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# Elastic Yielding in Cold Drawn Polymer Glasses Well below the Glass Transition Temperature

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# **Elastic yielding in cold drawn polymer glasses well below glass transition temperature**

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## **Abstract**

This Letter reports elastic-driven internal yielding in strained ductile polymer glasses. After cold drawing of two different polymer glasses to neck at room temperature, we show that the samples display considerable retractive stress when warmed up above the storage temperature but still considerably below their glass transition temperatures. We conclude that the elastic yielding arises from the distortion of backbones leading to chain tension in the network.

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Upon large deformation, polymers of high molecular weight exhibit a rich variety of nonlinear responses. At temperatures above the glass transition temperature  $T_g$ , their rheological behavior dictates processing and manufacturing efficiency of polymeric materials whose annual worldwide annual production is several hundred-billion pounds. Here polymer entanglement, arising from chain uncrossability, forms a rubbery network and plays an essential role in controlling the initial elastic deformation. Below  $T_g$ , the vitrification of all segments in the chain-like molecules introduces significant complication in the physics of polymer glasses. In addition to the chain network there is also a primary structure due to the immobilization of the segments upon the vitrification. The intricate coupling between inter-chain and intra-chain forces makes the description of deformation, yielding, strain localization and fracture in polymer glasses rather challenging to formulate. On the other hand, a microscopic understanding of mechanical behavior under large deformation may actually reveal useful information about the nature of the glass transition. The large deformation behavior of polymer glasses is important because nonlinear mechanical properties determine the performance of products made with glassy polymers [1-3].

In recent years there has been a significant resurgence of research interest to explore the origin of mechanical stress and nature of microscopic events taking place during large deformation of polymer glasses. New experiments [4-8], theories [9-15], and computer simulations [16-24] have been performed to delineate physical processes governing polymer glass deformation. The measurements of the local mobility [5, 6] reveal a greatly reduced relaxation time  $\tau$  upon yielding of the primary structure and rising of the local strain rate  $\dot{\epsilon}$ . On the other hand, when the sample slows down during its tensile creep under a constant load,  $\tau$  increases again, contradicting the basic formulation of plastic flow by Eyring [25]. Nevertheless, the consensus from the recent studies [20, 26] is that the dissipative plastic deformation generates the observed high mechanical stresses.

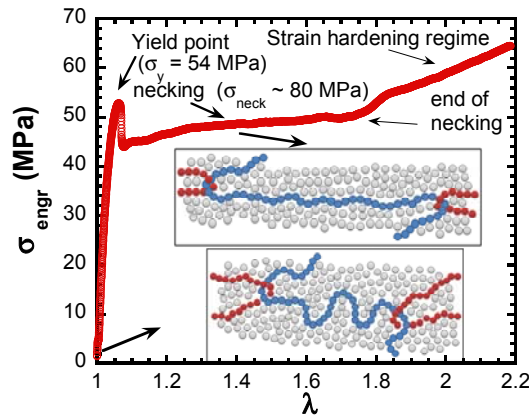


Fig. 1 Stress-strain curve of the PC glass undergoing startup uniaxial extension at 23 °C. The dog-bone shaped PC of original length  $L_0 = 39$  mm is extended at a constant crosshead speed  $V = 6$  mm/min. The inset cartoons depict straining of a load-bearing strand in the chain network.

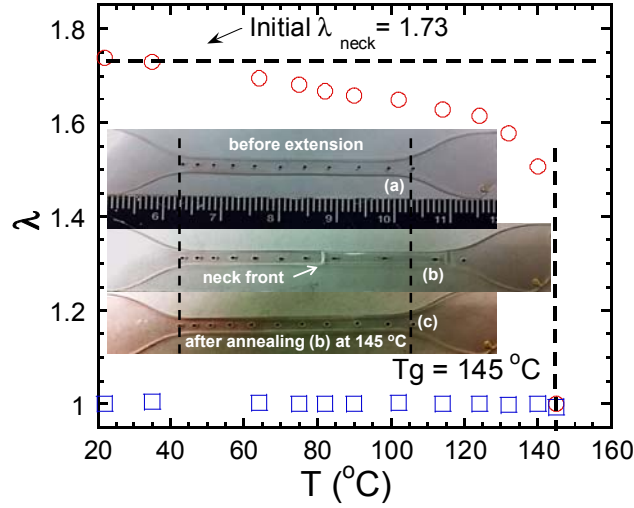


Fig. 2 Dimensional retraction upon warming up to the various temperatures including  $T_g = 145$  °C, denoted by the vertical dashed line. The pre-necked sample in photo (b) was made by first stretching a PC specimen in photo (a) at a crosshead speed  $V = 10$  mm/min at  $45$  °C to a natural draw ratio  $\lambda_{neck} = 1.73$  and then storing it at  $23$  °C for 24 hrs. After annealing at these discrete temperatures for 24 hrs, the length of the annealed specimens was measured. The circles represent an average over three repeated runs at each temperature. Photo (c) shows that annealing at  $T_g$  for 24 hrs allows the specimen to restore its original length.

The present work describes a series of new phenomena that may pertain to the nature of mechanical responses of a most common ductile polymer glass, polycarbonate (PC). PC can undergo considerable tensile extension before fracture. At large deformation, we can perceive the polymer glass as a hybrid [27], made of a primary structure due to the vitrification-induced jamming and a chain network, as shown in the inset of Fig. 1. After the yielding of the primary structure with increasing extension, shear yielding of the chain network takes place to initiate necking. The uniaxial extension shows in Fig. 1 that the tensile stress is remarkably flat during the neck front propagation, where the neck is stable in the sense that its dimensions remain constant before the completion of necking. In absence of any plastic deformation in the neck, what can produce the observed tensile stress level of  $\sigma = \sigma_{engr} \lambda_{neck} = 80$  MPa that far exceeds the yield stress  $\sigma_y = 54$  MPa (measured in Fig. 1) for the primary structure?

Upon unloading a necked PC specimen at room temperature, the strained PC retracts only a few percent instead of returning to its original dimensions. Because of re-vitrification during the stress release, additional retraction of the strained chain network is prevented by the inability of the segments to hop over one another. However, after annealing at the increasing temperatures for 24 hrs or longer, the pre-necked PC shows a growing amount of shrinkage as shown in Fig. 2. This dimensional change [28-34] at temperatures far below  $T_g$  is actually rather revealing: it must be caused by the strained chain network.

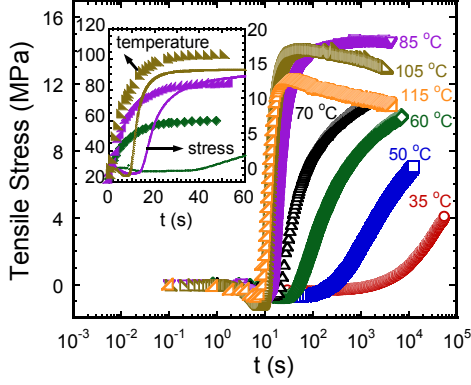


Fig. 3(a)

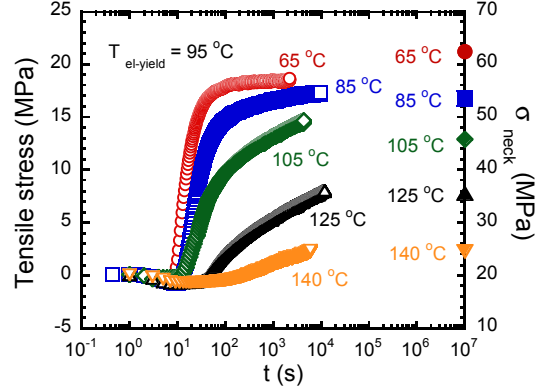


Fig. 3(b)

Fig. 3 (a) Elastic yielding phenomenon at different annealing temperatures. Cold drawn samples were prepared at 23 °C at constant crosshead speed  $V = 6$  mm/min. After storage under 23 °C for 24 hrs, the pre-necked sample was placed in an Instron tester and heated up. The rising temperature in the specimen causes it to slightly expand between the two clamps so that load cell picks up a negative force in the direction of pushing the clamps away from each other. While holding the clamps in their original positions, the specimen gradually starts to pull on the clamps, reflecting emergence of tension within the specimen. (b) The same measurements as in (a) for samples that were extended to neck at other temperatures of 65 °C, 85 °C, 105 °C, 125 °C and 140 °C respectively, involving the same  $V = 6$  mm/min. During unloading the sample was sprayed with icy water to quench. After storage under 23 °C for 24 hrs, the pre-necked samples were brought to 95 °C to observe the elastic yielding phenomenon.

The slight degree of specimen shrinkage has been seen before [28-35]. However, the explanation for the emergence of a "retractive stress" during annealing of cold drawn polymers as volume change [30] is entirely inconsistent with the present data. The focus of the present work is to probe the manifestation of the embedded elastic stress that causes the shrinkage. Instead of extending the PC to the point of breaking beyond  $\lambda = 2$ , we collect pre-necked specimens by stopping short of the onset of the "strain hardening" regime. After days of storage at 23 °C when the pre-necked PC no longer changes its dimensions and is thus apparently stress free, we mount the specimen at the storage temperature onto two clamps of an Instron tester that hold the specimen fixed at a constant length. Without any relative displacement of the clamps, no stress is detected. However, upon warming up the specimen to the different temperatures that are still far below  $T_g$ , considerable tension pulls the two clamps inward, as measured in Fig. 3(a). The emergence of the stress occurs more quickly at a higher temperature. For the same pre-necked specimens, the tension builds up three orders of magnitude faster as the annealing temperature increases from 35 to 85 °C. Upon further analysis, we find that the kinetics obey Eyring-Arrhenius like relation:  $\tau \sim \exp[(E - A\sigma)/RT]$ , where  $\tau$  is a characteristic time scale extracted from Fig. 3(a) and  $R$  is the gas constant and the activation energy  $E$  is estimated to be 155 kJ/mol.

The inset of Fig. 3(a) shows the temperature profiles (larger symbols) as well as corresponding stress signals. The initial negative stress reading occurs because of the thermal expansion of the specimen. (See the Supplementary Materials for a detailed description of the setup used to heat the specimen.) The specimen actually bent during the thermal expansion. Then, as the hidden chain tension grows to cause the unjamming of segments surrounding the load-bearing strands, the specimen retracts and straightens to produce the observed tensile stress. At the higher temperatures, the stress change is non-monotonic: At 105 and 115 °C, the elastic yielding is so severe that the residual stress was actually able to relax as the segments hop around under the driving force of the strained chain network.

The PC specimens drawn at other temperatures exhibit a similar phenomenon as shown in Fig. 3(b) where the PC glass was extended to neck at a crosshead speed  $V = 6$  mm/min at temperatures ranging from 65 to 140 °C and quenched with icy water to rapidly vitrify the necked glass. There is considerable and systematic drop in the driving force for elastic yielding with increasing cold-drawing temperature. The characteristic time  $\tau$  changes in a way consistent with the Eyring formula  $\tau \sim \exp(-A\sigma/RT)$ .

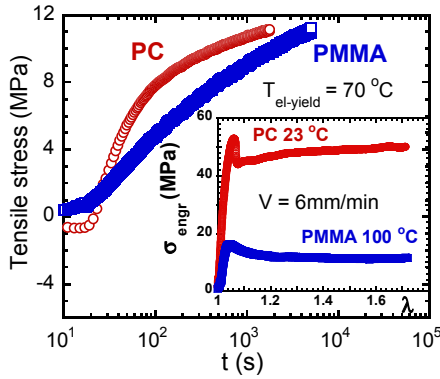


Fig. 4

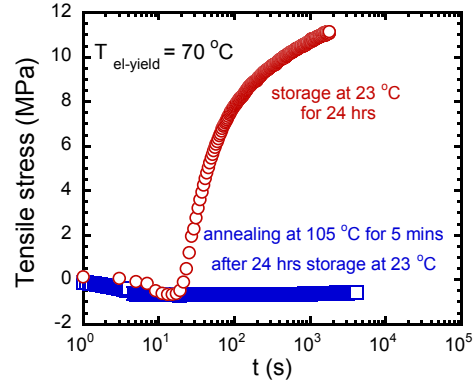


Fig. 5

Fig. 4 Growing tension (i.e., the elastic yielding phenomenon) at the elevated temperature  $T_{\text{el-yield}} = 70$  °C from a pre-necked PMMA glass prepared at 100 °C by uniaxial extension  $V = 6$  mm/min to an stretching ratio  $\lambda_{\text{neck}} = 1.72$ , subsequent thermal quenching with icy water before storage under 23 °C for 24 hrs, along with the data from a pre-necked PC (the same data from Fig. 1). The stress-strain curves of the "cold" drawing at 23 °C for PC and 100 °C for PMMA, are shown in the inset.

Fig. 5 Absence of elastic yielding (squares) at 70 °C after 5 min annealing (at  $T = 105$  °C, still 40 °C below  $T_g$ ) of the same cold drawn specimen as described in Figs. 2 and 3 that shows rising tensile stress (circles) over time (i.e., elastic yielding).

To test whether the elastic yielding phenomenon is specific to PC, we "cold draw" another common polymer glass: poly(methyl methacrylate) (PMMA) at 100 °C. Fig. 4 shows that a "cold" drawn PMMA also exhibits the retractive stress over time at  $T_{\text{el-yield}} = 70$  °C, which is 35 °C below its glass transition temperature  $T_g = 105$  °C. Thus, the remarkable emergence of retractive stress at temperatures well below  $T_g$

occurs despite the apparently dramatic difference between PC and PMMA. It is plausible that all ductile polymer glasses of high molecular weight is capable of displaying this elastic internal yielding phenomenon.

Solid-like deformation of polymers can occur both above and below  $T_g$ . Below  $T_g$ , the stress level is one to two orders of magnitude higher than that involved in melt deformation. The stable necking evidently demonstrates the ability of the chain network depicted in Fig. 1 to bear the load because the Cauchy well exceeds the yield stress at which the primary structure breaks down. In such an anelastic state, the tension in a load-bearing strand (LBS) is far greater than what the entropic elasticity (arising from chain conformational change) could account for. In other words, the straining in glassy state of the chain network may have the efficiency to stretch or bend or twist the covalent bonds in the backbone. Such backbone distortions apparently do not disappear as long as the storage temperature is well below  $T_g$ . The vitrification assures that the distorted bonds remain stuck in the highly energetically unfavorable states. Warming up such a strained polymer glass weakens the vitrification so that the primary structure can locally yield driven by the backbone tension, involving hopping of one segment over another. Such local unjamming allows the intra-chain tension to transmit along the LBS so that we observe the macroscopic tension.

In other words, chain conformational change is not a pertinent concept to describing large deformation of polymer glasses. We demonstrate this assertion with the following experiment. After the cold drawing of PC at room temperature to neck as described in Figs. 1-2 and storing the pre-necked specimen at 23 °C for 24 hrs, we annealed it at 105 °C (still 40 °C below  $T_g$ ) for five minutes. During the quick annealing the specimen shrank negligibly, i.e., by 3 %, so that the chain (uniaxial) deformation of 73 % remained little changed. Although the quick annealing preserved the chain conformation, the elastic yielding behavior disappeared as shown in Fig. 5: the specimen remained bent to produce a negative stress. Clearly, any embedded bond distortion produced by the cold drawing has vanished sufficiently so that there is insufficient chain tension to overcome the vitrification at  $T_{el-yield} = 70$  °C. Similarly, we show in Fig. S.2 in the Supplementary Materials that drawing above  $T_g$ , although resulting in equally large conformational changes, does not produce any effect of elastic yielding.

In conclusion, the remarkable elastic internal yielding phenomenon allows us to demonstrate the intra-chain component of the mechanical stress in tensile deformation of polymer glasses. The backbone distortion in the strained chain network seems necessary to cause yielding of the primary structure or unjamming of the vitrified segments upon warming up from the storage temperature to an elevated temperature where the polymer glass is still in a deeply glassy state, e.g., still 100 degrees below  $T_g$  in the case of PC. The elastic-yielded specimens display considerable tensile stress when held fixed between two points. A polymer glass extended to neck at a lower temperature show higher chain tension during the elastic yielding. The hidden tensile stress takes a shorter time to emerge at a higher annealing temperature. Thus, the phenomenon may be in spirit analogous to the

behavior of stress induced dynamic yielding in polymer glasses [36-39].

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