UNDERSTANDING MELT-DEFORMATION EFFECT ON MECHANICAL BEHAVIOR OF POLYMER GLASSES

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UNDERSTANDING MELT-DEFORMATION EFFECT ON MECHANICAL BEHAVIOR OF POLYMER GLASSES

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ABSTRACT

Polymer glasses play a key role in manufacture and industrial field in terms of their mechanical properties. Despite tremendous efforts in the past on exploring the mechanical instabilities of polymer glasses, it remains vague and under debate regarding the approach to improve mechanical properties of polymeric glass, the molecular origin of stress and the nature of the brittle-ductile transition.

In this dissertation, we investigate the effects of melt deformation on mechanical behavior of polymer glasses in two separate ways. In first project, we apply planar extension in melt state to induce anisotropic network structure. Such a pre-deformed sample is predicted to show anisotropic deformation or fracture depending the direction of compression. The observed mechanical responses extends our theoretical understanding of glassy polymer under large deformation. Specifically, these experimental findings illustrate the explicit role of chain networking in compression and support the idea that the lateral chain networking resists the transverse expansion. In second project, in terms of tensile responses, we examine how and why retractive stress could show up during annealing of melt-deformed sample in its glassy state. Melt stretching may have produced non-negligible distortions at the bond level as well as a reduction of energy barrier, resulting in a rejuvenated glassy state.
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4.28 Stretching of internal structure, in terms of the average end-to-end distance during melt extension at two Hencky rates corresponding to the product of Rouse time and rate, $W_{IR}$, equal to 1 and 30 respectively. The top curve represents the affine extension limit, given by $(\lambda^2/3+2/\lambda) <(r/r_0)^2−1$ for $|i−j| = 4$ or 36 represents the averaged end-to-end distance for all segments comprised of 4 or 36 beads.

4.29 Orientation function (P2) and average bond length of the backbone bond against time during deformation at 300 K (regime (1)), upon releasing at 300 K (regime (2)) and during elastic yielding upon annealing at 360 K (regime (3)).

4.30 Orientational correlation function against time in the pre-deformed and non-deformed systems at 360 K.

4.31 Stress relaxation from pre-yield extension as a function of time at four different temperatures from 60 °C to 90 °C for (a) PS319K and (b) PMMA125K.

4.32 Storage and loss moduli $G'$ and $G''$ as a function of frequency for (a) PS319K, (b) PMMA125K and (c) PS650K.
CHAPTER I

INTRODUCTION

Polymeric materials exist in one of the three states, the disordered liquid state, crystalline state and glassy state. Most molecular-level studies in the past four decades concentrate on the first liquid state, following the tradition pioneered by de Gennes\textsuperscript{1-4}, Doi and Edward\textsuperscript{5,6}. De Gennes firstly proposed a reptation model on the relationship between relaxation time, viscosity and molecular weight. Following by the reptation model, a very well-known tube model was developed by Doi and Edward and has been undergoing constant revision and improvement. Although well-established tube model was applied to describe nonlinear rheological behaviors, recent new phenomena such as shear banding in startup shear\textsuperscript{7-13} and non-quiescent relaxation under step strain\textsuperscript{14-16} have called for a fundamental revision of the current theoretical picture for nonlinear rheological behavior of entangled polymeric liquids. Although first principle theory for chain uncrossability of entangled polymer system is still under developing, new experimental result as well as latest understanding on polymer rheology were summarized in a recent published book\textsuperscript{17}. 
Contrary to large amount of effort and work on polymer liquid state, today’s textbooks hardly have any in-depth molecular-level discussion of mechanics of polymers in the glassy state. To make coherent understanding between macroscopic phenomenon and microscopic theory, Eyring purposed the idea that stress-induced lowering of the activation barrier for plastic deformation\textsuperscript{18-20}. Later, Haward and Thackray\textsuperscript{21} developed H-T model to illustrate yielding and strain hardening behavior in polymer glass based on Eyring’s activation theory\textsuperscript{18} and James and Guth’s rubber elasticity theory\textsuperscript{22}. Several other groups including Boyce and Buckley\textsuperscript{23-36} extended the H-T model to establish 3D constitutive equation to account for glassy polymer mechanical behavior.

Despite these pioneering work and study, a lot of fundamental questions are still unclear and unsolved. For example, given many polymer glasses with T\textsubscript{g} well above room temperature, why are some brittle and others ductile? For those ductile polymers, how and why could yielding take place to ensure a plastic deformation? On the other hand, why do these polymers turn from ductile to brittle upon cooling to a lower temperature, and vice versa? Although yielding and brittle-ductile transition phenomena are known for decades, what are the molecular-level physics behind them? In recent years, plastic flow in polymer glasses is generally understood as an activated process. Many studies in recent years including pioneering optical photobleaching experiments from Ediger’s lab\textsuperscript{37-43} and molecular dynamics simulation by Riggleman and coworkers\textsuperscript{44, 45} show that segmental dynamics are greatly accelerated upon yielding. As indicated by the theory of Chen and Schweizer\textsuperscript{46}, the applied stress lowers the confining potential barrier F\textsubscript{B} and thus speeds up the alpha relaxation, as shown by this expression for the alpha time. Since these studies
does not involve temperature into discussion. It’s still challenging to apply those activation ideas to understand brittle-ductile transition in polymer glasses.

The brittle-ductile transition (BDT) is an intriguing phenomenon that have yet received a satisfactory theoretical explanation. It is a textbook’s practice to describe the BDT in terms of the Ludwik-Davidenov-Wittman-Orowan (LDWO) hypothesis. This standard explanation regards plastic yielding and brittle fracture as independent and competing processes during tensile extension. According to the hypothesis, at a high temperature above the BDT temperature, yielding and plastic flow involve a tensile stress $\sigma_y$ lower than the brittle fracture stress $\sigma_b$ required to produce chain scission. The brittle stress $\sigma_b$ has much weaker temperature dependence than $\sigma_y$. Thus, $\sigma_y$ can eventually grow to reach $\sigma_b$ at the BDT. The LDWO hypothesis does not encompass any specific molecular picture and does not answer the basic question of why a polymer glass can yield and undergo plastic deformation. Moreover, because the strength of covalent bonds cannot multiply in presence of pressure it cannot explain the fact that pressurization causes $\sigma_b$ to increase multiple times. Thus, the LDWO hypothesis is rather powerless to describe the origin of the BDT.

Recently, a molecular model is proposed, trying to address the questions about yielding and brittle-ductile transition of polymer glasses. Inherited from the entanglement network in polymer melt state, this model claims the crucial role of chain network in polymer glass to ensure yielding and following ductile deformation. Moreover, large deformation must involve considerable intra-segmental interaction contribution. In this dissertation, we examine melt-deformation effects on mechanical behaviors of polymer
glass under both tensile and compression modes to unveil how chain network could control brittle-ductile transition under compression test and what is the nature of retractive stress displayed in melt-deformed polymer glass.

In Chapter II, we will introduce some basic features and different deformation modes on polymer glass. A series of literature works regarding nonlinear behavior of polymer glasses on experiment, theory and modeling will be went through, followed by a recent phenomenological molecular model for yielding and brittle-ductile transition of polymer glasses.

In Chapter III, we apply planar extension in melt state to affect the chain network structure in polymer glasses. Such pre-deformed sample shows expected anisotropic deformation and predictable crack formation under compression test. For example, by dilating the chain network areal density in the lateral dimensions, polymer glasses such as PS and PMMA can switch from ductile to brittle response. Conversely, by increasing the lateral network density, a brittle polystyrene can turn ductile. This work combines theoretical insights with new experimental design (melt squeezing to produce an anisotropic entanglement network) and quantitative characterization by molecular dynamics simulations. It builds on a recent molecular picture that offered a zeroth-order description for the subject of brittle vs. ductile behavior and shows that the mechanical responses can be accounted for in terms of the structure of the chain network. These experimental findings illustrate the explicit role of chain networking in compression and support the idea that the lateral chain networking resists the transverse expansion. Thus,
these compression experiments extend the previous understanding concerning extension of polymer glasses\textsuperscript{49}.

In Chapter IV, by characterizing the mechanical behavior we elucidate how melt extension of well-entangled polymers could result in a rejuvenated glassy state. Specifically, quenching of melt-stretched polystyrene and poly(methyl methacrylate) preserves the effect of pre-deformation in an apparent stress-free state; upon annealing the quenched polymer glasses display considerable retractive stress. Molecular dynamic simulation confirms that melt-stretching could produce non-negligible distortions at the bond level, the emergent retractive stress is due to molecular force imbalance at the elevated temperature where interchain repacking occurs because of the reduced energy barrier in the pre-deformed polymer glass.

In Chapter V, an overall summary of this work is presented.
CHAPTER II
CHARACTERISTICS OF POLYMER GLASSES

2.1 Glass Transition and Polymer Glasses

Polymer is large molecule composed of many repeat units and its physical properties are strongly temperature dependent. Polymer dynamic can so fast in the format of liquid state upon heating to the temperature well above melting temperature $T_m$ that longest length and time scales can be probed. Given a thermal quenching rate comparable to crystallization rate, polymeric liquid will have a high tendency to get chain folding and undergo first-order transition process to form crystal. However, if the cooling rate is much faster than crystallization rate, then the thermal motion will be insufficient for developing lamellae structure and crystallization process is largely suppressed. As a consequence, polymeric system becomes a supercooled liquid without reaching equilibrium state. Further quenching to lower temperature within experimental time scale results in a low dynamic non-equilibrium state in polymer system, where the specific volume and enthalpy will show different temperature dependences. The overall process is shown in Figure 2.1.
Because of the freeze of segmental motion in polymer chain due to thermal quenching, the mechanical behavior of entangle polymers significantly increases. In term of modulus, sitting at temperature well above $T_g$, there is a rubbery plateau corresponding to a modulus at around 1 MPa. Further decreasing the temperature below $T_g$ results in Young’s modulus which is 1 GPa level. There is 3 orders difference in modulus upon passing glass transition temperature, apparently, mechanical properties are strongly temperature dependent near glass transition regime. Figure 2.2 shows temperature dependence of modulus given different kinds of polymer systems. Low molecular weight unentangled chains display similar behavior like small molecules that without plateau modulus. By increasing molecular weight, rubbery plateau starts to show up and could last for different lengths of period.
Figure 2.2 Modulus as a function of temperature or time for polymers with different molecular weights. The starting point for rubbery plateau to drop down varies among polymer with different molecular weight.
2.2 Basic deformation modes for polymer melt and glasses

2.2.1 Mechanical deformation for polymer melt

Although there may be various kinds of deformation modes in industrial polymer melt processing, two most common modes are simple shear and uniaxial extension in research lab. Figure 2.3 depicts these two modes. In shear deformation, material is sandwiched and sheared between two parallel plates, shear stress is defined as

\[ \sigma = \frac{F}{A} \] (2.1)

where \( F \) is the measured force and \( A \) is material cross section area. Elemental shear strain is defined as

\[ \gamma = \frac{\Delta x}{H} \] (2.2)

where \( \Delta x \) is material travel distance, \( H \) is the gap between two plates. Then shear rate is defined as

\[ \dot{\gamma} = \frac{d\gamma}{dt} = \frac{v}{H} \] (2.3)

where \( v \) is the speed of moving plate.

In uniaxial extension, material is stretched along one direction, stretching ratio is defined as
\[ \lambda = \frac{L}{L_0} \quad (2.4) \]

where \( L_0 \) is sample initial length and \( L \) is instant length upon extension. Extension rate is called Hencky rate, and is defined as

\[ \dot{\varepsilon} = \frac{v}{L} = \frac{v}{vt + L_0} \quad (2.5) \]

where \( v \) is relative moving speed between sample two ends. Further derivative yields

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

integrating (2.6) yields

\[ \lambda = \exp(\dot{\varepsilon}t) = \exp \varepsilon \quad (2.7) \]

where \( \varepsilon \) is Hencky strain.

Engineering stress is used to measure mechanical response and is defined as

\[ \sigma_{engr} = \frac{F}{A_0} \quad (2.8) \]

where \( F \) is the force we applied and \( A_0 \) is the initial cross-sectional area of the sample.
2.2.2 Mechanical deformation for polymer glass

Mechanical properties of polymer glass can be evaluated through either uniaxial extension or compression test, as shown in the Figure 2.4. In extension test, a dogbone shape specimen is fixed between two clamps and is stretched at a constant crosshead speed along one axis. Similar as polymer melt uniaxial extension, we have

$$\lambda = \frac{L}{L_0} \quad (2.9)$$

and

$$\sigma_{en,gr} = \frac{F}{A_0} \quad (2.10)$$

In compression test, cylinder specimen is sandwiched between two metal plates where the external force is applied. Compression is going along one axis at a constant crosshead speed. In this case, compression ratio $\lambda$ is defined as the initial height divided by the realtime height during deformation, that is
\[ \lambda = \frac{H_0}{H} \quad (2.11) \]

Also, different from engineering stress that we usually use in extension test, true stress is a more preferred variable in compression test, defined as

\[ \sigma_{\text{true}} = \frac{F}{A} \quad (2.12) \]

where \( F \) is applied force and \( A \) is real-time cross-section area during deformation.

If we assume density and volume is constant during deformation, we could derivative the relationship between engineering stress and true stress as the following

\[ \sigma_{\text{true}} = \frac{F}{A_0} \cdot \frac{A_0}{A} = \frac{F}{A_0} \cdot \frac{H}{H_0} = \frac{\sigma_{\text{engr}}}{\lambda} \quad (2.13) \]
Figure 2.4 Polymer glass under deformation on (a) uniaxial extension and (b) uniaxial compression.
2.3 Nonlinear behavior of polymer glasses under deformation

In this part, we will discuss two major nonlinear mechanical behaviors in polymer glass: (a) yielding and plastic deformation and (b) brittle-ductile transition. Literature study regarding theory and explanation on these nonlinear mechanical behaviors will be reviewed.

2.3.1 Yielding and plastic deformation: an activation process

![Stress-strain curve of polymer glasses](image)

Figure 2.5 Stress-strain curve of polymer glasses undergoing uniaxial tensile (red curve) and compression (blue curve).

At room temperature, some polymer glasses exhibit ductile response and could undergo large deformation. For example, Figure 2.5 is a typical stress-strain curve for Polycarbonate...
(PC) under both uniaxial extension (red curve) and compression (blue curve). In both cases, at the beginning of deformation, stress grows linearly with strain, which is defined as elastic regime. After that, sample will undergo shear yielding where stress shows an overshoot called yield point and then followed by strain softening initialed by 45° shear plane. Different from compression test, necking could take place in extension test from a certain shear plane starting from where engineering stress is keeping constant along with necking propagation until reaches to the very end where necking completing. After that, stress could grow monotonically with strain which is called strain hardening regime. In terms of the overall mechanical behavior, uniaxial compression exhibits a higher yielding stress as well as a stronger strain hardening response. As a result, compression test is an ideal candidate to study strain hardening behavior thanks to the homogeneity deformation in absence of necking under uniaxial compression.

In recent years, yielding is generally understood as an activated process based on both experiment and computer simulation group. For example, Schweizer and coworkers have developed a nonlinear Langevin equation (NLE)- based microscopic theory for polymer glass under deformation\textsuperscript{46, 51, 52} and pointed out thermal density fluctuation $S_0$ is the key factor that control segmental dynamics upon deformation and explain how intersegmental interactions could cause segmental caging by erecting certain potential barrier $F_B$. In this language, applied stress upon external deformation could lower the $F_B$, lead $S_0$ to increase and speed up the alpha relaxation. For example, Figure 2.6 showed rate effect on thermal density fluctuation $S_0$ as well as the corresponding alpha relaxation time.
Figure 2.6 (a) Constant strain rate stress-strain curves for fixed $T = T_g - 30$ K and preaging time $t_{age} = 10^5$ s at strain rates $\dot{\gamma} = 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}$ and $10^{-1}$ s$^{-1}$. The corresponding strain dependence of the dimensionless density fluctuation amplitude, $S_0$, and logarithmic mean relaxation time (in seconds), $\log(\tau_\alpha)$, are shown in (b) and (c), respectively. (Reprinted of Figure 3 from Chen, K.; Schweizer, K. S. Macromolecules 2011, 44, (10), 3988-4000.)
Dr. Ediger carried out a series of work on optical photobleaching experiments\textsuperscript{37, 39, 42, 43}. By tracking the evolution of average segmental relaxation time during extension using optical probe reorientation measurements, result showed segmental mobility greatly speeded up after yielding. Such mobility increase is both temperature and external rate dependent. For example, Figure 2.7 and Figure 2.8 showed how temperature and rate affects the segmental dynamics of polymer glass under deformation. The value of $\tau_{1/e}$ in the post-yield regime depends upon temperature, with faster dynamics observed at higher temperature. Besides, the effect of temperature on segmental dynamics during deformation at a particular strain rate is significantly smaller than the effect of temperature in the PMMA glass in the absence of deformation. In the absence of deformation, $\tau_{1/e}$ differs between the lowest and highest temperature by a factor of 25; after yield, this decreases to a factor of 4.
Figure 2.7 Engineering stress plotted against global strain for cross-linked PMMA glasses deformed at a constant global strain rate of $3.1 \times 10^{-5}$ s$^{-1}$. Data are presented for experiments at four temperatures. *In-situ* experiment was carried out based on optical probe reorientation measurements. (Reprinted of Figure 1 from Hebert, K.; Bending, B.; Ricci, J.; Ediger, M. D *Macromolecules* 2015, 48, (18), 6736-6744.)
Figure 2.8 Evolution of segmental dynamics as a function of local strain for a PMMA glass during constant strain rate deformations. Average segmental relaxation time $\tau_{1/e}$ was measured using the probe mobility technique. (a) showed deformation at $T_g - 22$ K at four strain rates. (b) showed $\tau_{1/e}$ for tests with a local strain rate of $(1.3 \pm 0.2) \times 10^{-4}$ s$^{-1}$ at the four different temperatures. The arrows in (a) and (b) indicated the value of $\tau_{1/e}$ in the absence of deformation.

Many other experimental techniques such as NMR$^{54}$, dielectric spectroscopy$^{55, 56}$, positron annihilation lifetime spectroscopy$^{57}$ as well as mechanical testing$^{58-61}$ all had similar conclusion that segmental mobility can be greatly accelerated upon large deformation. Besides, distribution of the relaxation time got narrowed, indicating a
decrease of system dynamic heterogeneity during plastic flow. Molecular simulation works also reported higher segmental motion and elevated potential energy landscape emerged during mechanical deformation.
2.3.2 Brittle-ductile transition (BDT)

2.3.2.1 Basic phenomenon and LDWO hypothesis

Another well-known nonlinear phenomenon in polymer glass is brittle-ductile transition (BDT), the pressure and temperature effect on BDT was reported by Dr. Baer\(^62\). For example, Figure 2.9 showed temperature effect on BDT for glassy polymer PMMA. Although it is completely brittle at room temperature and below, it could turn into ductile and undergo plastic deformation by increasing temperature.

![Diagram of stress-strain relationship for PMMA under extension showing brittle and ductile responses at different temperatures.]

Figure 2.9 Temperature effect on brittle-ductile transition for PMMA under extension. PMMA showed brittle response under room temperature and below, while it exhibited ductile response at 40 °C and above.
However, over decades the physics behind BDT phenomenon is barely clear. It is a
textbook practice to explain BDT based on Ludwik-Davidenov-Wittman-Orowan (LDWO)
hypothesis. This hypothesis demonstrated the BDT phenomenon as shown in Figure 2.10
Breaking stress and yield stress as a function of temperature in the LDWO hypothesis.
This hypothesis regarded plastic flow and brittle fracture as two independent and
competing processes, either brittle failure or ductile yielding would take place when the
corresponding yielding stress ($\sigma_y$) or yielding stress ($\sigma_y$) was reached first. Because the
breaking stress ($\sigma_b$) had a lower temperature dependence than yielding stress ($\sigma_y$), these
two stress curves shared an intersection which defined as the brittle-ductile transition
(BDT) point. At certain temperature above brittle-ductile transition temperature, yielding
involved a tensile stress much lower than the breaking stress that required for chain
scission, thus yielding could take place instead of brittle failure. Conversely, below
transition temperature the preferable mechanical response is brittle fracture because the
breaking stress threshold was first reached. However, this hypothesis didn’t base on any
molecular foundation and later was found out to be contrary to the pressurization effect as shown in Figure 2.11. If we apply LDWO hypothesis concept, the transition point would
move to lower temperature by shifting the yield stress curve downward to lower stress level,
however, the experiment data indicated yielding stress shifted to higher value, resulting in
a higher brittle-ductile transition temperature. This inconsistence invalids the LDWO
hypothesis to explain the brittle-ductile transition phenomenon.
Figure 2.10 Breaking stress and yield stress as a function of temperature in the LDWO hypothesis.

Figure 2.11 Pressurization effect on the BDT of PS. Tensile deformation in a hydrostatic pressure condition can induce the brittle-to-ductile transition in amorphous polymers.
2.3.2.2 External factors that affect BDT

Besides temperature and pressure effect on BDT indicated by Dr. Baer, there are several other effects that are known to influence the characteristics of the BDT: (a) physical aging\textsuperscript{63}, (b) mechanical rejuvenation\textsuperscript{64}, (c) melt-stretching\textsuperscript{49} and (d) blending\textsuperscript{49}.

Adequate physical aging could even turn most ductile polycarbonate into brittle under extension test\textsuperscript{49}, as shown in Figure 2.12. Since polymer glass sat in a non-equilibrium state, physical aging could allow the system to evolve toward the equilibrium state and move into a deeper potential well, segmental dynamics dramatically slowed down during this process, which made polymer glass difficult to yield.

![Figure 2.12 Mechanical response of polycarbonate (PC) under extension at room temperature before and after aging. Aged PC showed brittle response while non-aged one could undergo yielding. Sample got aged at 147°C for 10 days under vacuum condition.](image-url)
By contrast, “cold” deformation such as twisting or roll-milling could induce a mechanical rejuvenation effect which has the opposite effect to physical aging. Such deformation could make segments repacking take place, lifting some segments over the potential barrier, resulting in system situating in a higher energy state. Literature reported\textsuperscript{48} brittle PMMA turned into ductile at room temperature after went through milling. Besides, pre-milled PC could undergo homogeneous deformation without shear yielding and necking\textsuperscript{48}.

Other intriguing effect on BDT is melt-stretching. For example, a recently study\textsuperscript{49} reported that by subjecting PMMA to fast melt extension and then followed by fast quench, such pre-treated PMMA exhibited ductile response at room temperature as shown in Figure 2.13. The physics behind this phenomenon was then illustrated under the recognition that melt stretching produced a geometric condensation effect. The detail will be discussed in section 2.4.3.
Figure 2.13 Stress versus elongation for melt-stretched PMMA under cold draw. Melt stretching is carried out at 135°C to Hencky strains ε= 0.6, 1.0, 1.4 and 1.8. Isotropic sample exhibited brittle response under extension, while highly melt-stretched sample showed ductile response.
Blending is also one way that could affect BDT. Experimental result indicated PC could become brittle after adding low-molar-mass component to develop a binary system, as shown in Figure 2.14. The explanation for this phenomenon based on molecular structure will be discussed in section 2.4.3.

Figure 2.14 Stress versus elongation for PC mixture (167 kg/mol and 7 kg/mol) with weight fraction of high molecular weight equals to 100% (circle), 80% (squares), 60% (diamonds) and 40% (triangles). Mechanical responses for 60% and 40% are brittle.
2.4 Experiments-inspired molecular model: hybrid structure in polymer glass

2.4.1 Searching for molecular model of polymer glasses: bridging the gap of $10^6$

In polymer physics, the most challenging task is to connect macroscopical experiment phenomenon (on 1mm scale) to microscopic structure (on 1nm scale). Although constitutive modeling is the first step to develop quantitative description of solid mechanics, it lacks molecular ingredients without first principle-based molecular theory. Besides, fracture mechanics is always applied to explain character of fracture behavior, however, fracture mechanical method does not deal with molecular origin of toughness and interpret dissipative mechanism under molecular level.

To explore the molecular machanisms of polymer glass under large deformation, we need to probe physic natures of the leading phenomena such as yielding, plastic flow and brittle fracture. Despite a lot of pioneering works carried out in the past, a coherent understanding under molecular-level to explain nonlinear mechanical behavior of glassy polymer such as yielding and BDT is still missing. Based on experiments inspiration and cognition of the unique nature of chain uncrossability and connectivity, a recent study purposed a molecular model to better understand polymer glass under large deformation.
Figure 2.15 Hybrid structure for polymer glass undergoing large deformation along Z direction. The light dots and short bars in between represent polymer segments connected by van der Waals intersegmental interaction, and a load-bearing strand (thin rings) start to emerge upon large deformation by pairing hairpins with other chains due to intermolecular chain uncrossability. (replot of Figure 12.1 Roth, C. B., Polymer Glasses. CRC Press, Taylor & Francis, 2016, p398)

2.4.2 Structural hybrid in polymer glass under large deformation: primary structure and chain network

Polymer glass with sufficient high molecular weight could undergo yielding and plastic flow, by contrast, glassy polymer of low molecular mass is completely fragile and only suffer brittle failure. Given this sharp contrast result from molecular weight, it is necessary to involve chain network into discussion when depicting mechanical behavior under large deformation. Specifically, polymer glasses with high molecular weight can be treated as a structural hybrid with a primary structure due to short-ranged van der Waals intersegmental
interaction and a chain network due to intra-segmental connectivity to form load-bearing strands (LBS) as shown by Figure 2.15. Notice within initial elastic deformation regime, all the segments belong to primary structure. Beyond that regime, chain network starts to emerge to make it possible for the glass to respond globally. Specifically, displacement of the load-bearing strands (LBS) activates the surrounding vitreous segments, lifting them out of their dormant state, macroscopic plastic flow can take place when most segments are no longer vitreous.
2.4.3 Role of chain network under large deformation

As delineated in the molecular model, chain network is essential for yielding and plastic deformation. Treating brittle-ductile transition (BDT) as the leading phenomenon, we will discuss why chain network is necessary and how it play a role in dictating mechanical behavior in terms of BDT.

The striking phenomenon that melt-stretched PMMA turned into ductile is mentioned in section 2.3.2.2. To truly understand the physics behind, we need to recognize that melt stretching produces a geometric condensation of load-bearing strands (LBSs) as illustrated in Figure 2.16. Melt stretching cause entanglement strands got condensed along the stretching direction, such pre-deformation effect can be preserved by fast quench polymer melt to its glassy state. As a result, the chain network areal density in a melt-stretched sample is much higher compared with an isotropic sample. Upon cold drawing, there are more LBSs in a pre-treated sample that could allow force transmits along covalent bonds to activate the surrounding segments and thus ensure ductile yielding.

![Figure 2.16 Geometric condensation of entanglement strands produced by uniaxial extension of polymer melt along Z axis, the straight lines represent entanglement strands that get condensed due to cross-sectional area shrinkage in XY plane.](image)
Given the concept about chain network, it is now clear to explain how blending could affect mechanical response in terms of BDT in section 2.3.2.2. Apparently, blending could alter the chain network structure. Mixture with different compositions would have different chain network areal density. Since the low molecular weight component cannot form its own network, the network density in mixture got dilated. In presence of sufficient low-molar-mass component, PC could turn into brittle as shown in Figure 2.14.

Since the chain network plays a key role in this molecular model to describe polymer glass under large deformation, we need to study its basic properties. Although the concept of chain network structure in polymer glass below \( T_g \) is inherited from entanglement network from the melt state, their structure characters are different. In terms of quantitative analysis, the areal density of entanglement strands is given by

\[
\psi_{\text{ent}} \sim \frac{1}{p^2} \quad (2.14)
\]

where \( p \) is packing length in the packing model and it is proportional to the size of an entanglement strand \( l_{\text{ent}} \), which is \( p \sim l_{\text{ent}} \). \(^{67,68}\)

While the critical (minimum) size of load-bearing strand \( l_{\text{LBS}} \) scale with Kuhn length \( l_k \), which is \( l_{\text{LBS}} \sim l_k \). And the areal density of load-bearing strand is given by

\[
\psi \sim \frac{1}{pl_k} \quad (2.15)
\]
Because the size of Kuhn length $l_k$ is larger than that of packing length $p$, the areal density of entanglement network $\psi_{\text{ent}}$ is higher than that of load-bearing strand. Figure 2.17 showed packing length dependence of these two areal densities.

![Figure 2.17](image)

Figure 2.17 Areal density $\psi$ of loading bearing strands (LBSs) in the Gaussian chain network and areal density $\psi_{\text{ent}}$ of entanglement strands of different polymers. The unknown prefactor in equation (2.15) is chosen in such a way to avoid overlaying the two quantities that show different scaling dependences on the packing length $p$. The data describe 12 polymers in order of increasing $p$: bpA-PC, PEEK, PE, PET, POM, PPO, PVAc, PMA, PMMA, $\text{PaMS}$, PS and PtBS. (replot of Figure 12.10 Roth, C. B., Polymer Glasses. CRC Press, Taylor & Francis, 2016, p 411)

It was postulated to calculate tensile stress $\sigma$ given by the product of chain network areal density $\psi$ and chain tension $f_{ct}$ in the load-bearing strands. Upon cold-draw, the chain tension $f_{ct}$ can continually increase from below 0.1 nN toward its threshold value called
chain pullout force $f_{cp}$ as long as the network is intact ($f_{cp}$ is sensitive to temperature near $T_g$, and saturated at $f^* \sim 0.25$ nN for different polymer glasses at far below $T_g$). Since the force to break a covalent bond is around 5 nN\(^6\), much higher than the chain pullout force as shown in Figure 2.18, chain pullout should be the dominant mechanism for the chain network failure.

Figure 2.18 Chain tension $f_{cp}$ at the BDT for both isotropic and melt-stretched PS, PMMA, and bpA-PC. The stretching ratios are $\lambda_{ms} = 1.5$, 2.2, and 2.7 for PS, $\lambda_{ms} = 1.8$ and 2.2 for PMMA, and $\lambda_{ms} = 1.7$, 2.1, 2.5, and 2.7 for bpA-PC. With increasing $\lambda_{ms}$, $T_{BD}$ shifts to lower temperatures for PS and PMMA (parallel) and to higher temperatures for bpA-PC (perpendicular). Also indicated is the level of molecular force for chain scission at 5 nN for carbon-carbon bonds. The chain tension in the necked state, $f_{ct}(neck)$, during cold drawing of bpA-PC at the different temperatures above the BDT, is also evaluated as a function of temperature T, as represented by the small dots.
3.1 Introduction

Extreme mechanical response of polymer solids to large external deformation can be challenging to explain. Brittle fracture and ductile failure are a disastrous outcome of materials’ inability to adjust to the imposed shape change. According to the Griffith criterion\textsuperscript{70}, structural defects cause stress concentration, so that the mechanical strength is always found in practice to be much lower than the theoretical limit. However, fracture mechanical analyses do not describe what microscopic physics governs the deformation-induced decohesion of glassy polymers. Moreover, it has been difficult to understand why some polymers can show ductile responses to large deformation under some conditions but brittle failure under other conditions. Such a wide range of mechanical responses renders the familiar von Mises and Tresca criteria\textsuperscript{71,72} less than helpful. Similarly, the Eyring-type idea of stress-induced lowering of the activation barrier for plastic deformation\textsuperscript{73,74} cannot explain or anticipate when and why a ductile glass loses its ability to yield upon lowering
the temperature. Such an idea fails because it does not address where the molecular forces originate from during macroscopic external deformation.

Until recently, it had been unclear just how chain entanglement would afford a glassy polymer the unique characteristic ductility and what the molecular mechanism operates to control the brittle-ductile transition that is commonly observed in all glassy polymers of high molecular weight. Upon synthesizing all the available information including the key observations that a brittle polystyrene turns ductile (a) upon hydrostatic pressurization or (b) after fast melt extension or (c) following mechanical rejuvenation, it was suggested that the key factor driving a glassy polymer to yield is chain networking. Experimental result shows that chain networking seems necessary to transmit the external deformation and mobilize the dormant segments in a macroscopic system while local segmental displacements alone are insufficient to bring about plastic macroscopic deformation. Specifically in compression test, despite the action of compression that squeezes on all segments, plastic deformation could not occur below \( T_g \) for amorphous polymers with inadequate chain networking. What does a chain network do in compression? We speculate that the network junctions presumably spread affinely in the lateral dimensions during compression. This is plausible because segments at the junctions are not free to slide past one another. It is the affine biaxial-like extension (on the scales of the mesh size) of the chain network that may displace and mobilize the non-networking segments. Yielding would take place if the network density is adequately high. Here the structure of network density is characterized by the areal density rather than volume density, defined as the number load-bearing strands per unit cross-sectional area.
In this work we apply planar extension in polymer melt state to affect the chain network structure in polymer glass and show how chain network density control the BDT behavior. These experimental findings illustrate the explicit role of chain networking in compression and support the idea that the lateral chain networking resists the transverse expansion. Thus, these compression experiments extend the previous understanding concerning extension of polymer glasses.
3.2 Experimental section

3.2.1 Sample preparation

The bisphenol A polycarbonate (PC) was Lexan TM 141 111 from Sabic (GE Plastic). PS319K was a commercial polystyrene from Dow (Styron 663). PS33K was from Scientific Polymer Products, Inc. PS650K was synthesized at The University of Tennessee. PMMA350K is from Aldrich chemistry. Their basic characteristics are listed in Table 3.1.

Table 3.1 Basic Parameters of Polymer glasses

<table>
<thead>
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<th>Polymer</th>
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<th>Me (kg/mol)</th>
<th>PDI</th>
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PS mixtures PS650K/PS33k with composition of 27.5%/72.5% was prepared by first dissolving PS650K and PS33K in THF to make a honey-like solutions, and most of THF was evaporated slowly by placing the homogeneous solutions under a hood for several days, and the rest of THF was removed in a vacuum oven at Tg-30 °C for 10 hours and Tg+40 °C for another 5 hours. TGA measurements reveal negligible THF in the final sample after this procedure.
Samples were compression molded using a Carver press in a mold with dimensions of H × W × L = 20mm × 5mm × 25 mm, sandwiched by two Kapton® polyimide films at 200 °C. The cooling of the molded sheets to reach room temperature takes minutes. No thermal annealing was applied.

3.2.2 Experimental methods

Planar extension of polymer melt was carried out using an Instron 5969, which was equipped with a custom-made oven with temperature control within ±0.5 °C. In each test, the oven was heated to the prescribed temperature, once reaching the setting temperature, 15 minutes were allowed to achieve thermal equilibration. The device depicted in Figure 3.1 in the main text was lubricated with silicone oil on all contacting surfaces including the two sidewalls during the melt squeezing. A melt-squeezed sample was immediately quenched by icy water after squeezing. The quenched sample can be cut into cube-like specimens by a high-speed cutter.

Uniaxial compression tests were performed at room temperature using Instron 5969. The Bluehill software allows us to perform compression tests with various constant cross-head speeds in the unit of mm/min, which were then normalized by initial height H₀ to indicate the initial compression rate V/H₀ (min⁻¹). All cube-shaped specimens were lubricated on the top and bottle surfaces with silicone oil during cold compression.

In order to carry out in situ monitoring of the anisotropic lateral expansion of the melt-squeezed samples, a piece of 1 inch thick glass was used as the bottom on which the sample
rests, and a CCD camera was employed to track the lateral dimensional increase upon compression as shown in Figure 3.1.

Figure 3.1 (a) side view sketch of the setup for in situ measurement of anisotropic lateral dimensional change during compression. (b) photo of the actual setup.
3.3 Result and discussion

3.3.1 Planar extension induced anisotropic chain network

For common polymers of high molecular weight including bisphenol A polycarbonate (PC), polystyrene (PS), it is straightforward to subject them to planar extension in melt state using a one-dimensional squeezing device shown in Figure 3.2 (a). As a result, the isotropic chain network (due to chain uncrossability) becomes anisotropic: The sample (polymer melt) height shrinks upon getting squeezed out of the channel of length L and width w. In the affine deformation limit, for a sample cut from the quenched pre-deformed-melt shown in Figure 3.2 (b), the entanglement network can be regarded as taking an anisotropic structure, as schematically illustrated in Figure 3.2 (b), in terms of the different areal densities ($\psi_C$, $\psi_U$ and $\psi_D$) of effective strands in each of the three cross-sections (faces), denoted by C (condensed), U (unchanged) and D (dilated), respectively. With adequate quenching we expect to partially retain the effect of pre-deformation on the network structure. Such a system provides us an opportunity to examine the roles of chain networking during “uniaxial” compression. Until now it has been unclear not only how chain network may influence the mechanical response but also what properties of the network affect the outcome, i.e., whether the areal density $\psi_D$ on the face D (being compressed) or $\psi_U$ and $\psi_C$ in the transverse "faces" are more important for the emergent compressive stress, the shape change and ductility.
Figure 3.2 (a) Sketch of the apparatus for planar extension realized in presence of lubrication by pushing downward (along z axis) the piston to squeeze the melt along x axis at a width W fixed by the two side walls. (b) The isotropic sample converts an anisotropic object after quenching the melt-deformed sample well below $T_g$ and cutting into cube-shape as shown, where the three different surfaces are labeled as face D, U and C, respectively. Shape changes are quantified by changes in $L_U$, $L_D$ and $L_C$.

3.3.2 Anisotropic deformation in pre-treated polycarbonate (PC)

The melt pre-deformation has afforded us an effective means to create anisotropic structures. As shown in Figure 3.2 (b), we have presumably $\psi_U = \psi_{iso}$, $\psi_D = \psi_{iso}/\lambda$ and $\psi_C = \lambda \psi_{iso}$ in the affine deformation limit, where $\lambda = L_{z0}/L_z$ represents the degree of the homogeneous planar extension in the melt state. In reality, such melt deformation would not be perfectly affine. Nevertheless, Figures 3.2 (a)-(b) depict a qualitative expectation. It is a valid and interesting question to ask how the lateral dimensions of such a sample change respectively upon cold compression on each of the three different faces.
Figure 3.3 *In-situ* measurements of the anisotropic lateral expansion of pre-deformed PC during face U compression in terms of the normalized dimensional changes, where the triangles show the isotropic expansion given by $(H_i/H)^{1/2}$. See Figure 3.9 (a) in Appendix for the rheological data describing the melt-squeezing to $L_{D}/L_{x}=2$.

We reason that the maximum anisotropic response occurs during face U compression because the anisotropy should be controlled by the ratio of areal network densities in the two lateral dimensions, $\psi_C/\psi_D \sim \lambda^2$, which is larger than the other two comparable ratios $\psi_U/\psi_D \sim \lambda$ and $\psi_C/\psi_U \sim \lambda$. Based on melt-squeezed PC, Figure 3.3 shows that $L_C$ is found to increase almost as strongly as $H_i/H$ and the lateral dimension $L_D$ remains little changed. Here $H_i$ denotes the initial sample height before cold compression. Thus, because of the structural anisotropy the "uniaxial" compression produces near planar extension without any physical constraint. The anisotropic spread of the sample in the lateral dimensions clearly reveals the key role that the anisotropic chain network plays in the ductile compression. In other words, the observation of anisotropic lateral expansion supports the idea that the chain network dictates the mechanical response. When the chain network is
structurally anisotropic, the lateral “biaxial” extension is also anisotropic: the sample spreads more along the mechanically and structurally weaker direction.

3.3.3 Crack formation and brittle-ductile transition

3.3.3.1 Turn ductile polymer into brittle glass

we subjected PS and PMMA to melt squeezing as depicted in Figure 3.2 (a)-(b) and subsequently carried out cold compression. Besides probing the universality regarding the behavior observed in Figure 3.3, such experiments allowed us to confirm predictions that are beyond the information presented in Figure 3.3. Specifically, we conducted four discrete tests: besides the uniaxial compression on an isotropic sample as the reference, we cold-compressed separately on face D, face C and face U of the quenched pre-melt-squeezed sample. The stress responses involving face D and face C are qualitatively predictable relative to the isotropic compression. Figure 3.4 shows these four tests on both PS and PMMA, universal mechanical behavior is found on these two polymer materials. It is seen that the stress is highest for face D compression apparently because \( \psi_C > \psi_{iso} \) and \( \psi_U = \psi_{iso} \), which is true in the affine deformation limit (which we adopt as approximation). Face C compression produces lower compressive stress than the compression of an isotropic sample because the lateral areal network densities are either \( \psi_D < \psi_{iso} \) or \( \psi_U = \psi_{iso} \). In absence of any structural failure, face U compression would produce the largest anisotropic lateral expansion as shown in Figure 3.3.
Figure 3.4 Compressive stress vs. compression ratio $H_i/H$ involving face D (diamonds), face C (circles) and face U (squares) compressions of (a) pre-deformed PS as well as the compression of the isotropic PS (triangles) and (b) pre-deformed PMMA as well as the compression of the isotropic PMMA. In Figure (a), the vertical arrows C and U show the strains at which cracks are first observed. See Figure 3.9 (b) and (c) in Appendix for PS and PMMA melt squeezing to $L_{x0}/L_z = 5$.

In reality, the face U compression of the pre-deformed sample produces a brittle response. Apparently, the lateral chain network can no longer enable sufficient segmental mobilization and resist crack initiation and growth. Since small cracks also emerged in the face C compression, it is clear that the directional weakening of the chain network made the samples susceptible to structural failure. In other words, the lateral network densities dictate not only the magnitude of the compressive stress but also the cohesive strength of the polymer glasses under compression. Face U compression is more disastrous plausibly because this configuration exposes the maximum contrast in the areal density among the two lateral directions (as demonstrated in Figure 3.3 based on the ductile face U
compression of PC). Specifically, the ratio of \( \psi_C/\psi_D \sim \lambda^2 \) is higher than \( \psi_U/\psi_D \sim \lambda \) for any value of \( \lambda > 1 \). There is a greater tendency for the sample to accommodate the face U compression by expanding more in the direction where the sample encounters the lowest network density \( \psi_D = \psi_{iso}/\lambda \).

3.3.3.2 Cold-compression rate effect

Face U cold compression is also conducted at different rates as shown in Figure 3.5, result data confirm the same point that sample accommodates face U compression by expanding more along the direction where the chain network density is lowest, so the sample after compression turns to be a rectangular shape with multiple cracks. By increasing rate, sample failures turn to be more severe with plenty of cracks developed due to directional weakening of the chain network.
Figure 3.5 (a) Compressive stress vs. compression ratio $H_i/H$ involving isotropic PS at cold-compression rate $V/H_i= 1 \text{ min}^{-1}$ (circle), pre-treated PS ($\lambda=4$) at cold-compression rate $V/H_i= 0.1 \text{ min}^{-1}$ (square) and $V/H_i= 1 \text{ min}^{-1}$ (triangle). (b) Snapshots of isotropic PS surface (left) after test as well as pre-treated PS surface U ($\lambda=4$) after test at cold-compression rate $V/H_i= 0.1 \text{ min}^{-1}$ (middle) and $V/H_i= 1 \text{ min}^{-1}$ (right).
3.3.3.3 Melt-squeezing ratio effect

To further examine melt-deformation effect, sample is melt-squeezed to different extents, then conducted face U cold-compression as shown in Figure 3.6. For sample that melt-squeezed to $\lambda = 3$, a contrast between two lateral chain network areal densities is given by the ratio of $\psi_C/\psi_D \sim \lambda^2 = 9$, in this case sample develops several cracks and the entire structure is barely maintained. Sample that melt-squeezed to $\lambda = 4$ suffers completely structure failure because here the contrast between two areal densities is more severe, almost double the first case, given by $\psi_C/\psi_D \sim \lambda^2 = 16$.

Figure 3.6 Compressive stress vs. compression ratio $H_i/H$ involving isotropic PS cold compression (triangle), face U cold compression on pre-treated PS that melt-squeezed to $\lambda=3$ (square) and $\lambda=4$ (circle).
3.3.3.4 Turn brittle polymer blend into ductile glass

Next, we anticipate a brittle glassy polymer to show ductile response to certain compression upon undergoing the same melt pre-deformation as depicted in Figure 3.2 (a). Figure 3.2 (b) shows that a denser lateral chain network is available when the compression is applied on face D. Increased network density should enhance the activation through the lateral molecular mobilization. As a test of the notion that sufficient lateral chain networking is required to ensure ductile response, we examined two samples, i.e., isotropic PS mixture labeled as PS650K(27.5)/PS33K(72.5) that is brittle in uniaxial compression and the same sample that has undergone melt-squeezing to develop "geometric condensation" as shown in Figure 3.2 (b). Instead of $\psi_{iso}$, the new areal densities are $\psi_U \sim \psi_{iso}$ and $\psi_C > \psi_{iso}$. Contrary to the phenomenon in Figure 3.4 where an isotropic ductile PS319K turned brittle after melt-squeezing upon face U compression, Figure 3.7 shows that during face D compression the isotropic brittle PS mixture became ductile after sufficient melt-squeezing.
Figure 3.7 Compressive stress vs. compression ratio for the isotropic PS mixture and face D compression of the melt-squeezed PS mixture. See Figure 3.9 (d) in Appendix for the stress-strain curve of the melt squeezing to $L_{0y}/L_z = 6$. 
3.4 Further discussion: molecular dynamic (MD) simulation study

To further elucidate the explicit roles of the chain network in controlling the mechanical responses, we carried out MD simulation based on a coarse-grained model\textsuperscript{81} for PS. We investigate how such pre-deformation as that shown in Figure 3.2 (a) causes the sample to respond to compression on the different faces. In the MD simulation a melt of chain length $N = 500$ was subjected to considerable planar extension and quenched fast to below $T_g$. The quenched glassy systems along with the reference (that did not undergo melt deformation) were respectively compressed at $T = 300$ K on each of the three faces in six separate MD simulation runs.

The simulation results resemble the experimental data. Specifically, as shown in Figure 3.8 (a), the compressive stress is highest for face D compression (diamonds), and the face C compression (circles) produces the lowest stress. The reference system shows in Figure 3.10 (a) that strain hardening (stress increase in post-yield regime) is much weaker than the face D compression but stronger than face U and face C compressions, in agreement with the experimental trend in Figure 3.4. The MD simulations also illustrate in Figure 3.3 significant anisotropic responses in terms of the ratio of the expansion ratios. Further analysis of these MD results shows that the compressive stress stem from intersegmental repulsion. However, it is the chain networking that resists the lateral expansion. The lateral areal density of load-bearing strands in the chain network plays an important role in the stress growth beyond the yield point. For example, the sharp contrast between the diamonds and the rest of the three symbols in Figure 3.8 (a) shows that the mechanical resistance to
the face D compression is highest due to the geometric condensation shown in Figure 3.2 (b).

Figure 3.8 (a) Compressive stress vs. compression ratio H/H for the melt-squeezed system on each of the three faces, all at 300 K. (b) Corresponding anisotropic shape changes characterized by the ratio of the lateral dimensional expansion for each of the three compressions. (c) Mass density change as a function of compression ratio. (d) Bond length increase due to lateral network straining where the inset is a snapshot from face D compression at H/H = 2.5 near the end of the compression. The images show how strands with different degrees of bond stretching emerge throughout the sample during the compression where the red color (online) indicates a large stretching of 7%.
The areal densities of lateral load-bearing strands after the melt-squeezing also determines how the mass density builds up during compression as shown in Figure 3.8 (c): The highest density increase accompanies the highest compressive stress growth seen in Figure 3.8 (a). This is a consequence of the enhanced lateral chain network, with \( \psi_C > \psi_{iso} \) and \( \psi_U \sim \psi_{iso} \). The causal relation presumably goes as follows. The higher lateral resistance arises from the higher areal network densities, leading to higher compressive stress buildup. The higher mass density arises from the higher compressive stress. In the end, the higher density and compressive stress lead to more significant bond level distortion, i.e., greater covalent bond length stretching. Specifically, Figure 3.8 (d) confirms that bond stretching is strongest for the face D compression in comparison to all the other scenarios. Figure 3.10 (b) and (c) show similar trends for the mass density and bond stretching in the reference system.
3.5 Conclusion

In this work, we have several objectives. First, using planar extension above T_g we show how a glassy polymer can be made to have an anisotropic chain network. Second, we illustrate that because of the different areal densities in each of the three orthogonal cross-sections, the melt-pre-deformed polymer can exhibit anisotropic responses to compression. Third, besides the anisotropic shape change, we illustrate how structural characteristics can be used to predict the mechanical response. Specifically, we demonstrate that after melt-pre-deformation a previously isotropic ductile polymer glass can turn brittle in compression along a certain direction with respect to the melt-planar extension direction. Conversely, after subjecting an isotropic brittle glassy polymer to planar melt extension, the pre-deformed glassy polymer can yield and undergo ductile compression along particular direction. Fourth, we perform molecular-dynamics simulation to elucidate the molecular origin of stresses and describe the observed anisotropic responses.

In conclusion, we predict anisotropic shape changes and mechanical responses based on the structural anisotropy introduced in glassy polymers by pre-melt deformation. Ductile polymers can turn brittle and vice versa after specific melt deformation. Conversely, the anisotropic mechanical behaviors, also observed in the MD simulation, support the notions that (1) the resistance to compression varies with the structural characteristics of the chain network and (2) the lateral areal density of load-bearing strands in the network controls the dimensional changes and determines whether or not yielding can successfully emerge to avoid macroscopic fracture during compression.
3.6 Appendix

3.6.1 Mechanical behavior for melt squeezing

The lubricated melt squeezing amounts to applying planar extension. Depending on the directional relation between the melt-squeezing direction and cold-compression direction, the melt-deformation amounts to either geometric condensation or dilation of the chain network in the lateral dimensions. The sample studied in Figure 3.3 underwent the melt squeezing recorded in Figure 3.9 (a). Figure 3.4 is based on the sample prepared with melt squeezing whose stress-strain curve is given in Figure 3.9 (b) and (c). In unidirectional compression shown in Figure 3.7, the brittle PS mixture turns ductile after melt squeezing illustrated by the stress vs. strain curve in Figure 3.9 (d).
Figure 3.9 (a) stress-strain curve of PC63K melt undergoing planar extension (cf. Figure 3.3) at 150 °C. (b) stress-strain curve for PS319K melt undergoing planar extension at 125 °C. (c) stress-strain curve for PMMA350K melt undergoing planar extension at 125 °C. (d) stress-strain curve for the PS mixture (PS650K/PS33K) undergoing planar extension at 120 °C.

3.6.2 Molecular dynamic simulation detail

Molecular dynamics simulation was done using the recent coarse-grained model of polystyrene. In this model one repeat unit of polystyrene is represented by 2 beads where the backbone bead represents the CH group directly bonded to the phenyl ring and half of each neighboring CH$_2$ group and the side bead represents the phenyl ring.
A system containing 500 polystyrene chains of each 500-mers (1000 beads per chain) was generated by randomly distributing the polystyrene chains in a periodic box. The system was first subjected to a homemade Monte Carlo (MC) code for density equilibration. The MC simulation follows the method introduced by Rolf Auhl et.al\(^8\) where five typical MC moves (translation, rotation, reflection, inversion and exchange) were used to decrease the density fluctuation until the structure factor of the system \(S(q)\) in the limit \(q \to 0\) was reduced to about one percent of the initial value. The system was then equilibrated using MD at 700K for 5.6 ns to density around 0.82g/cm\(^3\). All the MD simulations were performed using the LAMMPS simulation package.\(^8\)

The melt squeezing (cf. Figure 3.2) was done at 700K where the “width” of the cubic simulation box (w’ by w’ by w’) was held fixed at \(L_y = w’\) while a compressional deformation was applied in the z-direction at a rate of 0.5/\(\text{ns}\) to \(w'/L_z=2\). The system was then run for an additional 1 ns at 700 K with the box allowed to adjust in the z-direction but was fixed in the x- and y-direction so as to retain the anisotropy of the chain network. A quenching rate of 10K/\(\text{ns}\) was then applied to cool the system down to 500K with box dimensions held fixed in both x and y direction, effectively preventing the fast elastic recoil in the melt state. No constraint was applied in quenching the system from 500 K to 300 K since the chains do not recoil within the time scale of the quenching rate. At 300 K, in terms of the width \(w\), the system has a height of \(H_0 = w/1.84\) and length \(L_x = 1.61w\), where \(w\) is around 360 Å, and the density is around 1.052 g/cm\(^3\).
A reference system was generated by quenching the isotropic cubic box from 700K to 500K with the same quenching rate of 10K/ns and the same constraint on both x and y dimensions (i.e., held fixed during quenching). No constraint was applied in quenching the system from 500 K to 300 K so that the quenching protocol is identical to that adopted to prepare the melt squeezed system. Due to the constraint during the quench, the control system is not fully isotropic and cubic, measuring to be $w \times w \times H_0$ where $H_0 = w/1.12$ with $w = 358$ and density equal to $1.053 \text{ g/cm}^3$.

The pre-deformed melt system and the reference were subjected to various unidirectional compressions at a constant compression rate of 0.5/ns, resulting in the observations presented in Figure 3.8 (a)-(d) in the main text for the pre-deformed melt system. The control system data are presented here as shown in Figure 3.10 (a)-(c).

Figure 3.10 (a) Compressive stress vs. compression ratio $H_i/H$ for the reference system on each of the three faces, all at 300 K. (b) Mass density change as a function of compression ratio. (c) Bond length increase due to lateral network straining.
CHAPTER IV

EMERGENCE OF RETRACTIVE STRESS IN MELT-STRETCHED POLYMER GLASSES

4.1 Introduction

While the nature of glass and the glass transition remain an unsolved problem in condensed matter physics, organic polymeric glasses possess additional variables, making them even more interesting to study. Unlike all other organic glasses of low molecular weight such as non-crystalline sugar, glassy polymers can be ductile and thus undergo considerable external deformation without fracture.\textsuperscript{47, 75, 76} Significant mechanical stress can be embedded in the glassy state after large ductile deformation at temperatures much lower than the glass transition temperature $T_g$. 
Conceptually analogous to deformation-induced crystallization in certain semi-crystalline polymers, the molecularly deformed polymer glasses differ from their undeformed isotropic state in at least one way: The stress-containing polymer glasses exhibit elastic yielding\textsuperscript{85-87}. After ductile cold drawing (at room temperature) to a sufficient extent and unloading to permit stress relaxation in an unconstrained manner, the specimen attains an apparent stress-free state after days of storage at room temperature without mechanical constraint. However, when annealed at temperatures above the storage temperature (e.g., room temperature) yet still substantially below $T_g$, considerable retractive stress may emerge after an induction period that depends on the annealing temperature and the condition of cold drawing.

Melt deformation (above $T_g$) of high-molecular weight polymer is usually understood within the framework of rubbery elasticity theory\textsuperscript{88}. For non-crosslinked entangled melts, significant chain stretching is possible due to polymer entanglement arising from intermolecular uncrossability. In the conventional description, the stress is assumed to be entropic in origin, and the internal energy changes negligibly with extension. The conformational entropy change occurs due to chain deformation at the level of the entanglement strand (spacing) that is the building block (mesh size) of the entanglement network. Taking the basic unit (sub-Gaussian chain) to have a coil size (end-to-end distance) $l_{ent}$, the elastic melt plateau modulus $G_{pl}$ is dictated by this structure, given by $G_{pl} = k_B T / p (l_{ent})^2$, with $p$ being the packing length\textsuperscript{89}. During affine melt deformation, the stress level is therefore set to a magnitude comparable to $G_{pl}$. For example, for uniaxial extension, the tensile stress may be quantified by the neo-Hookean expression $\sigma = \ldots$
\[ G_{pl}(\lambda^2-1/\lambda), \] where \( \lambda \) is the stretching ratio. This level of stress implies that little chain stretching takes place on length scales much smaller than \( l_{\text{ent}} \).

The present work attempts to marry the two subjects of elastic yielding in glassy state and uniaxial extension in melt state in order to acquire more insights concerning the essential questions in each of the two topics. In combination, we can more effectively explore the origin of the retractive stress during annealing; we can determine what kind of polymer deformation is required to produce the elastic yielding, i.e., emergence of retractive stress in a pre-deformed polymer glass at temperatures (\( T_{\text{el-yield}} \)) elevated from the storage temperature that are still below \( T_g \). We discover that melt-stretched polymer glasses display retractive stress upon annealing at \( T_{\text{el-yield}} < T_g \). Based on the combined data of melt extension and elastic yielding we propose that even rubbery melt extension at temperatures well above \( T_g \) can produce conformational distortion at the covalent bond level in polystyrene and poly(methyl methacrylate).
4.2 Materials and Apparatus

4.2.1 Materials

Poly(methyl methacrylate) (PMMA) and polystyrene (PS) with different molecular weight as well as amorphous PLA are studied here. The basic characteristics are listed in Table 4.1. GPC measurements were carried out using THF-based GPC equipped with Wyatt Dawn Eos multi-angle laser light (MALLS) Detector and Waters Model 2414 differential refractometer concentration detector. Glass transition temperatures were characterized by TA Instruments Q2000 and Q200. DSC ramping at 10 °C/min to Tg + 80 °C followed by the same rate for cooling after thermal histories were erased.

Pellet-like resins are first placed in a dog-bone shaped mold with dimensions L × W × T equal to 10 mm × 3 mm × 1mm, sandwiched by two Kapton® polyimide film in a high vacuum press (Technical Machine Products Inc. Cleveland, OH) at temperature Tg + 60 °C.
Table 4.1 Basic Parameters of Polymer Glasses

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<td>Pressure Chemical</td>
</tr>
</tbody>
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4.2.2 Apparatus

Uniaxial melt extension is carried out above their glass transition temperature by using Instron 5543 with an environment chamber. The tests were conducted over a range of temperatures above glass transition temperature. For the experiments carried out above room temperature, after mounting the samples onto the Instron and closing the oven door, at least ten minutes were used to assure thermal equilibration. The Merlin software allows us to perform extension tests with various constant cross-head speeds V in the unit of mm/min. Dogbone specimen is loaded between clamps and melt stretching takes place under constant speed at certain temperature. After stretched to assigned elongation ratios, the stretched specimens are quickly quenched to glassy state by icy water to preserve the
melt-stretching effect, taking PS319K as an example, Figure 4.1 shows the mechanical stress response upon quenching, it takes the sample only 2.5 seconds to build 3MPa stress, which is much faster than its relaxation time. All the melt-stretched samples were stored at room temperature for 12h before annealing experiments were carried out at certain temperature which was realized by a homemade temperature controller with temperature accuracy of ±0.5 °C. The description of the heater design is available in Reference 90. Specifically, in section 4.4, PMMA35K was melt-deformed based on the squeeze device that introduced in section 3.3.3. As a reference for comparison, PMMA125K was also deformed in this way.

Linear viscoelastic properties PS and PMMA were characterized by small-amplitude oscillatory shear (SAOS) measurements on an ARES G2 rheometer at different temperatures with parallel disks of 8 mm diameter. Polymer samples with 1 mm in thickness were first heated up to sufficiently high temperatures above $T_g$ to achieve good adhesion between the samples and the steel disks. The strain amplitude for SAOS was set to be 5% for the typical temperature range from $T_g + 50 °C$ to $T_g + 5 °C$ while the frequency ranges from 100 to 0.05 rad/s. To access the $\alpha$ segmental relaxation ($\tau_\alpha$) dynamics, the frequency sweep amplitude was gradually decreased to 0.01% for near and below $T_g$ temperature range using frequency range from 1 to 0.05 rad/s. In this study, $\tau_\alpha$(SAOS) was obtained from the reciprocal of the third crossover frequency by $\tau_\alpha$ (SAOS) = $1/\omega_\alpha$. SAOS data for PS319K, PS650K and PMMA125K are available in Appendix.
Figure 4.1 Isotropic specimen first undergoes thermal equilibrium at 130 °C for 15 min and ice water was applied after Instron mechanical testing system started recording for 15 seconds.
4.3 Experimental studies

4.3.1 Basic features

Melt extension is expected to produce initial elastic response similar to that of a crosslinked rubber with modulus $G_{pl}$. However, entanglements do not survive at high strains presumably because of the molecular force imbalance\textsuperscript{91,92}. Consequently, yielding emerges, evidenced at low rates by the peak in the engineering stress $\sigma_{\text{engr}} = \sigma/\lambda$ and at high rates by a sharp downward deviation of the growing stress from the affine deformation response, i.e., the neo-Hookean expression. Figure 4.2 (a) shows the yielding characteristics for three effective rates that characterized by initial Rouse Weissenberg numbers given as the product of Hencky rate $(V/L_0)$ and Rouse time $\tau_R$. For the first two lower rates, $\sigma_{\text{engr}}$ shows distinctive peaks, indicating that affine extension ceases at rather low strains. Casting it in the form of rubber elasticity formula $\sigma_{\text{engr}} = G(\lambda)(\lambda-1/\lambda^2)$, we interpret the engineering stress decline as due to the collapse of the entanglement network. Yielding is signified by the effective decreasing modulus $G(\lambda)$. A gradual rather than steep stress decrease presumably implies that the residual network is still undergoing extension. With increasing effective rate, the onset of the stress decrease is postponed. While $\sigma_{\text{engr}}$ peaks at $\lambda_y = 5$ for $Wi_R = 1.27$, it does not decrease up to $\lambda = 8$ for $Wi_R = 12.7$, where $Wi_R$ denotes the initial Rouse-Weissenberg number. Thus, more molecular deformation can take place with increasing rate.
Figure 4.2 (a) Stress-strain curve of PS650K that melt-stretched to different draw ratios at 140 °C under different initial Rouse Weissenberg numbers. Black line indicates rubber elasticity $\sigma_{\text{engr}} = G_{\text{pl}} (\lambda - 1/\lambda^2)$. (b) Retractive tensile stress as a function of annealing time at annealing temperature 90 °C for PS650K melt-stretched specimens.

To examine how chain stretching grows during melt extension we carried out the following unusual experiment. At the end of melt extension, we thermally quench the specimen sufficiently quickly below $T_g$ to preserve the melt-stretched state. After days of storage of such melt-stretched samples at room temperature, we mounted these samples onto an Instron mechanical testing system (MTS) at room temperature and attempted to detect any emergent tensile retraction as a function of time. As shown in Figure 4.2 (b), there is no stress before a custom-designed heater was introduced to surround and heat up the melt-stretched specimen from room temperature to $T_{\text{el-yield}} = 90$ °C. Once the specimen warms up, the Instron-MTS first recorded a compressive force because of the thermal expansion. For the specimen labeled as $W_i_R = 0.25$, Figure 4.2 (b) shows that the stress never turned retractive. The sample actually stayed bent due to the thermal expansion. The stress relaxes under the compressive condition since the alpha relaxation time is quite short.
at 90 °C. To our surprise, during the same annealing that produces nothing but thermal expansion as indicated by the specimen labeled as $W_{IR} = 0.25$ in Figure 4.2 (b), the more strongly melt-stretched samples became straight over time and produced considerable retractive stresses on time scales shorter than one minute.

As a control experiment, we then apply PS and PMMA specimens that un-deformed but still quenched from melt state to run elastic yielding test at anneal temperature 90 °C. As shown in Figure 4.3, the record of Instron machinal testing system first shows a compressive force because of the thermal expansion and then stress relaxation takes place since the alpha relaxation for both of the two polymers at 90 °C are quite short as shown in section 4.6.1. The stress never goes retractive within experimental time because the specimen is bent all the time. The snapshots from Figure 4.4 further confirm that the un-deformed specimen stayed bent while the pre-deformed specimen goes fully straighten after annealing at 90 °C for 1000s.
Figure 4.3 Retractive tensile stress as a function of annealing time for PMMA125K and PS319K at an annealing temperature 90 °C. The specimen is first loaded between two clamps under 130 °C for 15min without stretch and then quenched by ice water before unloading.

Figure 4.4 Side view of snapshots for specimens that loaded between clamps after annealed for 1000s at 90 °C. (a) is the melt-stretched PS319K specimen, it stays straighten due to the retractive force showing up upon annealing. (b) is the un-deformed PS319K that quenched from 125 °C, it remains bended after annealing at 90 °C.
4.3.2 Annealing temperature effect

PS319K specimen is first stretched in the melt state at 125 °C with an initial Hencky rate $V/L_0= 1 \text{ s}^{-1}$, specimen after stretched is immediately quenched to preserve melt-stretching effect, as shown in Figure 4.5 (a). A set of specimens that undergo the same pre-deformed procedure are then mounted between clamps and annealing under different temperatures. Basic elastic yielding behavior is shown in Figure 4.5 (b), the initial negative stress that first shows up is due to thermal expansion, after certain induction time, a considerable retractive tensile stress could build up within the experimental time. Higher tensile stress as well as shorter induction time could take place for a specimen that annealed at higher temperature. Sizeable retractive stress can show up even at 70 °C which is well below $T_g = 103 \text{ °C}$. At the higher temperatures, such as 100 °C or 105 °C, the elastic yielding is so severe that the residual stress is able to relax over time because of force imbalance.

Figure 4.5 (a) Stress-strain curve for a polystyrene melt at 125 °C. The uniaxial melt extension is carried out with an initial Hencky rate $V/L_0=1 \text{ s}^{-1}$ to $\lambda=8$, a spray of ice water is applied to quickly quench the specimen to room temperature before unloading. (b)
Retractive tensile stress as a function of annealing time at various annealing temperature from 70 °C to 105 °C for a melt-stretched PS.

4.3.3 Melt-stretching condition effect

4.3.3.1 From different melt-stretching temperature

We verified the authenticity of the discovery made in Figure 4.6 by examining the effect of melt stretching at different temperatures. Figure 4.6 (b) shows that at the same initial Hencky rate \( V/L_0 = 0.4 \text{ s}^{-1} \) melt stretching at a lower temperature produces a stronger elastic yielding effect, characterized by a shorter induction time and higher magnitude of the retractive stress. At 120 °C, polystyrene could apparently form a temporary network due to short-ranged intersegmental interactions that can respond to melt extension at a stress level far exceeding a level determined by the ordinary rubbery elastic modulus. Up to \( \lambda = 5 \), the stress is considerably higher than the affine deformation limit of the entanglement network. For example, at \( \lambda = 2 \), the stress is twice as high as given by the neo-Hookean formula \( \sigma_{\text{enr}} = G_p(\lambda - 1/\lambda^2) \), which is the rubber elasticity line. The unusual, much stiffer initial stress response in Figure 4.6 (a) has recently been studied both experimentally\(^93\) and theoretically\(^94\). We speculate that chain deformation has reached a more local length scale at 120 °C. Conversely, the attainable stress is considerably lower at 130 °C and even lower at 140 °C.
Figure 4.6 (a) Stress-strain curve for PS319K under initial Hencky rate V/L₀=0.4 s⁻¹ at various temperatures above T_g. Black line indicates rubber elasticity \( \sigma_{\text{engr}} = G_{\text{pl}} (\lambda - 1/\lambda^2) \), plateau modulus \( G_{\text{pl}} \) for polystyrene is typically 0.22 MPa measured by small-amplitude oscillatory shear (SAOS). (b) Retractive tensile stress as a function of annealing time at annealing temperature 90 °C. The inset shows tensile stress that built up after annealed for 1000s under 90 °C versus Cauchy stress that built up after melt-stretched to certain draw ratio \( \sigma_\text{Cauchy} = \sigma_{\text{engr}} \lambda \).

To quantify the magnitude of retractive tensile stress, we plot emergent retractive stress as a function of Cauchy stress that built up after melt-stretched to certain draw ratio in logarithmic scale in the inset of Figure 4.6 (b). After draw a diagonal line as a reference where retractive stress equals to Cauchy stress, we find the retractive stress is always lower than the Cauchy stress since the Cauchy stress sets the upper bound for the observable retractive stress. Besides, the retractive stress slowly approaches to the level of the Cauchy stress as the melt-stretched temperature gets lower, which is consistent with our speculation that chain deformation reached a more local length scale at 120 °C.
4.3.3.2 From different melt-stretching ratio

Given a sufficient high initial Rouse-Weissenberg number at 120 °C, i.e., the product of initial rate and Rouse time, PS319K specimens could undergo uniaxial extension to different draw ratio with a glassy-like initial mechanical response as discussed in Figure 4.7 (a). Elastic yielding phenomenon in Figure 4.7 (b) shows specimen that undergoes higher chain stretching ratio, manifests larger retractive stress. By plotting Cauchy and retractive tensile stress as a function of draw ratio, data points show the trend that retractive stress is much smaller than the Cauchy stress at low stretching draw ratio. For example, at draw ratio λ = 2, the retractive stress is only one third of the Cauchy stress. Although Cauchy stress that built up at λ = 2 is unusual high due to the transient intersegmental network, the intrasegmental chain stretching contribution is quite low due to a limited stretching ratio at this time, which leads to a huge difference stress level between Cauchy stress and retractive stress.
Figure 4.7 (a) Stress-strain curve for PS319K melt that uniaxial stretched at 120 °C with a Rouse Weissenberg number $W_{iR} = 100$. The specimens are melt-stretched to different draw ratio from $\lambda = 2$ to $\lambda = 6$. Also plot rubber elasticity line as a reference, given by $\sigma_{\text{engr}} = G_p(\lambda - 1/\lambda^2)$. (b) Retractive tensile stress of melt-stretched specimens with different draw ratios as a function of annealing time at annealing temperature 90 °C. Inset is tensile stress that built up after annealed for 2000s under 90 °C and Cauchy stress that built up after melt-stretched to certain degree ($\sigma_{\text{Cauchy}} = \sigma_{\text{engr}} \lambda$) as a function of different melt-stretched draw ratio.

PS2M is subjected to melt extension at a high temperature 150 °C, the modulus recovers to rubber elasticity limit in this case. The stress is monotonically built up without yielding under a sufficient high Rouse Weissenberg number $W_{iR} = 32$. Again, we examine the relationship between the Cauchy stress and retractive stress. Compared with the inset in Figure 4.7 (b), although they share a same trend, i.e., retractive stress is much smaller than the Cauchy stress at low stretching draw ratio, the inset of Figure 4.8 (b) shows there is still much difference between these two stress levels even at high draw ratio. For example,
at $\lambda = 8$, inset of shows retractive stress is almost close to the Cauchy stress while the retractive stress is relatively only half of the Cauchy stress. At high enough temperature such as 150 °C, it is difficult to preserve sufficient chain stretching since the relaxation time is so short.

Figure 4.8 (a) Stress-strain curve for PS2M melt that uniaxial stretched at 150 °C with a Rouse Weissenberg number $W_{Ir} = 32$. The specimens are melt-stretched to different draw ratio from $\lambda = 5$ to $\lambda = 8$. (b) Retractive tensile stress of melt-stretched specimens with different draw ratios as a function of annealing time at annealing temperature 90 °C. Inset is tensile stress that built up after annealed for 2000s under 90 °C and Cauchy stress that built up after melt-stretched to certain degree ($\sigma_{Cauchy} = \sigma_{engr} \lambda$) as a function of different melt-stretching ratio.

To make a comparison between the effects of transient glassy response and rubbery melt response, we then conducted melt extension of PS650K under both 120 °C and 140 °C as shown in Figure 4.9 and Figure 4.10, with an initial Rouse Weissenberg number equals to 100 and 8.94, respectively. To quantitively determine the melt-stretching effect under these
two conditions, retractive stress is plotted as a function of Cauchy stress in each case in logarithmic scale within the same range of draw ratio from $\lambda = 5$ to $\lambda = 7$ as shown in Figure 4.11, the ratio between retractive stress and Cauchy stress for PS650K remains around 0.83 given by the melt-stretched temperature 120 °C while the ratio shifts from 0.48 to 0.86 under melt-stretched temperature 140 °C. In other words, the slope in the case of 140 °C is much milder than that of 120 °C. Local scale bond distortion might be more effective in the case of uniaxial extension at 120 °C than that at 140 °C.

Figure 4.9 (a) Stress-strain curve for P650K melt that uniaxial stretched at 120 °C with a Rouse Weissenberg number $W_R = 100$. The specimens are melt-stretched to different extent from $\lambda = 5$ to $\lambda = 8$. (b) Retractive tensile stress of melt-stretched specimens with different stretching ratios as a function of annealing time at annealing temperature 90 °C.
Figure 4.10 (a) Stress-strain curve for PS650K melt that uniaxial stretched at 140 °C with a Rouse Weissenberg number \( W_{IR} = 8.94 \). The specimens are melt-stretched to different extent from \( \lambda = 3 \) to \( \lambda = 7 \). (b) Retractive tensile stress of melt-stretched specimens with different stretching ratios as a function of annealing time at annealing temperature 90 °C.

Figure 4.11 Tensile stress that built up after certain amount of annealing time under 90 °C versus Cauchy stress that built up after melt-stretched to certain degree (\( \sigma_{\text{Cauchy}} = \sigma_{\text{engr}} \lambda \)) for PS650K that melt-stretched under 120 °C and 140 °C, respectively.

Next, we examine the universality of the elastic yielding behavior after melt stretching by studying a second polymer glass. Specifically, we subjected poly(methyl methacrylate)
(PMMA) to melt extension at a sufficiently high temperature (150 °C) where it displays the distinct yielding characteristic (i.e., a maximum in $\sigma_{\text{engr}}$) as shown in the inset of Figure 4.12. Confirming the phenomenon like polystyrene, we see more retractive stress at a larger stretching ratio. Besides, it indicated that the effect of melt stretching is greater at higher stretching ratios despite the decline of $\sigma_{\text{engr}}$ beyond $\lambda = 4$.

![Graph showing retractive stress during annealing at Tel-yield = 90 °C for PMMA](image)

Figure 4.12 Retractive stress during annealing at Tel-yield = 90 °C for PMMA that experienced melt stretching at five different melt stretching ratios from 3 to 7. At an initial Hencky rate $V/L_0 = 0.67$ s$^{-1}$, the inset shows peaking of $\sigma_{\text{engr}}$ as a function of stretching ratio $\lambda$, where the thin line is the neo-Hookean expression $\sigma_{\text{engr}} = G_{\text{pl}}(\lambda - 1/\lambda^2)$ with $G_{\text{pl}}$ being shear melt plateau modulus.

4.3.3.3 From different melt-stretching rate

Melt extension is applied on PMMA125K under the same temperature with different effective rates indicated by initial Rouse Weissenberg number ranging from 5.6 to 200 as shown in Figure 4.13. Specimen that undergoes melt stretch with lower rate also shows a lower retractive stress upon annealing. We quantify the magnitude of retractive stress as a
function of Rouse Weissenberg number \((W_iR)\) to further study the rate effect on melt stretching. The filled circle firstly converges to the filled square under low \(W_iR\) and then diverges as \(W_iR\) gets larger. Under low enough \(W_iR\) such as 5.6 and 10, yielding prevents sufficient chain stretching which leads to a less effective bond distortion. Within the range of high enough \(W_iR\), effect of transient network lead to a glassy-like mechanical behavior. Although the Cauchy stress available at \(\lambda =5\) is high, majority of the mechanical stress result from the viscous stress which is intersegmental in origin, it is has nothing to do with entanglement network, i.e., chain stretching, therefore the difference between Cauchy stress and retractive stress gets larger.
Figure 4.13 (a) Stress-strain curve for PMMA125K that melt-stretched under 130 °C with different Rouse Weissenberg numbers. (b) Retractive stress of melt-stretched specimens that uniaxial stretched under different Weissenberg number as a function of annealing time at annealing temperature 90 °C. Inset is tensile stress that built up after annealed for 1000s under 90 °C and Cauchy stress that built up after melt-stretched to certain degree (\(\sigma_{\text{Cauchy}} = \sigma_{\text{enr}} \lambda\)) as a function of Weissenberg numbers of melt-stretching.

4.3.4 Pre-annealing effect

Before mount the pre-deformed specimen to record the retractive stress, we leave the specimens into a chamber with a stress-free state under certain temperatures below its elastic yielding temperature for 5 min. The specimen after pre-annealed varies in induction time, for example, after took pre-annealing at 80 °C for 5min, the induction time shifts from 10s (as indicated by the control sample) to 60s. As shown in Figure 4.14 Although induction time is sensitive to the pre-annealing temperature, the tensile stress plateau is relatively unaffected.
Figure 4.14 Retractive tensile stress of melt-stretched specimens as a function of annealing time at annealing temperature 90 °C. Specimens are first annealed with stress-free under different temperature for 5 min before load between clamps. Inset is stress-strain curve of PS319K that uniaxial stretched under 125 °C.

4.3.5 Mechanical cycling

Cycling test can be achieved by heating up specimen and then cooling down as shown in Figure 4.15. Specifically, heating can be either siting at a constant temperature or gradual increasing in every cycle. For cycling carried out at 90 °C, the retractive stress plateau kept constant around 2 MPa and was not affected by cycling as shown in Figure 4.15 (a). Figure 4.15 (b) shows cycling test with step gradual temperature from 80 °C to 100 °C. Little retractive stress plateau difference was found between 90 °C and 100 °C.
Figure 4.15 (a) Retractive tensile stress of melt-stretched specimens as a function of annealing time at annealing temperature 90 °C. The heater is removed out after 1000s with the specimen loading between clamps under room temperature for 5 min and then move the heater back, the same procedure is repeated by three times. (b) Retractive tensile stress of melt-stretched specimens as a function of annealing time at several different annealing temperatures. The specimen is first annealed under 80 °C for 1000s before the heater is removed with the specimen loading between clamps under room temperature for 5 min and then move the heater back with a temperature of 90 °C, following by the same procedure with the heater back under 100 °C. Several numbers that in the plot indicate the tensile stress the specimen reaches at that time.

4.4 Further discussion

4.4.1 Study the nature of retractive stress based on experiments

4.4.1.1 Ruling out intersegmental viscous stress contribution

To study the nature of retractive stress upon annealing, we carried out the following experiments. Two specimens were subjected to melt extension under different conditions
to match a similar Cauchy stress ($\sigma_{\text{Cauchy}} = \sigma_{\text{engr}} \lambda$) at the end of stretching. We first apply different temperatures under the same rate. Straight line indicated Cauchy stress level in each case in Figure 4.16 (b). For melt stretching with the draw ratio $\lambda = 2$ under 120 °C, retractive stress is less than one third of the Cauchy stress, in the other case that melt stretching with the draw ratio $\lambda = 8$ under 140 °C, the retractive stress almost approaches the upper bound. Along the same line, we then match similar Cauchy stress by tuning rate under same temperature as shown in Figure 4.17. The result is the same under these two sets of testing. Higher draw ratio under melt-stretching leads to a larger magnitude of retractive stress. In either case, melt-stretching with $\lambda = 8$ induced much more chain deformation resulting in a larger amount of segmental distortion than that from the melt-stretching with $\lambda = 2$, therefore a higher level of retractive stress can be achieved.
Figure 4.16 (a) Stress-strain curve of PS319K that melt-stretched to different draw ratios at the same rate under 120 °C and 140 °C, respectively. (b) Retractive tensile stress of specimens that pre-deformed at 120 °C (square) and 140 °C (circle) under annealing temperature 90 °C. Straight line indicates the upper boundary that the tensile stress can built up by calculating the Cauchy stress buildup in melt state ($\sigma_{\text{Cauchy}} = \sigma_{\text{engr}} \lambda$).
Figure 4.17 (a) Stress-strain curve of PS319K that melt-stretched to different draw ratios at 120 °C with two different rates. (b) Retractive tensile stress of specimens that pre-deformed under rate 0.4 s⁻¹ (square) and 0.017 s⁻¹ (circle) upon annealing temperature 90 °C. Straight line indicates the upper boundary that the tensile stress can built up by calculating the Cauchy stress buildup in melt state \( \sigma_{\text{Cauchy}} = \sigma_{\text{engr}} \lambda \).

Another way to study the nature of the elastic yielding is to apply melt extension at a low draw ratio. As shown in Figure 4.18, transient glassy response is achieved under each case. Larger effective rate leads to a greater gap between Cauchy stress and retractive stress, which prove the viscous stress contribution in the Cauchy stress could not participate in the retractive stress, in other words, intersegmental viscous stress itself could not induce the elastic yielding phenomenon.
4.4.1.2 Molecular weight effect on retractive stress

To further study intersegmental stress buildup in melt deformation had contribution on the retractive stress emergence upon annealing, we conducted tests based on PMMA with different molecular weight. PMMA35K is a short chain system that is barely entangled given entanglement molecular weight $M_c=13$Kg/mol compared with PMMA125K. To confirm their difference on their entanglement levels, we first conducted melt-deformation under squeezing reaching to the same $\lambda = 7$ as shown in Figure 4.19 (a). After quenched these pre-treated samples, we heated them up at 150 °C to carry out a recovery test. While PMMA125K could take 431% shrinkage after 5 minutes, PMMA35K could only shrink 229%, which indicating there is a much higher entanglement level of PMMA125K than that of PMMA35K. Specifically, instead of heating these sample well above $T_g$, we can
also anneal such melt-deformed samples at 80 °C well below $T_g$ as shown in Figure 4.19 (b), there was no retractive stress show up in PMMA35K. By contrast, pre-treated PMMA125K showed normal elastic yielding phenomenon. The experimental result is consistent with our understanding that well-entanglement polymer system is the origin of elastic yielding behavior.

Figure 4.19 (a) Stress-strain curve of PMMA35K that melt-squeezed at 120 °C with initial rate 0.2 s$^{-1}$ (square) and PMMA125K (circle) that melt-squeezed at 130 °C with initial rate 0.02 s$^{-1}$. (b) Retractive tensile stress of melt-squeezed PMMA35K (square) and PMMA125K (circle) as a function of annealing time at annealing temperature 80 °C.
4.4.1.3 Shrinkage of melt-deformed sample upon annealing

Chain deformation could reach different levels corresponding to different origin of force buildup in melt state. For example, Entropic force arises when a chain is deformed. Deformation involves orientation of backbone bonds but no distortion at bond level, i.e., no bond stretching and no bond angle change. Conversely, when the chain deformation is more severe so that bond length increases, enthalpic force emerges corresponding to an increase in the internal energy of intrachain origin. Upon annealing, we would like to study the difference between pre-treated samples with different melt-stretching condition that involve either enthalpic or entropic force buildup. Two different stretching conditions were carried out as shown in Figure 4.20.
Figure 4.20 PMMA125K melt deformation at 130 °C under a strong condition involving a Rouse Weissenberg number $W_R = 52.5$ to $\lambda = 5$ (circle) and under a mild condition involving Rouse Weissenberg number $W_R = 0.25$ to $\lambda = 3.5$ (square).

After sample underwent deformation in the melt state, upon annealing, instead of recording mechanical data in terms of retractive stress, we can anneal sample and track its shrinkage. As shown in Figure 4.21, upon annealing such pre-deformed sample, sample length first increases due to thermal expansion, after reaching thermal equilibration, shrinkage takes place (dash lines in Figure 4.21 indicate the shrinkage start point). Shrinkage measurements were carried out at four different temperatures and then normalize the data from the shrinkage starting point as shown in Figure 4.22.

Figure 4.21 Real time specimen length over its initial length as a function of time for (a) pre-deformed sample upon annealing at different temperatures after underwent melt stretching involving a Rouse Weissenberg number $W_R = 0.2$ to $\lambda = 3.5$ and (b) pre-deformed sample upon annealing at different temperatures after underwent melt stretching involving a Rouse Weissenberg number $W_R = 52.5$ to $\lambda = 5$. 
Figure 4.22 Normalization of specimen length by percentage as a function of time starting from the shrinkage point (dash line in Figure 4.21) after reaching thermal equilibration for (a) pre-deformed sample upon annealing at different temperatures after underwent melt stretching involving a Rouse Weissenberg number $W_iR = 0.2$ to $\lambda = 3.5$ and (b) pre-deformed sample upon annealing at different temperatures after underwent melt stretching involving a Rouse Weissenberg number $W_iR = 52.5$ to $\lambda = 5$. 
Since we have two cases that under either mild or strong melt-stretching condition, comparison can be made about how long it takes for these two kinds of pre-treated sample to reach the same percentage of shrinkage, solid line shown in Figure 4.22 is the moment for specimen shrank 0.75% amount and the corresponding times it took under different temperatures. Time that required for 0.75% shrinkage is then plot as a function of temperature as shown in Figure 4.23. Result shows sample that melt-deformed under strong condition \((W_{IR} = 52.5 \text{ to } \lambda = 5)\) could shrink much faster than the other case, at 90 °C, the contrast between two cases can be almost one order difference. Alpha relaxation time based on pre-yield relaxation behavior measurement in section 4.6.1 can be also plotted together in terms of shifting factor for temperature dependence comparison as shown in Figure 4.24. Mild case was found to \((W_{IR} = 0.2 \text{ to } \lambda = 3.5)\) share a similar temperature dependence with alpha relaxation time, while there is a stronger temperature dependence in the other case.
Figure 4.23 Time required to take 0.75% shrinkage under different temperatures for (a) pre-deformed sample upon annealing at different temperatures after underwent melt stretching involving a Rouse Weissenberg number $W_i R = 0.2$ to $\lambda = 3.5$ (square) and (b) pre-deformed sample upon annealing at different temperatures after underwent melt stretching involving a Rouse Weissenberg number $W_i R = 52.5$ to $\lambda = 5$ (circle).
Figure 4.24 Shifting factor as a function of temperature for alpha relaxation time (square), mild melt-stretching case with a Rouse Weissenberg number \( W_iR = 0.2 \) to \( \lambda = 3.5 \) (diamond) and strong melt-stretching case with a Rouse Weissenberg number \( W_iR = 52.5 \) to \( \lambda = 5 \) (circle).

To examine the universality of such behavior, PS650K is also studied in a similar way. Sample is first subjected to melt-extension under two conditions as shown in Figure 4.25.
Figure 4.25 PS650K melt deformation at 140 °C under a strong condition involving a Rouse Weissenberg number \( Wi_R = 10 \) to \( \lambda = 5 \) (circle) and under a mild condition involving a Rouse Weissenberg number \( Wi_R = 0.2 \) to \( \lambda = 3 \) (diamond).

Pre-treated sample is then annealed at different temperatures and shrinkage measurement was conducted, followed by further normalization from the shrinkage starting point as shown in Figure 4.26.
Figure 4.26 Real time specimen length over its initial length as a function of time for (a) pre-deformed PS650K upon annealing at different temperatures after underwent melt stretching involving a Rouse Weissenberg number $\dot{W}_R = 0.2$ to $\lambda = 3$ and (b) pre-deformed PS650K upon annealing at different temperatures after underwent melt stretching involving a Rouse Weissenberg number $\dot{W}_R = 10$ to $\lambda = 5$. Normalization of specimen length by percentage as a function of time starting from the shrinkage point after reaching thermal equilibration for (c) melt-stretched PS650K involving a Rouse Weissenberg number $\dot{W}_R = 0.2$ to $\lambda = 3$ and (d) melt-stretched PS650K involving a Rouse Weissenberg number $\dot{W}_R = 10$ to $\lambda = 5$. 
To compare how long it takes for these two kinds of pre-treated sample to reach the same percentage of shrinkage 0.55% (solid line in Figure 4.26 (a) and (b)), time required for that amount of shrinkage as well as alpha relaxation time is plotted as a function of temperature as shown in . Result in Figure 4.27 shows alpha relaxation relatively scale with the mild melt-deformation case ($W_{IR} = 0.2$ to $\lambda = 3$). Besides, specimen that melt-deformed under strong condition ($W_{IR} = 10$ to $\lambda = 5$) could shrink much faster than the other case, at 90 °C, the contrast can be more than one order difference between these two cases.

Figure 4.27 (a) Time required to take 0.55% shrinkage under different temperatures for pre-deformed PS650K upon annealing at different temperatures after underwent melt-stretching involving a Rouse Weissenberg number $W_{IR} = 0.2$ to $\lambda = 3$ (square) and for pre-deformed PS650K upon annealing at different temperatures after underwent melt-stretching involving a Rouse Weissenberg number $W_{IR} = 10$ to $\lambda = 5$ (circle) as well as alpha relaxation time on different temperatures (diamond).
Based on the experimental results on both PMMA and PS, we concluded that entropic force buildup in a mildly deformed case resulted in a slower shrinkage upon annealing such pre-treated sample, by contrast, shrinkage is much faster for the strong deformed case because of enthalpic force buildup in melt state. Entropic driving force could be alpha relaxation time dependent, while enthalpic force has a stronger temperature dependence.

4.4.2 Study the nature of retractive stress based on Molecular dynamics simulation

To see how segmental stretching took place during melt extension, we carried out bead-spring-model based molecular dynamics (MD) simulations of melt extension for $Wi_R = 1$ and 30. Figure 4.28 indicates that startup extension at $Wi_R = 1$ produces measurable chain stretching on the scale of several beads. If we take a segment of $n$ beads to be part of a free chain, not a part of an entanglement strand, then its relaxation time might be given by $\tau_n = \tau_R (n/N)^2$ where $N$ is the chain length and $\tau_R$ is the Rouse time of the whole chain. At $Wi_R = 1$, the level of segment deformation would be around $(n/N)^2$. For $n = 4$ and $N = 500$, this magnitude $(4/500)^2 < 0.01\%$. Instead, we observed considerable deformation ($> 1\%$) at $n = 4$ as shown in Figure 4.28 and the magnitude of the deformation increases nearly linearly with $\lambda$. It suggests that all local deformation is enslaved by the network deformation at the level of entanglement strand. Consequently, despite a relatively low Hencky rate considerable distortion can take place within each entanglement strand and monotonically grow with $\lambda$. 

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Figure 4.28 Stretching of internal structure, in terms of the average end-to-end distance during melt extension at two Hencky rates corresponding to the product of Rouse time and rate, $Wi_R$, equal to 1 and 30 respectively. The top curve represents the affine extension limit, given by $(\lambda^2/3+2/\lambda)$. $<(r/r_0)^2−1>$ for $|i−j| = 4$ or 36 represents the averaged end-to-end distance for all segments comprised of 4 or 36 beads.

To elucidate the origin of retractive stress observed during annealing, MD simulations were carried out based on a coarse-grained model for polystyrene. The system was first uniaxially extended at 300 K to a draw ratio $L/L_0 = 2.2$. The data analysis shows that the tensile extension produces significant bond stretching. The unloading at the end of extension, i.e., setting the system constraint-free, allows the partial bond retraction and disorientation, as shown in Figure 4.29. An apparent stress-free state is reached and the system stops shrinking when the intrachain retractive forces are balanced by intermolecular compression. At this point, within the time scale of our simulation, the potential barrier against relocating to another energy minimum on the energy landscape is too high to climb over. Nevertheless, because of the mechanical rejuvenation (by the extension to $L/L_0$
= 2.2), the height of the energy barrier between the present local energy minimum and a neighboring local minimum is expected to be lower than the barrier height in an undeformed system. The reduced barrier height would allow the annealing to cause more rapid interchain re-packing. Specifically, upon annealing at 360 K, interchain re-packing takes place, causing force imbalance between the distorted load-bearing strands and the vitreous surroundings while the bond length and orientation remain constant.

Figure 4.29 Orientation function (P2) and average bond length of the backbone bond against time during deformation at 300 K (regime (1)), upon releasing at 300 K (regime (2)) and during elastic yielding upon annealing at 360 K (regime (3)).

The lower barrier height in the rejuvenated state produced by the pre-deformation may imply that there is higher molecular mobility. In terms of the orientational correlation, Figure 4.30 shows that the decorrelation indeed occurs much earlier in the pre-deformed state relative to the non-deformed system. Thus, the MD simulation confirms that upon annealing of a pre-deformed polymer the emergence of retractive stress stems from the force imbalance arising from structural adjustment. The sufficient pre-deformation altered
the energy landscape, making it possible for the thermal fluctuation to rearrange segmental packing.

Figure 4.30 Orientational correlation function against time in the pre-deformed and non-deformed systems at 360 K.
4.5 Conclusion

In conclusion, by examining the mechanical behavior of pre-deformed polymers in their glassy state based on experiment as well as molecular dynamic simulation, we show that rubbery melt-stretching results in considerable bond distortions on repeat unit scale. Given the reduced potential energy barrier, the system is no longer stable during annealing against significant interchain repacking. As a result, melt-deformed polymer glasses show considerable retractive stress after certain induction time in their glassy state. This work systematically investigates how characteristics of induction time and magnitude of the tensile stress change as a function of the temperature at which melt stretching is carried out, the degree of melt stretching, the annealing temperature. The conclusion that melt-stretching can cause bond distortion on the scale of repeated units is consistent with the past studies and should inspire more theoretical development of molecular models on melt deformation.
4.6 Appendix

4.6.1 Stress relaxation from pre-yield deformation.

Tensile deformation of 1% strain was applied on stress relaxation test for PS319K and PMMA125K as shown in Figure 4.31.

![Figure 4.31 Stress relaxation from pre-yield extension as a function of time at four different temperatures from 60 °C to 90 °C for (a) PS319K and (b) PMMA125K.](image)

KWW fitting was then applied to provide alpha relaxation time ($\tau_\alpha$) data in Figure 4.24 and Figure 4.27.

KWW equation given by

$$\sigma(t) = \sigma(t = 0) * a * \exp[-(t/\tau_\alpha)^\beta]$$  \hspace{1cm} (4.1)
4.6.2 Small amplitude oscillatory shear (SAOS)

Terminal relaxation time $\tau$ for each polymer material is determined from small amplitude oscillatory shear (SAOS) as shown in Figure 4.32. Measurements were carried out at different temperatures to generate a master curve by both vertically and horizontally shifting the data collected at each temperature.
Figure 4.32 Storage and loss moduli G’ and G’’ as a function of frequency for (a) PS319K, (b) PMMA125K, (c) PS650K.
CHAPTER V

SUMMARY

Understanding polymer dynamic and behavior under melt deformation is an important topic. Extended the idea from classical rubber elasticity theory\textsuperscript{22, 101}, transient network models\textsuperscript{102, 103} indicated chain entanglement is the key rheological feature. Packing model\textsuperscript{104, 105} and percolation model\textsuperscript{106} were purposed to depict the onset of chain entanglement. Further development on molecular-level description of entanglement dynamics involved pioneering work on reptation model by de Gennes\textsuperscript{3} and tube model of Doi and Edwards\textsuperscript{6}. Molecular-model-based research on polymer melt over four decades has consumed tremendous effort from generations of polymer scientists. By contrast, much less efforts were paid to study and understand mechanical behavior of polymer glass. Given the fact that polymer glass sitting on a non-equilibrium and nonergodic state, it is really challenging to establish a molecular level understanding on polymer glass under large deformation. Thus, pioneering work from Dr. Ediger and coworker\textsuperscript{39, 107}, studies based on molecular dynamic (MD) simulation\textsuperscript{43, 108}, and microscopic Nonlinear Langevin Equation (NLE) theory developed by Chen and Schweizer\textsuperscript{109-112} are particularly notable.
Recently, based on the knowledge on melt rheology and inspired by the formation of polymer glass. A molecular model was purposed to better understand polymer glasses under large deformation. The model regards polymer glasses of sufficiently high molecular weight as a structural hybrid, with a primary structure due to short-ranged van der Waals intersegmental interaction and a chain network due to chain connectivity and uncrossability. In terms of nonlinear behaviors of polymer glass under large deformation, chain network is essential for yielding and plastic flow.

By bridging the knowledge between polymer melt and polymer glass, this work carried out various experimental tests including extension and compression deformation as well as the assistance of computer simulation to test structural hybrid molecular model and to understand melt-deformation effect on mechanical behavior of polymer glass.

In Chapter II, a brief introduction about glass transition and polymer glasses was reviewed. Typical testing methods such as tensile and compression methods to characterize the mechanical behaviors in terms of stress and strain were described. Different nonlinear behaviors including yielding, necking, strain hardening as well as brittle and ductile transition were introduced. Next, literature work about nonlinear behaviors of polymer glass on both experiments and theories along with test structural hybrid molecular model were reviewed.

In Chapter III, planar extension was applied in melt state to introduce structural anisotropy in various polymer glasses and probe their mechanical responses under compression. Both experiment and molecular-dynamics simulation demonstrate sharply
anisotropic plastic deformation and preferential crack formation. For example, by dilating the chain network areal density in the lateral dimensions, polymer glasses such as PS and PMMA can switch from ductile to brittle response. Conversely, by increasing the lateral network density, a brittle polystyrene can turn ductile. The experimental findings confirm the existence of chain network as well as illustrate its role in compression and support the idea that the lateral (areal) network density resists the horizontal expansion and determines whether or not crack can form and result in brittle fracture in a specific plane. Thus, these compression experiments extend the previous understanding concerning extension of polymer glasses.

In Chapter IV, we carried out mechanical testing to elucidates how melt extension results in a rejuvenated glassy state. Whether melt stretching produces sufficient enthalpic stress that would show up during annealing of such pre-treated glassy polymers (e.g., polystyrene and PMMA). Specifically, quenching of melt stretched polystyrene and PMMA is shown to trap significant chain tension: Upon annealing the samples show measurable retractive tensile stress. Molecular dynamics simulation confirms that the emergent retractive stress is due to molecular force imbalance at the elevated temperature where interchain repacking occurs because of the reduced energy barrier in the pre-deformed polymer glass. Melt stretching may have produced non-negligible distortions at the bond level, corresponding to a significant non-entropic force.
BIBLIOGRAPHY


