau = 30$ therefore, $Wi = 6$.

Looking at engineering stress we find that as a function of strain, engineering stress does not increase monotonically. In fact, the engineering stress levels off and goes through a maximum, similar to shear. This maximum also has the same meaning as the
stress overshoot in shear and is referred to as the yield point. Before the yield point the sample is undergoing both flow and elastic deformation. The elastic deformation in this regime is only somewhat recoverable. After the yield point the sample has undergone irreversible plastic flow. In this regard, engineering stress can give us an idea of the state of the entanglement network.

2.3.2 ELASTIC REGIME

When the rate $\dot{\varepsilon} >> 1/\tau$ or the Weissenberg number $Wi >> 1$, molecular diffusion is grossly inadequate in terms of rearranging the chain in order to relax stress. A great deal of stretching ($\lambda >> \varepsilon$) can happen in a time $t < \tau$. In this case, since the network cannot deform indefinitely, yielding must occur. Up to the yield point, the measured tensile force results from the elastic retraction force from each load bearing strand between entanglements. At some point the retraction force is equal the intermolecular gripping force, and if strain is continued, sliding of the chains past each other can occur. This causes tensile force to stop increasing, and sufficient sliding leads to chain disentanglement and a decrease in tensile force.

2.3.2.1 RUPTURE REGIME

Since we are examining the effects of melt stretching on the mechanical properties of glasses, we hoped to perform experiments where the effects of melt stretching where the most severe. In doing this, most of the melt extension in this document takes place in the rupture regime. This regime was first described by Malkin and Petrie where they referred to this as the rubber-to-glass transition. This name is
misleading since this rupture like behavior can be found far from the glassy state.\textsuperscript{32} This regime is characterized by a constant increase in engineering stress $\sigma_{\text{eng}}$ with increased strain as seen in figure 2.12. In the rupture regime the entanglement points are locked in, in such a way that chain sliding does not seem possible. This leads to non-Gaussian stretching where the chains are stretched far from their preferred Gaussian coil. In this regime chain scission could occur before the needed force imbalance to cause chain slippage, leading to a monotonically growing tensile force followed by catastrophic failure. This failure behavior with no engineering stress overshoot and chain scission has been called rupture,\textsuperscript{32-33} hence, the name “rupture regime”.
In the rupture regime a great deal of entanglement network deformation is expected. At Weissenberg Numbers as high as $Wi = 500$ the sample can be strained $\lambda = \exp(Wi) = \exp(500)$ in time $\tau$. This implies that molecular diffusion is negligible compared to the applied strain and nearly all of the strain is transferred to molecular deformation, in turn, leading to non Gaussian stretching of the polymer chains. When stretching in this regime we use only a small fraction of $\tau$, $(t \sim \tau / 100)$ to complete the
deformation, followed by rapid thermal quenching into the glassy state where the deformation is trapped by the vitrification of the glass. We can then examine the effects of this melt stretching on the physical properties of the polymer glass.

2.4 NETWORK APPROACH TO MELT STRETCHING

Recent advancements in the theory of melt stretching\textsuperscript{32-33} allow us to explain the mechanical responses of a melt stretched samples in various regimes. In the flow regime the sample is affected very little by the melt stretching. Let $\psi$ be the number of load bearing strands in the sample cross section. Upon melt stretching in the flow regime $\psi$ remains unchanged since the chains can move around through thermal diffusion at a similar speed to the melt stretching. On the other hand, when melt stretching in the rupture regime, $\psi$ is greatly affected. In the rupture regime, extension is happening much faster than the polymer chains can hope to sort themselves out with thermal diffusion. Due to noncrossability the chains form a network that is deformed with the applied deformation. Figure 2.13 depicts the deformation of the entanglement network when deformed in the affine deformation limit. The crosshatch is a 2-D schematic representation of the entanglement network undergoing an affine deformation of $\lambda$ along the Z-axis. The blue dots represent a monomer of a load bearing chain, where the white dot represent a non load bearing monomer in the direction of concern. The non load bearing monomers can be, for example: chain ends, hairpins, and monomers of chains whose backbone direction is perpendicular to melt stretching.
From the above picture, the effects of melt stretching can be described. In the direction of melt stretching (along Z) in the XY plane the number of load bearing strands $(\psi_{||})$ is increased by a factor of $\lambda$ or $\psi_{||} = \lambda \psi$. However, in the YZ plane the number of load bearing strands is decreased by $\lambda^{-1/2}$ or $\psi_{\perp} = \lambda^{-1/2} \psi$. We suspect this anisotropy in the entanglement network can cause a change in the glassy state physical properties of the polymer. Before we look at how melt stretching effects these properties, an understanding of the past work on the physical properties of glasses is needed.
3.1 POLYMER GLASSES

In this study, the physical properties of amorphous polymer glasses will be explored in detail. Amorphous glasses were chosen because they show more distinct changes in mechanical behavior with temperature than semi-crystalline polymers.\(^2,9-10\) Also, amorphous polymers structure can be thought of as uniform, relative to a semi-crystalline material that has amorphous regions and crystalline regions. Without the complications of crystallinity the effects of melt stretching on the mechanical properties of polymer glasses should be easier to delineate.

3.1.1 EFFECTS OF TEMPERATURE ON THE MECHANICAL PROPERTIES OF ENTANGLED POLYMERS

The effects of temperature on the physical properties of entangled polymers are of utmost importance because rubbers and glasses often display very large changes in mechanical properties with change in temperature.\(^2\) For instance, you wouldn’t want your tire to become hard and brittle at low temperatures, or your beverage cup to become soft and flow with a hot liquid inside it. Therefore, it is very important to know the mechanical properties of these materials across all possible usage temperatures. In order to look at how the mechanical properties of the glass, such as modulus, change with
temperature, it is convenient to apply a SAOS at fixed frequency to the material and shift temperature.\textsuperscript{2} Figure 3.1 shows how the modulus of a typical polymer changes as a function of temperature. When measuring the modulus $G^*$ as a function of changing temperature there is large change in modulus, often around 3 orders of magnitude, in a small temperature window. This transition is referred to as the glass transition\textsuperscript{2, 5, 10-11, 51} and will be discussed in detail in the next section.

Figure 3.1  Modulus as a function of Temperature for a typical polymer.

### 3.1.2 GLASS TRANSITION.

The glass transition or alpha transition occurs at a temperature below which long range segmental motion in the polymer chains are frozen.\textsuperscript{2, 52} The result of this suppression is an increase in the modulus of the material and an increase in the viscosity.
on the order of $10^6$ Pa s. The change in modulus arises due to the fact above $T_g$, a small deformation simply deforms the Gaussian chain a small amount resulting in a loss of entropy. This rubbery material has a modulus $G^* \sim 1$ MPa. On the other hand, when deforming a material below $T_g$, segmental motions, and certainly full molecular motions, are frozen. In the glassy state the stiffness of the material is related to stored elastic energy that comes from perturbing the molecules away from their equilibrium positions. In this state the material is much stiffer than the rubbery state with a modulus $G^* \sim 1$GPa.

The fact that upon changing temperature, polymers can exhibit two distinctly different types of mechanical behavior has long been known. Above the glass transition the material is a soft flexible rubber, and below the glass transition the material is a hard, rigid plastic. Beyond the obvious change in modulus at the glass transition, it is often fitting to look at the dielectric relaxation behavior at the glass transition, as a similar change is often seen. Many things affect a polymers $T_g$ and no theory can accurately predict the $T_g$ of a broad range of polymers. Molecular changes that shift $T_g$ include: main chain structure, side groups, polarity, small molecules, and cross-linking. How $T_g$ is effected by these things is certainly important for engineering applications, although it is beyond the scope of this study.

3.1.2.1 MEASURING $T_g$

When looking at the mechanical properties of polymer glasses or melts it is important to know where $T_g$ is located relative to the experimental temperature. When taking mechanical measurements in the melt state, one wishes to stay away from $T_g$ to avoid any effects of vitrification on the material. The same goes for glassy properties,
around \( T_g \) material properties often change drastically, for instance, the failure behavior of a material can change as \( T_g \) is approached.\(^3\) The importance of the glass transition means that it is equally important to be able to accurately and easily find this temperature experimentally. Common methods include: Differential Scanning Calorimetry (DSC), Specific Volume Measurements, Dynamic Mechanical Analysis (DMA), and Dielectric spectroscopy.\(^{77}\) Although all are important experimental methods, in this dissertation DSC was used to obtain all quoted \( T_g \) values, so it will be discussed in detail.

DSC is perhaps the most commonly used and simplest way to measure the glass transition of a polymer.\(^{51,53}\) In DSC a small sample of polymer and a reference sample are placed on two separate heating blocks and probed with thermocouples. The reference sample is chosen so that it has no transition and a well defined heat capacity in the temperature range of the experiment. The samples are heated at a constant rate through a set temperature range, and the amount of heat required to heat the sample relative to the reference is monitored. Knowing the heat capacity of the reference allows one to determine the heat flow needed to raise the temperature of the polymer as a function of temperature. At \( T_g \) the sample has a change in heat capacity which is captured in a plot of heat flow as a function of temperature. Figure 3.2 has a curve obtained from a DSC measurement of PMMA. When performing DSC measurements it is important to first erase all thermal and mechanical history from the sample.\(^{53}\) This is done by heating the sample well above \( T_g \) followed by a period of equilibration. After the sample has equilibrated the temperature can be lowered at a set rate and the heat capacity as a function of temperature can be obtained. Having knowledge of the location of \( T_g \) allows us to discuss the physical properties of polymer glasses deep in the glassy state.
Figure 3.2  Heat flow as a function of temperature for a PMMA sample. Sample was heated at 10°C per min to 150°C for 20 min, followed by a quench at a rate of 10°C per min where the data was obtained.

3.2 PHYSICAL PROPERTIES OF POLYMER GLASSES

In the glassy state entangled polymers respond to external deformation in one of two ways: brittle failure or ductile failure. Brittle failure happens at low strain ~ 5% while stress is still growing monotonically.² Brittle failure is preceded with microscopic structural changes called crazes.⁴ Ductile failure occurs after the stress strain curve
passes through a maximum. Figure 3.3 illustrates the difference in stress strain behavior for a brittle and ductile polymer.

![Stress vs. Strain Graph]

Figure 3.3 Illustration of stress as function of strain for both a brittle and ductile polymer.

For example, polystyrene (PS) often fails in a brittle manner at room temperature with a strain at failure less than 5%. On the other hand, well entangled polycarbonate (PC) fails in a ductile manner at room temperature. PC exhibits shear yielding which initiates necking. This allows the sample to be stretched to double its original length before failure. It is of great interest how and why polymers fail in a ductile or brittle manner and there are currently many researchers conducting research on the subject.\textsuperscript{54-69}

The past research on the physical properties of polymer glasses can be loosely classified into three research categories: Ludwik\textsuperscript{70}, Davidenoff\textsuperscript{71}, Whitman, and
Orowan\textsuperscript{72} theory and the brittle-ductile transition temperature, crazing and microstructural features\textsuperscript{4}, and strain hardening\textsuperscript{25}. The following sections will focus on each of these past treatments in detail.

3.2.1 LUDWIK, DAVIDENOFF, WHITMAN, AND OROWAN HYPOTHESIS

The Ludwik, Davidenoff, Whittman, and Orowan (LDWO) hypothesis concludes that brittle fracture occurs when the yield stress is greater than a critical value.\textsuperscript{72} This theory was developed mid-century to describe the failure behavior of metals and makes several essential assumptions. LDWO assumes that the brittle failure and plastic flow are two different processes, giving rise to separate curves for brittle failure (fracture stress $\sigma_b$) and plastic flow (yield stress $\sigma_y$). It is then assumed that whichever process occurs at a lower stress is the process chosen by the system.\textsuperscript{2} Figure 3.4 illustrates the transition from brittle failure to ductile failure as described by the LDWO hypothesis.
The temperature where the brittle stress ($\sigma_b$) and the yield stress ($\sigma_y$) cross is defined as the brittle-ductile transition temperature ($T_{bd}$). This point is very important since it represents the temperature above which the brittle material becomes ductile. The stress at this point can also be defined: $\sigma_b(T_{bd}) = \sigma_y(T_{bd}) = \sigma_B$. In the LDWO hypothesis the brittle strength $\sigma_B$ is thought to be given by the areal density of backbone bonds. This strength would have little temperature dependence, since density is not greatly affected by temperature changes below $T_g$, as shown in figure 3.4. The yield strength $\sigma_y$ corresponds to the stress at which the glassy network made up of intermolecular forces can be broken. This network is very weak above $T_g$, at $T_g$ it increases a great deal and with further decrease in temperature this network continues to increase in strength causing it to cross the brittle strength at some point. A consequence of this is that at low enough
temperatures brittle failure always occurs. The brittle ductile transition temperature $T_{bd}$ is a relevant intrinsic material property, and is especially useful in engineering applications. PS has a $T_{bd} \approx 90^\circ C$, so at room temperature PS fails in a brittle manner. On the other end of the spectrum, PC has a $T_{bd} \approx -140^\circ C$, so it is ductile at room temperature, and one must go to liquid nitrogen temperatures to find brittle behavior.\textsuperscript{3}

Vincent performed pioneering work on the brittle-ductile transition in the 1960’s.\textsuperscript{3} Using a diagram similar to figure 3.4 he discussed the relationship between yield strength $\sigma_y$ and brittle strength $\sigma_B$ of a variety of polymers. Vincent examined the effects of rate and a host of material variables including $M_w$, side groups, additives (plasticizers), crystallinity, crosslinking, and molecular orientation on the brittle-ductile transition. Vincent found a correlation between $\sigma_B$ and the areal density of backbone bonds ($\varphi$):

$$\varphi = \frac{\rho l_0}{M_0} \approx 2 \text{ nm}^{-2}$$

(3.1)

where $M_0$ is the molecular weight of a repeat unit, $\rho$ is the polymer density, and $l_0$ is the length of a repeat unit, for a dozen common polymer glasses. Vincent concluded that the brittle failure at $\sigma_B$ was due to chain scission. This reasoning is questionable since the stress to break all chains $\sigma_{\text{break}} = f_b \varphi \approx 10 GPa$ and the $\sigma_B \approx 100 MPa$ (assuming a carbon-carbon bond breaks at $f_b = 5$ nN).\textsuperscript{74} Not all chains across the sample bear load, so Vincent’s use of areal density of molecules is definitely an over estimate of the breaking stress. Vincent was also among the first to explore the failure behavior of bi-axially melt-stretched Poly(methyl methacrylate) PMMA. He found a shift from brittle failure in the non-melt-stretched sample to ductile behavior in the melt-stretched PMMA. The areal density of molecules $\varphi$ cannot be appreciably changed by melt stretching, since melt
stretching conserves volume, so Vincent’s correlation cannot adequately explain how PMMA became ductile upon melt stretching.

Several other researches also used the LDWO hypothesis to understand the mechanical behavior of polymers. Berested\textsuperscript{75} claimed that whether a polymer glass is brittle or ductile “depends chiefly on the intrinsic strength of the material in tension, which is postulated to be dependent on the entanglement network density.” It is also worth noting that Wards classic book on the mechanical properties of solid polymers contains an entire section on the merits of describing the failure behavior of polymer glasses with the LDWO approach.

Also within the LDWO analysis, studies suggested that ductile behavior and yielding of the network made up of van der Waals forces was due to adequate molecular mobility under the given test condition.\textsuperscript{76-78} Implying the segmental relaxation characteristics of the polymer glass are responsible for how the glass failed.\textsuperscript{77} Some researchers have gone so far as to correlate ductile failure behavior with existence of a secondary relaxation (Beta or Gamma) below $T_g$.\textsuperscript{79-83} The idea of secondary relaxations being solely responsible for ductile behavior was long ago discounted by Vincent who cited several examples to the contrary. For example, Polytetreflouroethylene’s (PTFE) last secondary relaxation occurs at 176K yet PTFE is still ductile at 77K. The lowest secondary relaxation in Polyethylene occurs at 140K, however, high molecular weight polyethylene is ductile at 77K. Vincent found that polycarbonate of bisphenyl A was ductile at 77K even though its lowest relaxation occurs at 200K. On the other hand, poly(cyclohexyl methacrylate) is brittle at room temperature and has two secondary
relaxations at -80°C and -20°C. These counter examples show that there is no simple correlation between failure behavior and secondary relaxations.

Others paid more attention to how the entanglement network provided the polymer glass strength. Aharoni was first to explore the relationship between the entanglement volume and the activation volume for the glass transition and its correlation with ductility. He found that when the entanglement volume is less than the activation volume the sample was ductile, and if the opposite was true, the sample was brittle. Aharoni also argued against the ductility being a result of sub-\(T_g\) relaxation phenomena. Despite the ubiquity of the LDWO approach, a sentiment came about that the physical properties of glasses could not be properly understood unless microstructural properties such as: crazing and shear banding, and their effects on crack propagation where elucidated.

3.2.2 CRAZING AND MICROSTRUCTURAL PHENOMENA

Brittleness in polymer glasses under tensile stress can be traced to formation of small crack like defects called crazes. The difference between these crazes and cracks is that crazes have many small fibrils bridging the gap. These fibrils on the size of 5nm - 30nm bear load and allow force transfer across the gap. When crazes breakdown cracks are formed, this process of craze breakdown and crack formation is assisted by the high true stress in the fibril. Since crazing is at the heart of failure behavior in brittle polymer glasses knowledge of the process is exceedingly important.

Craze nucleation is delayed from the initial onset of stress, and often crazes form at defects in the sample. Common defects that induce craze formation include: grooves
in the sample surface, dust in the sample, phase separation, and chain alignment near the sample air interface. Crazes start out as localized plastic strain. If the material is able to, it will shear yield on a macroscopic scale and necking will take place, and the sample will not fail until after a large strain. If shear yielding does not occur the localized plastic strain will induce voids which turn into fibrils and crazing has occurred. These voids are formed by the sample undergoing localized plastic deformation without being able to deform the sample globally. Figure 3.5 illustrates the process of small voids turning into crazes.

![Diagram of crazing process](image)

Figure 3.5 Illustration of voids becoming crazes.

More often than not, the first craze to form does not lead to catastrophic failure. A great deal of energy is consumed creating the craze, and the material strain hardens upon deformation and plastic flow. This strain hardening stabilizes the craze and allows another craze to form, at another defect, and the process repeats itself. Eventually one of the crazes becomes a crack and the sample fails in a catastrophic manner. Interestingly, the formation of voids, crazing, and failure by crack propagation all happen in just a few percent global strain.
Beyond just the process by which crazing occurs, Kramer and co-workers studied how material properties and experimental procedures effect crazing. Their studies found a strong connection between entanglement density and the characteristics of crazes. The number of entanglements per unit volume can be given by:

\[ \nu_e = \frac{\rho N_A}{M_e} \]  

(3.2)

where \( N_A \) is Avogadro’s number and \( M_e \) is the entanglement molecular weight. They observed that polymers with low entanglement density such as PS readily form crazes and fail in brittle manner. Polymers with a high entanglement density are less likely to form crazes, and the crazes that they due form are under lower stress. Highly entangled polymers instead prefer to undergo shear yielding.

Other than entanglement density, Kramer realized that the theoretical maximum chain extension \( \lambda_{\text{max}} \) between entanglements:

\[ \lambda_{\text{max}} = \frac{L_c}{l_{\text{ent}}} \]  

(3.3)

where \( L_c \) is the contour length between entanglements and \( l_{\text{ent}} \) is the distance between entanglements is an important parameter. Figure 3.6 illustrates stretching the polymer chain by \( \lambda_{\text{max}} \). He observed that brittle polymer glasses tend to have a large \( \lambda_{\text{max}} \) and the opposite is true for ductile polymers. Another observation was that polymers with a large \( \lambda_{\text{max}} \) have a larger extension in the craze zone \( \lambda_{\text{craze}} \). They also noted that tensile stress on the fibrils \( \sigma_{\text{fib}} \) is enhanced by a factor of \( \lambda_{\text{craze}} \) relative to the applied tensile stress \( S \):

\[ \sigma_{\text{fib}} = \lambda_{\text{craze}} S . \]  

(3.4)

The enhancement factor \( \lambda_{\text{craze}} \) comes from a change in density in the craze zone caused by the voids between fibrils. It is now clear why larger \( \lambda_{\text{max}} \) polymers tend to fail in
brittle manner. These polymer form crazes with larger $\sigma_{fib}$ which are more likely to turn into cracks and cause catastrophic failure. Kramer et al.\textsuperscript{4} concluded “a useful way to increase the brittle fracture stress and decrease the ductile-to-brittle transition temperature of a glassy polymer is to decrease its entanglement contour length $L_c$.” A notable exception to Kramer’s observation $\lambda_{max} - \lambda_{craze}$ is PMMA.

Figure 3.6  Illustration of stretching a coiled chain to full extension.

3.2.3 STRAIN HARDENING

The most recent approach to explaining failure behavior, that is still be actively pursued by a number of groups, is related to strain hardening.\textsuperscript{54-69} This line of research focuses on the observation that in compression ductile polymers possess a qualitatively different stress-strain curve from brittle polymers. These studies focus on how after yielding strain hardening transpires, i.e., after yielding the stress grows with imposed strain. A great deal of effort was invested in this type of treatment and researchers looked to find the origin of this strain hardening. Kramer reminded the community that the origin of strain hardening is not entropic chain elasticity; the stress level is two orders of magnitude greater and decreases with increasing temperature.\textsuperscript{86} More recent work in the field is prompted by the sentiment that strain hardening is necessary to avoid brittle
failure. van Melick et al.\textsuperscript{25} concluded “stable or unstable neck growth (is) dependent on the ratio between yield stress and hardening modulus.” For example, they found that in compression PS had a high yield stress ~ 100 MPa and a low strain hardening modulus ~ 13 MPa making the ratio of yield stress to hardening modulus around 8, of course PS is known to be a brittle material. For a ductile material, poly(2,6-dimethyl-1,4-phenylene-oxide) (PPO) the yield stress was very similar ~ 100 MPa and the hardening modulus was 75 MPa. This resulted in a ratio of 1.25, in line with their conclusion that the degree of strain localization, which leads to brittle failure, is related to the ratio of yield stress and hardening modulus. One flaw with such experiments is the fact that they do not look at how polymer glasses transition from being ductile to brittle.

3.2.4 INTRIGUING PHENOMENA

In order to look at the merit of each of the aforementioned approaches, it is enlightening to review several interesting phenomena and whether or not they can be explained by past methods. First, (1) it has long been known that ductile polymers including PC can become brittle upon sufficient aging\textsuperscript{87} through adequate annealing near \(T_g\). Second, (2) the application of a adequately large hydrostatic pressure causes brittle polymers, for instance PS, to behave in a ductile fashion.\textsuperscript{85, 88} (3) Lowering the temperature of a polymer glass sufficiently will cause a ductile polymer such as PC to change from ductile behavior to brittle failure.\textsuperscript{3, 73} Lastly, (4) brittle glasses, for example PS and PMMA, can become ductile if they are first subjected to sufficient pre-deformation above \(T_g\).\textsuperscript{3, 21-24, 89-96} That same melt-stretched PS can be stretched nearly 100% in tensile deformation along the direction of melt stretching. Let us look at how
each past approach might encounter some difficulty explaining the phenomena listed above.

Aging or annealing a polymer sample cannot significantly change the entanglement structure, so any ideas based on the observed correlation between ductility and entanglement density cannot explain this aging effect. Aging cannot change the strength of C-C bonds so correlating brittle failure with the areal density also seems to have trouble explaining aging phenomenon.

Increasing the hydrostatic pressure on a sample raises $T_g$ and has been found to increase the yield stress\textsuperscript{85} of the pressurized sample. In order for the LDWO hypothesis to explain the change in failure behavior from brittle to ductile, it would imply that $\sigma_y$ is shifted to lower stresses. Relating entanglement density with ductility fails to capture the effects of pressurization since entanglement density is not appreciably changed.

Temperature changes below $T_g$ have a major effect on the failure behavior of polymer glasses.\textsuperscript{3, 73} Changing the temperature (below $T_g$) cannot significantly alter the entanglement structure. This leaves the correlations between ductility and entanglement density lacking in explanation. Also, raising the temperature lessens strain hardening as defined by van Melick \textit{et al.}\textsuperscript{25} Yet, with increasing temperature, many samples become ductile when their brittle-ductile transition is passed, so it appears strain hardening cannot explain the temperature effect either.

The observed effects of melt stretching on the polymer glass have a variety of explanations from all of the different groups. The strain hardening researchers\textsuperscript{54-59} assert that “the observed ductility of polystyrene originates from the reduction of strain softening and not from the molecular orientation.” Kramer found that pre-deformed
samples of PS had crazes with a smaller $\lambda_{\text{craze}}$, therefore, there was less stress in the fibrils so they were less likely to break. He asserted that the predeformation changed the polymers $\lambda_{\text{max}}$ from equilibrium values to smaller values in the stretched direction and larger values perpendicular to melt stretching. Several studies on pre-deformation of brittle glasses used birefringence to conclude that ductility was related to the orientation of the chains. One group concluded that such a phenomenon occurs in PS because of a change in molecular packing upon pre-deformation. This effect is not unique to PS; in fact, Vincent found that bi-axially oriented PMMA could become ductile.

It is clear that there is no consensus on how melt stretching can change failure behavior. Also clear, is the fact that much of the past work has trouble explaining all or even a fraction of the phenomena mentioned above. It is for this reason we have decided to explore the effects of melt stretching in hope that it will lead us to a better understanding of polymer glasses in general.
CHAPTER IV
MELT STRETCHING

4.1 INTRODUCTION

It has been known since the mid 20th century that some kind of melt stretching can cause brittle polystyrene to become ductile.\textsuperscript{22-23} In the present study we want to systematically explore the effects of melt stretching on the polymer glass. Using the ideas introduced in section 2.2-2.3 we hope to effectively stretch the sample in the flow regime, viscoelastic regime, and the rupture regime. After stretching, we will capture the sample in its deformed state by thermal quenching to below \( T_g \). In order to effectively stretch the samples in each of the flow regimes we must first have knowledge of the linear viscoelastic properties of each material. These properties were obtained through small amplitude oscillatory shear and are discussed in detail in the materials section of this chapter. After finding \( \tau \), one can easily stretch the sample in each of the regimes by using an appropriate Weissenberg number. In this study it was often more convenient to use temperature to effectively change the rate in accord with time temperature superposition. Beyond the effects of rate, we also wanted to explore the result of changing the strain before thermal quenching, in the rupture regime. As we will see in this chapter, each of the above mentioned stretching regimes can easily be achieved by change in temperature. Also, strains from \( \varepsilon = 0.6 \) – rupture can be realized on SER.
4.2 EXPERIMENTAL

This section will describe the materials used in this study, the apparatuses used for stretching, and the experimental methods used to achieve our desired state of melt stretching.

4.2.1 MATERIALS

The materials used in this study were, for the most part, commercial polymer glasses including Polystyrene (PS), Polycarbonate (PC), Poly(methyl methacrylate) (PMMA), poly(styrene acrylonitrile) (SAN). The PS studied is Dow Styron 663. The PC is Lexan TM 141 111 obtained from Sabic (GE Plastic). The PMMA is Plaskolite brand, item number CA-86. The SAN was graciously donated to us by Diamond Polymers is item number SAN 51. The SAN used in this study has a 33% acrylonitrile content. The applicable chemical and mechanical properties are listed in table 4.1.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>M_w (kg/mol)</th>
<th>PDI</th>
<th>τ (s)</th>
<th>Temp (°C)</th>
<th>T_g (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>319</td>
<td>1.44</td>
<td>1000</td>
<td>130</td>
<td>103</td>
</tr>
<tr>
<td>PMMA</td>
<td>125</td>
<td>1.41</td>
<td>2250</td>
<td>135</td>
<td>113</td>
</tr>
<tr>
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<td>1.59</td>
<td>400</td>
<td>130</td>
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</tr>
<tr>
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<td>63</td>
<td>1.58</td>
<td>NA</td>
<td>155</td>
<td>149</td>
</tr>
</tbody>
</table>

The terminal relaxation τ was obtained through small amplitude oscillatory shear measurements (SAOS) measurements of the storage modulus (G’) and the loss modulus (G”) as a function of frequency. The SAOS was carried out with an Anton Paar Physica MCR 301 rheometer using 15mm parallel plates. A SAOS for Polystyrene at 150°C is shown in figure 4.1. Figure 4.2 contains the time temperature superposition sifting factors used to obtain the relaxation time at given temperatures. Temperatures listed in...
the 5th column of table 4.1 are the temperatures at which values of $\tau$ are quoted. These temperatures correspond to the temperatures at which the melt stretching occurred for the strain dependence. Similar SAOS and time temperature superposition experiments were for all the polymers listed in table 4.1 with exception of PC. The temperature at which PC was melt stretched ($155^\circ$C) is only slightly above $T_g$ so the dynamics at this temperature are difficult to obtain.

Figure 4.1 Small amplitude oscillatory shear of polystyrene at 150°C.
Figure 4.2  Time temperature superposition shifting factors for polystyrene using 150°C as a reference. Note that at 130°C the dynamics are 50 times slower than at 150°C.

The molecular weight and polydispersity were found using GPC. The size exclusion chromatography was done using a Wyatt Dawn Eos multi-angle laser light (MALLS) detector in conjunction with a Waters model 2414 differential refractometer concentration detector. This was coupled with Wyatt Astra V 4.73.04 software and 3 waters HR styrogel columns. THF at 35°C flowing at 1ml/min passed through the setup. The glass transition temperatures were found using a TA Instruments Q2000 DSC. A
consistent procedure was used to obtain accurate glass transition temperatures. The sample temperature was ramped from low temperature to well above $T_g$ at 10°C per minute. The sample was allowed to equilibrate for 20 minutes at high temperature, followed by a ramp down in temperature at 10°C per minute. Figure 4.3 shows the DSC curve of PC.

Figure 4.3  Heat Flow as a function of Temperature of PC from 190°C to 50°C.
4.2.2 SAMPLE PREPARATION

Uniform samples were prepared for melt stretching by compression molding. First, a Mylar film was placed on top a thick steel plate. A mold is placed on top of the Mylar film and is filled with sample. Another film of Mylar is placed on top of the filled mold, followed by another thick steel sheet. Figure 4.4 contains a schematic of the compression molding setup. The apparatus is then placed into a Carver Brand Press and heated to well above Tg. Molding temperatures were as follows: PS 160°C, PMMA 170°C, SAN 160°C, and PC 200°C. After allowing the samples to become soft, the samples are then pressed for 1 minute and the stress is let off for one minute. This press and release is repeated 5 times followed by a final compression for 30 minutes during which the sample is allowed to relax. The samples are removed from the press and placed between two room temperature steel plates. These plates gently cool the sample back to room temperature while applying a nominal amount of normal force to the sample. After reaching room temperature, the Mylar sheets can be peeled away and the sample can be removed from the mold. The mold produces sheets of sample with dimensions 120mm x 120mm x 0.5mm. Samples of size 8mm x 25mm x 0.5mm were then cut from the sheets to be used on the SER.
4.2.3 MELT STRETCHING TECHNIQUE AND APARATUS

Melt stretching of PS, SAN, and PMMA (brittle polymers) took place on a first generation Sentmanat Extension Rheometer (SER). The SER was coupled with an ARES MCR 301 rotational rheometer and a Rheometric Scientific Oven accurate to 0.1°C. The above mentioned 8 mm x 25 mm x 0.5 mm sheets were adhered to the drums of the SER using commercially available Krazy Glue (super glue). The glue was allowed to dry for 10 min followed by heating in the oven to the prescribed experimental temperature. After the oven reached its set temperature, the sample was allowed to equilibrate for 5 min, after which extension took place. Following melt stretching; the samples were quickly thermally quenched using a mist of cool water from a common spray bottle. Subsequent to melt stretching, the sample dimensions were approximately 0.2 mm x 3
mm in their cross section, and a length between drums ($L_0$) of 15 mm. The brittle polymer glasses were melt-stretched in the same direction that they will be stretched in the glassy state, so the small sample size is acceptable for the tensile test in the glassy state. However, PC is already ductile, so we wanted to see how melt-stretching PC in the direction perpendicular to the direction of the glassy state tensile test affects its failure behavior. In order to prepare samples in this manner a different technique of melt-stretching is needed.

When preparing a sample where the cutting direction is perpendicular to the melt stretching direction, the sample must have one large cross-sectional dimension. This allows the piece cut from the sample to have appropriate dimensions for tensile testing in the glassy state. The SER is mounted on a commercial rotational rheometer which has a limited maximum torque, so melt stretching a large sample on the SER is out of question. PC sheets with dimensions 120 mm x 60 mm x 0.5 mm were prepared by the aforementioned compression molding technique. Holes were then drilled in the sample using a spade drill bit and specially made clamps where fitted to the sample. After fitting the clamps to the sample, the dimensions of the sample between the clamps were 30 mm x 120 mm x 0.5 mm. This larger sample size is melt-stretched at 155°C using an Instron model 5567 equipped with an Instron oven model 3119-406 accurate to 0.1°C. The model 5567 Instron coupled with Bluehill Software allows stretching at a constant Hencky Rate by increasing the crosshead speed exponentially in accord with the lengthening sample. Dog bone shaped samples were then cut from the melt-stretched sheets perpendicular to the direction of melt-stretching. Figure 4.5 illustrates melt-stretching and how the sample is cut relative to the direction of melt-stretching.
4.3 MELT EXTENSION OF PS, PMMA, SAN, AND PC

This section describes the melt extension of PS, PMMA, SAN, and PC. First, the brittle sample melt stretching on SER at different rates to a fixed Hencky Strain is described, followed by melt stretching to different strains at a fixed Hencky Rate. Finally, the melt stretching data of PC will be presented.

4.3.1 MELT STRETCHING OF POLYSTYRENE IN DIFFERENT FLOW REGIMES

In order to examine the effects of uniaxial melt-stretching across a broad range of stretching conditions PS was melt stretched to a final Hencky Strain $\varepsilon = 2$ ($\lambda = 7.4$) at temperatures ranging from 125°C – 150°C in 5°C increments, and with a Hencky Rate $\dot{\varepsilon} = 0.002$ s$^{-1}$ or 0.2 s$^{-1}$. Figure 4.6 contains stress-strain data for polystyrene stretched under these conditions. Shifting temperature from 125°C to 150°C has a large effect on the dynamics of the sample. The terminal relaxation time $\tau$ changes by factor of 250 from 20 s at 150°C to 5000 s at 125°C. This implies we have effectively changed the rate...
by a factor of 250 by changing temperature and using the same applied rate. At 125°C the Weissenberg Number $Wi = 5000 \, s^{-1} \times 0.2 \, s^{-1} = 1000 >> 1$. This high Weissenberg Number coupled with the large increase in engineering stress $\sigma_{\text{eng}}$ with increasing strain (see figure 4.7) are signs that the stretching is taking place in the rupture regime. In fact, these conditions are known to be in the rupture regime of PS because at the same temperature-rate combination, rupture occurs at strains between $\varepsilon = 2.2 - 2.4$. On the other hand, at 150°C the relaxation time is only 20 s and the lowest rate used was 0.002 s$^{-1}$, so $Wi = 0.04 < 1$. At this low Weissenberg Number the sample is in the flow regime as characterized by the stress overshoot and relatively low stress at the stress maximum as seen in figure 4.6. Between these two extremes there are intermediate effective rates where $Wi \sim 1$, such as 150°C at $\dot{\varepsilon} = 0.2$ and 145°C at $\dot{\varepsilon} = 0.2$. Having melt-stretched across a broad range of effective rates it is possible to see how stretching in each regime effects the physical properties of the polymer glass.
Figure 4.6 Melt stretching of polystyrene at various temperatures and rates to a fixed Hencky Strain $\varepsilon = 2.0$.

4.3.2 MELT STRETCHING TO VARIOUS STRAINS

Beyond melt stretching at different Weissenberg Numbers we want to investigate the results of melt stretching the sample to different strains. The rupture regime, where
\( \sigma_{\text{eng}} \) is monotonically increasing with strain, was chosen to perform the strain dependence study since the entanglement network is more effectively stretched in this regime.

Step Uniaxial extensions at \( \dot{\varepsilon} = 0.2 \, \text{s}^{-1} \) ranging in strain from \( \varepsilon = 0.6 - 2.2 \) were preformed for PS, PMMA, and SAN. Figure 4.7 contains the stress-strain data for PS melt stretched at 130°C and \( \dot{\varepsilon} = 0.2 \, \text{s}^{-1} \) for strains from \( \varepsilon = 0.6 - 2.2 \). At strains higher than 2.2 the PS fails in brittle manner at these testing conditions. Figure 4.8 contains the stress-strain data for PMMA at 135°C and \( \dot{\varepsilon} = 0.2 \, \text{s}^{-1} \) for strains \( \varepsilon = 0.6 - 1.8 \). When PMMA is subjected to a Hencky Strain \( \varepsilon > 1.8 \) rupture occurs under these testing conditions. Figure 4.9 contains the melt stretching data for SAN at 135°C and \( \dot{\varepsilon} = 0.2 \, \text{s}^{-1} \) for strains \( \varepsilon = 0.6 - 2.2 \). SAN fails at strains \( \varepsilon > 2.2 \) under these testing conditions. It is worth noting the strong monotonic increase in \( \sigma_{\text{eng}} \) for all of the strain dependence tests.

Also, the Weissenberg Numbers are 200, 450, and 80, all \( >> 1 \), for PS, PMMA, and SAN respectively. The last data point for each strain in figures 4.7 - 4.9 indicate the point of extension cessation.
Figure 4.7 Uniaxial melt-stretching of polystyrene at 130°C and $\dot{\varepsilon} = 0.2$ s$^{-1}$ for strains $\varepsilon = 0.6 - 2.2$. 
Figure 4.8 Uniaxial melt-stretching of poly(methyl methacrylate) at 135°C and $\varepsilon = 0.2$ s$^{-1}$ for strains $\varepsilon = 0.6 \text{ – } 1.8$. 
Figure 4.9  Uniaxial melt-stretching of poly(styrene acrylonitrile) at 135°C and $\varepsilon = 0.2$ s$^{-1}$

1 for strains $\varepsilon = 0.6 – 2.2$. 
4.3.3 MELT STRETCHING POLYCARBONATE

In order to cut samples in the direction perpendicular to melt stretching, one dimension of the samples cross section must be large enough to accommodate the length of the sample needed for Instron testing. This implies samples need a post stretched cross sectional dimension around 25mm. Given this large size, not to mention torque limitations, the SER cannot melt stretch samples this size. Sheets of PC with dimension 120 mm x 60 mm x 0.5 mm had four holes drilled in each side with a special spade shaped drill bit and were fitted with specially made clamps on each end. These clamps allowed the sample to be fitted to an Instron model 5567 equipped with an oven model 3119-406 accurate to 0.1°C.

After preparation, the polycarbonate samples were loaded onto the Instron and the oven was heated to 155°C. During heating a great deal of care must be taken adjusting the crosshead position to accommodate the thermal expansion of the sample and, more importantly, the crosshead shaft. To eliminate any tensile stress and/or slack in the sample that arises from thermal expansion the cross head must constantly be moved up keeping the tensile force zero until melt stretching begins. After the oven reaches 155°C the sample is allowed to equilibrate for 5 min followed by melt stretching. Constant Hencky Rate can be achieved using the Instron model 5567 and Bluehill software. Using true rate, the software changes the speed of the crosshead exponentially to keep the rate constant with the lengthening sample. The Instron has a maximum crosshead speed of 8.5 mm/s so care must be taken to not exceed this speed when melt stretching. Since our samples are relatively long $L_0 = 30$ mm, at $\lambda = 2.5$ the rate is 2.5 larger than the initial rate. To keep speed low relative to the machines capacity PC was melt-stretched at
155°C and \( \dot{\varepsilon} = 0.05\, \text{s}^{-1} \) to a Henky strain \( \varepsilon = 0.56 \) and \( \varepsilon = 0.91 \). Figure 4.10 contains the stress-strain data obtained from melt stretching on Instron. It should be noted that at strains above \( \varepsilon = 0.91 \) the sample ruptures during melt stretching. Samples were not stretched to the same high strains as the brittle polymers because rupture occurs in PC at \( \varepsilon = 1 \) under these conditions.

![Stress-strain curve](image)

Figure 4.10  Uniaxial melt-stretching of polycarbonate on Instron at 155°C and \( \dot{\varepsilon} = 0.05\, \text{s}^{-1} \) for strains \( \varepsilon = 0.56 \) and 0.91
4.3.4 PREPARING MELT-STRETCHED SAMPLES FOR GLASSY STATE

INSTRON STRETCHING

After melt-stretching PC on Instron, the sample is a large sheet and ASTM “dog bone” samples with dimensions 12.7mm x 3mm x 0.5mm can easily be cut out using a Relco Atom Punch Press. The brittle glasses melt-stretched on SER are not as simple to prepare. When the samples are wrapped onto the drums they form a “dog bone” shape. The ends of the samples wrapped on the drums form a cylindrical shape that must be straitened out before the sample can be loaded onto the Instron. If the ends are left curved the samples will break when the clamps are tightened. The curved ends of the samples are straitened by using pliers heated with a heat gun. Pressing the sample between the hot, flat surfaces of the pliers straightens the sample so it can be loaded onto the Instron. The center 15mm of the sample is never touched with the heated pliers, so effects of melt stretching are not disturbed by the straitening. After the samples are melt-stretched, thermally quenched, and straitened they can be loaded onto Instron so the effects of melt stretching can be explored.
CHAPTER V
GLASSY STATE UNIAXIAL STRETCHING

5.1 INTRODUCTION

This chapter presents the results of Instron style uniaxial extension of both isotropic (non-melt-stretched) and melt stretched polymer glasses. First, the results of the isotropic glasses will be presented. Next, the results of the pre-melt-stretching brittle glasses will be presented, followed by the PC melt-stretched in the direction perpendicular to the glassy state tensile testing.

5.2 UNIAXIAL EXTENSION OF ISOTROPIC GLASSES

To establish how the glasses used in this study behave under uniaxial extension before melt stretching all of them are stretched in the isotropic state. All samples where prepared by the methods mentioned in section 4.2.2, except the samples where cut with a die into a “dog bone" shape. Figure 5.1 contains the stress-strain data for all of the isotropic brittle glasses PS, PMMA, and SAN. In all of these samples failure occurs at a low strain and failure happens before shear yielding or non-uniform deformation occurs with stress increasing monotonically until failure. It is interesting to note that SAN and PS fail at a strains less than 5% where PMMA can be stretched to 9%. Figure 5.2 contains stress-strain data for ductile PC. PC undergoes shear yielding near the yield point (σ₀) followed by cold drawing to a large strain and failure at \( \frac{\Delta L}{L_0} = 1.4 \). Now that
we have elucidated the extension behavior of the isotropic sample we can investigate how melt stretching affects the failure behavior.

Figure 5.1 Stress-strain data for isotropic brittle polymers PS, SAN, and PMMA. The samples were stretched at \( V = 5 \text{ mm/min} \) and had an initial length \( L_0 = 12.7 \text{ mm} \).
5.3 TURNING BRITTLE GLASSES INTO DUCTILE POLYMERS

After each of the polymer glasses were melt-stretched, rapidly quenched, and had their edges straitened, we carried out displacement mode deformation on Instron at room temperature. In examining the effects of melt stretching on the deformation, yielding and failure behavior of PS, PMMA, and SAN we intend to show that melt-stretching has a significant effect on the polymer glass regardless of the polymer microstructure.
5.3.1 GLASSY STATE TESTING OF SAMPLES PRE-MELT-STRETCHED AT DIFFERENT RATES

We first present the Instron room temperature glassy state extension data for PS stretched at different temperatures (effective rates) to a fixed Hencky Strain $\varepsilon = 2.0$ (melt data shown in figure 4.6). The Instron extended the samples at a constant speed $V = 1$ mm/min until failure, represented by the final point on the plot. Velocities around 1mm/min where chosen because they easily allowed video tapping of the sample during extension. Video taping allows us to correlate different features of the stress-strain curves with macroscopic sample deformation. Figure 5.3 shows the effect of melt-stretching at different rates on the mechanical response of the polymer glass. Note that when stretching the sample with $\dot{\varepsilon} = 0.002$ s$^{-1}$ at 150°C the Weissenberg number of the deformation $Wi = 0.04 >> 1$, and this rate is in the flow regime and very little network deformation takes place, so the sample fails in a brittle manner. On the other hand, increasing the rate by factor of 100 at the same temperature 150°C, the sample now fails in a ductile manner. At 150°C and $\dot{\varepsilon} = 0.2$ s$^{-1}$ the Weissenberg Number of the stretching $Wi = 4$, at this rate the network is deformed. Continuing to lower temperatures, or effectively increasing rate, the sample shows increasing stretchability. As the temperature is lowered from 150°C to 125°C the rate is effectively changed by a factor of 250 as shown in chapter 4. The PS that experienced the more effective melt stretching shows higher yield stress and a greater degree of stretchability, increasing from $\frac{\Delta L}{L_0} = 0.4$ when pre-melt-stretched at 150°C to $\frac{\Delta L}{L_0} = 0.8$ when pre-melt-stretched at 125°C. The
yield stress $\sigma^y$ also increases from around 55 MPa when pre-melt-stretched at 150°C to 65 MPa when pre-melt-stretched at 125°C.

Figure 5.3  Engineering stress versus deformation $\frac{\Delta L}{L_0}$ in tensile deformation of the pre-melt-stretched samples shown in figure 4.6. The information in the legend refers to the samples pre-melt-stretching conditions.
This transition in failure behavior from brittle to ductile occurs in the form of shear yielding and necking. Here, necking refers to non-uniform extension. Figure 5.4 contains the same data as figure 5.3 for pre-melt stretching at 140°C, with photos of the sample during various stages of non-uniform deformation. The first photo is of the sample before deformation occurs. The second photo is taken at the point where shear occurs; this is the point where necking is initiated. The third photo is taken at a strain around $\frac{\Delta L}{L_0} = 0.3$ where the sample has drawn a large neck, note the thin center with a transition to a larger width at the top and bottom. The final photo is of the sample after breakdown in fibril-like manner. Our discussion of the details of the failure behavior will be deferred to Chapter 6.
Figure 5.4  Data for PS pre-melt-stretched at 140°C with $\dot{\varepsilon} = 0.2 \text{ s}^{-1}$. Pictures show the sample at various stages during the melt stretching.

5.3.2 PRE-MELT-STRETCHED TO DIFFERENT STRAINS

Beyond melt stretching at different extension rates, samples were melt-stretched to different strains at a constant Hencky Rate in the rupture regime. The stress-strain plots presented below correspond to samples pre-melt-stretched in figures 4.7-4.9. All of the samples melt-stretched to different strains were stretched on an Instron model 5567 at a constant velocity $V = 5\text{mm/min}$. Again, the sample was video taped during stretching so non-uniform extension and sample breakdown could be monitored.

Figure 5.5 contains the extension stress-strain data for glassy state polystyrene stretched at 130°C with $\dot{\varepsilon} = 0.2 \text{ s}^{-1}$. Similar to the melt stretched PS at 130°C in figure 5.3, the sample failure behavior changes from brittle to ductile. Upon increase in melt strain the glassy state stress-strain curve changes drastically. Upon increased melt strain the yield stress increases, although, the yield stays at a similar strain as the brittle failure in the isotropic state. Also, upon increased strain, the glassy stress plateau ($\sigma_{pl}$) increases with increased strain. The stretchability, or strain at break of the sample increases up until $\varepsilon = 1.8$ followed by decrease with further strain. Table 5.1 contains glassy state data for PS.
Figure 5.5 Glassy state stress-strain data for PS which was pre-melt-strained between $\varepsilon = 0.6 – 2.2$. Stretching in the glassy state was performed at $v = 5\text{mm/min}$. This glassy state data corresponds to the melt data in figure 4.7.

Figure 5.6 contains the extension stress-strain data for glassy state PMMA stretched at 135°C with $\dot{\varepsilon} = 0.2 \text{s}^{-1}$ to strains $\varepsilon = 0.6 – 1.8$. With PMMA the yielding is not as pronounced as PS and SAN although similar trends as mentioned above occur with
Table 5.1 Glassy state data for PS melt stretched to different strains

<table>
<thead>
<tr>
<th>Melt Strain</th>
<th>Yield Stress (MPa)</th>
<th>Yield Strain</th>
<th>Yield Stress Error (MPa)</th>
<th>Strain at Break</th>
<th>Initial Slope (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>3.7</td>
<td>0.038</td>
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</tr>
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</tr>
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</tr>
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</tr>
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<td>0.044</td>
<td>6.1</td>
<td>0.38</td>
<td>2580</td>
</tr>
</tbody>
</table>
increased melt strain; increased yield stress, increased plateau, and increased stretchability at strains up to $\varepsilon = 1.4$.

Figure 5.6 Glassy state stress-strain data for PMMA which was pre-melt-strained between $\varepsilon = 0.6 – 1.8$. Stretching in the glassy state was performed at $v = 5\text{mm/min}$.

This glassy state data corresponds to the melt data in figure 4.8.

Figure 5.7 contains the extension stress-strain data for glassy state SAN stretched at $130^\circ\text{C}$ with $\dot{\varepsilon} = 0.2 \text{s}^{-1}$ to strains $\varepsilon = 0.6 – 2.2$. At the lowest strain $\varepsilon = 0.6$ the sample has little stretchability but the stress passes through a yield point and is ductile in this
regard. At larger strains the sample becomes quite stretchable similar to PS. The yield strain of this material is similar to the failure strain in the isotropic state, which is common among all pre-melt-stretched samples. The SAN pre-melt-stretched to $\varepsilon = 1.8$ has an exceptionally jagged stress-strain curve which is caused by multiple necks being drawn at once, when the necks combine or drawing moves to another portion of the sample tensile stress increases or decreases. This behavior is also seen in well stretched polystyrene samples in both figures 5.5 and 5.3.
Figure 5.7  Glassy state stress-strain data for SAN which was pre-melt-strained between $\varepsilon = 0.6 – 2.2$. Stretching in the glassy state was performed at $v = 5\text{mm/min}$. This glassy state data corresponds to the melt data in figure 4.9.
5.3.3 YOUNG’S MODULUS

Upon pre-melt stretching the brittle samples, yield stress $\sigma^y$ increased while the yield strain stayed around the same value. This implies that there was a change in initial Young’s modulus of the material. To highlight this change in Young’s Modulus, several of the above figures are replotted only showing strains up to the yield stress. Figure 5.8 contains stress-strain data for PS corresponding to figure 5.5. The pre-melt-stretched samples show a marked increase in Young’s Modulus compared to the isotropic PS. For instance, the isotropic PS has an initial modulus $E_y = 1.5$ GPa and after being pre-melt-stretched to $\varepsilon = 2.0$ the modulus has approximately doubled to $E_y = 3$ GPa. The increase in modulus come from an increase in the contribution of bonded forces and has been noted in the past.$^3, 24$ Magnifying the initial portion of the plot also allows us to see that yield strain occurs between $\frac{\Delta L}{L_0} = 0.04$-0.05, which is near the breaking strain of the isotropic PS.
Figure 5.8 Glassy state stress-strain data for PS highlighting the initial response of the material to uniaxial extension. Data corresponds to the stretching performed in figure 5.5.

The change in glassy state uniaxial stretching initial response, after pre-melt-stretching, is perhaps most patent in PMMA. Figure 5.9 contains the initial behavior of the PMMA equivalent to figure 5.6. With PMMA, the change in Young’s Modulus is incremental, increasing with greater strain in the melt state and changes by more than a factor of 3 between isotropic and $\varepsilon = 2.0$. These data show that the deformed network plays a large role in the linear elastic properties of the glass.
Figure 5.9  Glassy state stress-strain for PMMA data highlighting the initial response of the material to uniaxial extension. Data corresponds to the stretching performed in figure 5.6.

5.4 GLASSY STATE POLYCARBONATE STRETCHING

Polycarbonate is a known ductile polymer\textsuperscript{3-4}, so we were interested in changing its failure behavior from ductile to brittle. We predicted in section 2.4 that melt stretching would have an adverse effect on the network in directions perpendicular to the direction of melt stretching. To test this idea, we melt stretched PC samples and cut the
specimen, to be tested in the glassy state, orthogonal to the direction of melt stretching. The samples then underwent a uniaxial tensile test on Instron at 5mm/min. Figure 5.10 contains stress-strain data of PC pre-melt-stretched to $\lambda = 1.75$ and $\lambda = 2.5$, corresponding to the pre-melt-stretching data in figure 4.10, with the photos showing how the specimens looked post failure. It is worth noting the drastic difference in failure strain upon pre-melt-stretching. When stretched to $\lambda = 1.75$ the sample is fails at $\frac{\Delta L}{L_0} = 0.32$ compared to failure at $\frac{\Delta L}{L_0} = 1.35$ for isotropic PC. The sample neck was not nearly as large as isotropic PC, which eventually encompasses the entire sample before failure, and the stress plateau value is not as large. Upon further pre-melt-stretching to $\lambda = 2.5$, the sample fails in a brittle manner at $\frac{\Delta L}{L_0} = 0.1$. The stress-strain curve does not pass through a maximum and no neck is drawn as is evident from the photograph of the post failure sample. Also, with increasing melt strain the yield stress continually decreases. The yield behavior and initial Young’s Modulus is best investigated by looking at figure 5.11, which is the same data as figure 5.10 concentrating on the low strain region. Initial slope (Young’s Modulus) is decreasing with increasing strain in the perpendicular direction. This lessening is in sharp contrast to what was seen in section 5.3.3, and, again, displays the deformed networks importance to the Young’s Modulus of the material.
Figure 5.10 Glassy state stress-strain plot for PC pre-melt-stretched in a direction perpendicular to glassy state stretching. Uniaxial extension took place at $v = 5\text{mm/min}$. 
Figure 5.11 Glassy state stress-strain for PC data highlighting the initial response of the material to uniaxial extension. Data corresponds to the stretching performed in figure 5.10.

5.5 CONCLUSIONS

Melt-stretching a polymer glass and quickly quenching it into the glassy state can have a great affect on the physical properties of the polymer glass. Brittle specimens pre-melt-stretched in the direction of glassy state extension can be made ductile upon sufficient melt stretching. Ductile specimens pre-melt-stretched in the direction perpendicular to glassy state extension can be made brittle upon sufficient melt stretching.
The Young’s Modulus of the sample increases with pre-melt-stretching in the direction of glassy state stretching, and decreases when pre-melt-stretched in directions perpendicular. Melt stretching also shifts the yield stress and plateau stress higher in the direction of glassy stretching and decreases them in directions perpendicular. From this data it is clear that the changes in the entanglement network during melt stretching are hugely important in determining the physical properties of the glass. The next chapter will discuss how the double network picture, and melt stretching depiction, along with further experiments, can elucidate the mechanical properties of these glasses.
CHAPTER VI
DOUBLE NETWORK PICTURE

6.1 INTRODUCTION

This chapter presents the foundation of the double network depiction of polymer glasses and shows how it can be used to describe their mechanical behavior. First, the basics of the double network picture are described. Second, the double network picture combined with our picture of melt stretching will be used to describe the various melt stretching phenomena. Next, we explore more cases where polycarbonate becomes brittle, through aging and blending, and how the double network picture can be used to describe these processes. Finally, a summary of results and conclusions are presented.

6.2 INTRODUCTION TO THE DOUBLE NETWORK PICTURE

Our perception of an amorphous polymer glass is a mechanical double network as depicted in figure 6.1, where the blue is the inter-segmental van der Waals interactions and the red represents the covalent bonded entangled chain network. The double network is composed of these two components and arises as follows. In the melt state of well entangled polymers, there is the entanglement network created by chain uncrossability that renews itself through thermal diffusion on the time scale of reptation. Upon cooling the well entangled polymer glass below the glass transition temperature \( T_g \), the chain network freezes and cannot freely move without external deformation. At temperatures
lower than $T_g$, a second network emerges made up entirely of non-bonded intermolecular interactions, i.e., van der Waals forces. We have named this non-bonded network the “primary structure” of the polymer glass. As thermal fluctuations become more suppressed with decreasing temperature the primary structure becomes stronger. During external deformation the primary network breaks down first. The load has to then transfer to the chain network.

Figure 6.1 Illustration of the double network picture for polymer glasses. The blue dashed lines represent the inter-segmental van der Waals interactions and the red represents the covalently bonded chain network.
If the glass is ductile, i.e., at temperatures above the brittle-ductile transition temperature $T_{bd}$, the primary structure readily breaks apart, and the failure behavior is dictated by the chain network. Conversely, the breakdown of the primary structure in the brittle glass leads to crazing and fracture at temperatures below $T_{bd}$. In other words, we find the realistic phase diagram for the depiction of the brittle-ductile transition to be contrary to the one based on the LDWO approach shown in Figure 3.4.

To reiterate, just below $T_g$, the primary structure is weak relative to the chain network, that is, the van der Waals “bonds” can easily be destroyed, allowing movement of the polymer segments. At a few percent tensile strain the primary structure is “fluidized”, and further strain causes deformation of the chain network. Often times in the ductile regime ($T_g > T > T_{bd}$) the polymer glass suffers shear yielding. This occurs when the tensile stress $\sigma$ reaches a level of sufficient shear stress $\sigma_{12}$ to cause shear yielding of the chain network through sub-chain sliding. Figure 6.2 illustrates the force decomposition along a shear plane for an applied tensile force. Shear yielding initiates global necking. In other words, the yielding occurs along a shear plane approximately 45° to the direction of tensile stretching. The necking front quickly becomes perpendicular to the stretching direction as the front begins propagating through the non-yielded region of the specimen. As the necking front expands, the extension in the majority of sample is negligible with the exception of the propagating front where the necked region continues to consume the non-necked sample. On the other hand, decreasing the temperature below $T_{bd}$ leads to a primary network that is so strong the stress required to cause failure is greater than can be born by the chain network. When
this occurs the primary network is the dominant structure in the sense that its collapse initializes global failure of the sample. Upon the failure of the primary structure, the chain network undergoes sever tensile strain localization in the form of crazes. In the craze, the chain network has undergone significant deformation while the rest of the polymer glass has hardly undergone any strain. Brittle fracture quickly follows due to the lack of load bearing ability in the crazed region. To summarize, in the regime near $T_g$ the deformation of the chain network is the dominant feature in tensile deformation, since the inter-segmental forces are relatively weak. On the other hand, at low temperatures below the $T_{bd}$ the primary network is the dominating factor because upon its breakdown the sample suffers crazing and subsequent fracture. Thus, the revised phase diagram should be the opposite of Figure 3.4 as shown in Figure 6.3.
Figure 6.2  Schematic representing tensile force decomposition along a shear plane. The
stress on the plane (σ₁₂) is related to the angle between the plane and the tensile direction
(θ), the area of the plane (A’), and the tensile force (F).

\[ \sigma_{12} = \frac{F \cos \theta}{A'} \]
\[ = (\frac{\sigma}{2}) \sin 2\theta \]

\[ A' / \sin \theta = A' \]

\[ \sigma = \frac{F}{A} \]
Figure 6.3  Generic failure behavior phase diagram constructed using our depiction of a polymer glass as a double network.

The double network picture can go further in explaining brittle failure. As mentioned, upon failure of the primary structure, the load must shift to the entangled polymer chain network. If the Young’s modulus $E$ of the glass (which is associated with the primary network) is much greater than the modulus of the chain network $E_{cn}$, i.e., $E \gg E_{cn}$, then strain localization will occur as follows. Suppose the primary structure breaks down at a stress $\sigma_p = E(\lambda_y - 1) = E\varepsilon_p$, where $\lambda_y$ is the extension ratio at the yield point of the primary structure and $\varepsilon_p$ is the corresponding strain. When the load is transferred to the chain network, the strain of the chain network is: $\varepsilon_{cn} = \sigma_p/E_{cn} = (E/E_{cn})\varepsilon_p$. This strain $\varepsilon_{cn}$ cannot occur globally since the global strain is at the level of $\varepsilon_p$ at the yield point. The only option is for a small portion of the sample to undergo high extension of $\varepsilon_{cn}$ and allow the rest of the sample to continue to deform at the applied rate.
In other words, the breakdown of the primary network can cause severe strain localization i.e., crazes.\textsuperscript{4} Crazes have been well studied\textsuperscript{4,12-20} and there is sufficient evidence that strain localization occurs on the micron scale, as a precursor to brittle failure.

6.3 EFFECTS OF MELT STRETCHING ON THE DOUBLE NETWORK

The brittle glasses (PS, PMMA, and SAN) can become ductile upon sufficient melt stretching as shown in Chapter V. The systematic data indicate that without raising the temperature above the brittle ductile transition temperature these glasses behave in a ductile fashion. This implies that the melt stretching has changed the structure of the chain network in such a way as to allow shear yielding, instead of brittle failure. It is clear that the chain network was strengthening in the melt stretching direction and weakened in the direction perpendicular to melt stretching. When the chain network is strengthened, the primary network no longer appears so strong, in relative terms, and it can fail without causing severe strain localization. We believe these changes in ductility can be explained using our picture on the effects of melt stretching highlighted in Chapter II.

When melt stretched, in the direction of tensile testing, there is condensation of load bearing strands $\psi_\parallel = \lambda \psi$. We presume that upon thermal quenching of the samples below $T_g$, we are able to trap this condensation of the entanglement network in the sample. Assuming the deformation is affine, and that $E_{cn} \sim \psi$, we can use the above analysis to describe the reduction in the propensity for the sample to undergo brittle failure $\varepsilon_{cn\parallel} = (E/\lambda E_{cn}) \varepsilon_p$, which is a factor $1/\lambda$ less than the isotropic state. Also, the yield stress ($\sigma^\gamma$) where the network undergoes shear yielding is enhanced with continued melt stretching.
In other words, the chain network is stronger by a factor $\lambda$, so the tensile strain localization may be reduced. On the other hand, when pre-melt-stretched in the direction perpendicular to glassy state tensile deformation, the number of load bearing strands is reduced $\psi_\perp = \lambda^{-1/2} \psi$. Using the same analysis, $\epsilon_{cn,\perp} = (E \lambda^{1/2} / E_{cn}) \epsilon_p$, which increases by a factor of $\lambda^{1/2}$. In the perpendicular stretching case, the entanglement network is weakened by the melt stretching, enhancing the chances of strain localization. These results bear out Chapter V, where pre-melt-stretched PS, PMMA, and SAN no longer fail in a brittle manner, and PC pre-melt-stretched perpendicular becomes brittle. In terms of the double network picture, the failure behavior phase diagram can describe these melt stretching phenomena well.

Our experimental data show several interesting things happen upon pre-melt-stretching in the direction of glassy stretching. First, the failure behavior of the material is changed from brittle to ductile. In other words, the brittle ductile transition temperature $T_{bd}$ is shifted to a temperature lower than room temperature. Also, there is a modest increase in the Young’s modulus, and a clear enhancement of the entanglement network related to the increase in $\sigma^Y$. Using these two facts, a failure behavior phase diagram for pre-melt-stretched PS will be constructed that bears out a shift in $T_{bd}$. Figure 6.4 contains a phase diagram for melt stretching in the direction of glassy state extension. A shift in the brittle stress, and a large shift in the yield stress, alters the $T_{bd}$ in such a way that it is now below room temperature.
Figure 6.4 Failure behavior phase diagram for pre-melt stretched PS, relative to the behavior of the isotropic PS, of where the material has become ductile at room temperature (RT).

Conversely, when pre-meltstretched in the direction perpendicular to glassy state extension the failure behavior phase diagram shifts the $T_{bd}$ to a higher temperature. This is primarily due to the lowering of the yield stress or weakening of the chain network.

Figure 6.5 contains the phase diagram for melt stretching PC in the direction perpendicular to glassy state deformation. By shifting both the brittle stress and yield stress, the post-melt-stretching brittle ductile transition temperature $T_{bd}'$ is now below room temperature as found experimentally.
Figure 6.5  Failure behavior phase diagram for PC melt stretched in the direction perpendicular to glassy state stretching. Note, $T_{bd}$ is below room temperature for isotropic PC and is shifter to $T_{bd}'$, above RT after melt stretching.

6.4 BLENDING AND AGING OF POLYCARBONATE

With our notion of the double network, long, well entangled polymer chains are needed to support the transfer of load onto the chain network. So, to further test the idea that a dilation of load bearing strands can change the failure behavior of PC, we blended a low molecular weight PC with a high molecular weight PC. We also looked at the effect aging PC just below $T_g$ has on its failure behavior. Finally, we will see how the how the double network picture treats these two phenomena.
6.4.2 BLENDING POLYCARBONATE

High molecular weight PC was prepared by precipitating the as-received commercial PC. A dilute solution of PC ~ 1% was prepared in chloroform, and methanol was stirred in. When the solution turned cloudy methanol addition was ceased. The solution was heated until clear again and allowed to slowly cool, inducing precipitation. We repeated this procedure three times collecting the precipitated PC. The chemical properties of this PC are listed in table 4.1. Low molecular weight PC was received from Fei Lin of Dr. Mathew Becker’s Group at The University of Akron. We ended up with a high molecular weight component with \( M_w = 167 \text{ Kg/mol} \) and a low molecular weight component \( M_w = 6 \text{ Kg/mol} \). The two PC then blended in 4 different weight fractions of the high molecular weight \( \phi, \phi:(1-\phi) \). These include: 100:0, 80:20, 60:40, 40:60.

Beyond blending, sample preparation for glassy state tensile stretching was the same as in section 4.2.2. Figure 6.6 contains the engineering stress as a function of strain data for the samples blended to different ratios. Drastic changes occur in the stress-strain behavior of blended polycarbonates. Looking at 80:20, the sample is no longer as stretchable and the strain at failure is reduced from \( \frac{\Delta L}{L_0} = 0.9 \) to \( \frac{\Delta L}{L_0} = 0.2 \). The yield stress \( \sigma^y \) is also decreased by adding just 20% short chains. With the next blend, 60:40, there was a complete change in failure behavior from ductile to brittle and low strain at failure \( \frac{\Delta L}{L_0} = 0.8 \). The final blend, 40:60, is again brittle and fails at a strain \( \frac{\Delta L}{L_0} = 0.05 \). Interestingly, the Young’s Modulus of the sample is not noticeably changed by blending. This implies
that the primary network is unaffected by the blending, while the chain networking is severely weakened, as can be seen by the change in failure behavior.

Figure 6.6 Engineering stress as a function of strain for blended PC. The sample becomes more brittle as the amount of short chains is increased.
6.4.3 AGED POLYCARBONATE

In order to examine the effects of aging on the failure behavior of polycarbonate, a sheet of polycarbonate was aged at 145°C for 10 days. After 10 days, the oven was slowly cooled back to room temperature over a 24 hour period. Dog bone shaped samples with dimension 12.7mm x 3mm x 0.5mm were cut from the sheet. The specimen was then tested in tensile deformation on the Instron with \( v = 5\text{mm/min} \) at RT. Figure 6.7 contains the engineering stress as a function of strain for the aged PC plotted along with non-aged PC. The inset pictures are of a large neck drawn in non-aged PC and negligible necking in aged PC. The yield stress \( \sigma^y \) of the aged samples is increased significantly over the non-aged sample. Aging pushes the sample further towards an equilibrium glass and increases the energy barrier to remove segments from their equilibrium potential. This increases the yield stress, since the plastic deformation of the chains is more difficult. In a way, aging the glass is equivalent to lowering the temperature of the tensile test towards the brittle ductile transition. The sample fails shortly after yielding; this is due to an increase in the vitrification of the glass without any enhancement of the chain network. When the load is transferred from the primary structure to the chain network the stress is too large, and the chain network quickly breaks down causing specimen failure.
Figure 6.7  Engineering stress as a function of strain for aged (blue) and non-aged (red) polycarbonate. The pictures are of a large neck drawn in the non-aged PC and the negligible necking in the aged PC.

6.4.4 DOUBLE NETWORK TREATMENT OF BLENDING AND AGING

Changes in the double network can account for both the blending and aging phenomena. To begin, blending lowers the breaking stress $\sigma^*$ and significantly weakens the chain network. Figure 6.8 contains a failure behavior phase diagram for blended PC.
The tensile tests illustrate with increased blending; both the yield stress $\sigma^y$ (80:20) and the breaking stress $\sigma^*$ (60:40 and 40:60) is lowered. In other words, when blended to 40% and 60% short chains, the brittle-ductile-transition temperature $T_{bd}$ is shifted to above room temperature RT.

![Figure 6.8 Schematic failure behavior phase diagram for blended PC. The solid lines represent long chain PC, where the $T_{bd}$ is below RT. The dashed lines represent blended PC, where the $T_{bd}$ is above RT.](image)

The aging phenomenon can also be expressed by the double network picture. To review, the aging increased the strength of the primary network through annealing. This annealing has little effect on the chain network, and when the primary network fails the chain network cannot sustain the force and breaks down shortly after the yield point. Figure 6.9 contains a schematic of the failure behavior phase diagram for aged PC. The aged sample is represented by the dashed lines, and the non-aged PC is represented by the
solid lines. From the experimental evidence it is clear the aging shifted the $T_{bd}$ near RT since the sample fails around the yield point.

Figure 6.9 Schematic failure behavior phase diagram for aged PC. The solid lines represent non-aged PC, where the $T_{bd}$ is below RT. The dashed lines represent blended PC, where the $T_{bd}$ is around RT.

6.5 CONCLUSIONS

We have studied the effect of melt stretching on the tensile extension of several polymer glasses including: polystyrene, poly(methyl-methacrylate), poly(styrene-acrylanitrile), and polycarbonate. Many key phenomena were noted. According to figure 5.3, upon melt stretching brittle PS to a large strain at a sufficient rate, the glassy state failure behavior of the material changed drastically; from brittle failure to ductile yielding. However, when the rate was in the terminal regime $Wi << 1$, no change in failure behavior was noticed. Second, upon deformation at high rates $Wi >> 1$ (section 5.3.2),
brittle glasses underwent ductile yielding in glassy state testing for melt strains as low as \( \varepsilon = 0.6 \). In the same melt stretching regime, with increasing strain, the yield stress \( \sigma^y \) of the material increased. Our melt stretching picture explains that the melt stretching effects are caused by a condensation of load bearing strands in the stretching direction. This change in failure behavior is equivalent to shifting the brittle ductile transition temperature \( T_{bd} \) below room temperature. The double network picture of polymer glasses shows, qualitatively, how this shift in \( T_{bd} \) is possible based on changes to the primary structure and chain network.

Upon melt stretching polycarbonate perpendicular to the direction of glassy state tensile testing, a different phenomenon is seen: the ductile polycarbonate is made brittle when pre-melt-stretched to \( \varepsilon = 0.91 \). Also, the yield stress \( \sigma^y \) of the material is continually decreased, with increasing strain. Our melt stretching picture explains this as being caused by a dilation of load bearing strands in the tensile direction. This change from ductile behavior to brittle failure is equivalent to shifting the \( T_{bd} \) to above room temperature. The double network picture demonstrates how this is possible by lessening the strength of the chain network, relative to the primary network.

To further test the idea of our melt stretching picture, i.e. that a dilation of load bearing strands can cause brittle failure, polycarbonate blends were prepared with long and short chains. With sufficient dilation of the long chains (60:40 and 40:60), the sample becomes brittle, just as with melt stretching. This further solidifies our position on the mechanism of melt stretching changing the structure of the entanglement network. Again, the double network picture of polymer glasses can be used, in a similar way to
perpendicular melt stretching, to explain the shift of the $T_{bd}$ to temperatures less than room temperature upon blending.

Aging polycarbonate has long been known to affect its failure behavior. After aging, we found polycarbonate to be nearly brittle, failing at small strains $\frac{\Delta L}{L_0} = 0.12$. In our double network picture, this is caused by an increase in the strength of the primary network with negligible increase in the strength of the chain network.
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DSC ramp at 10 °C per min for PS pre-melt stretched at 130 °C to $\varepsilon = 2.0$, followed by a ramp of the same sample to highlight the effects of melt stretching on the glass transition.