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

Shiwang Cheng and Shi-Qing Wang*

Maurice Morton Institute of Polymer Science and Engineering, University of Akron, Akron, Ohio 44325, USA
(Received 26 October 2012; revised manuscript received 30 November 2012; published 7 February 2013)

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 intra-segmental tension in the chain network.

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 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 chainlike molecules introduces significant complication in the physics of polymer glasses. In addition to the chain network, there is also a primary structure owing to the immobilization of the segments upon the vitrification. The intricate coupling between interchain and intrachain 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 τ upon yielding of the primary structure and rising of the local strain rate $\dot{\varepsilon}$. On the other hand, when the sample slows down during its tensile creep under a constant load, τ 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.

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 owing to the vitrification-induced segmental 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 the 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)?

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 revitrification in the external-stress-free state, additional retraction of the strained chain network is prevented by the
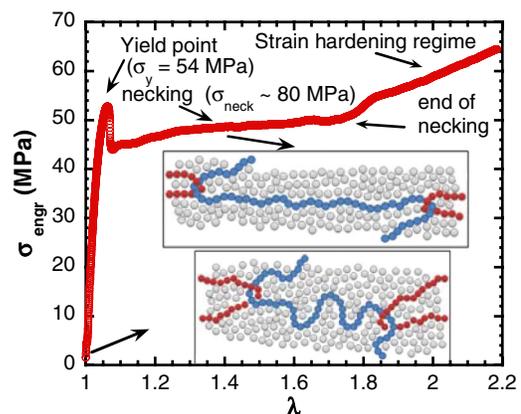

FIG. 1 (color online). Stress-strain curve of the PC glass undergoing startup uniaxial extension at 23 °C. The dog-bone-shaped PC of original length $L_0 = 39$ mm is extended at a constant crosshead speed $V = 6$ mm/min. The inset cartoons depict straining of a load-bearing strand in the chain network.
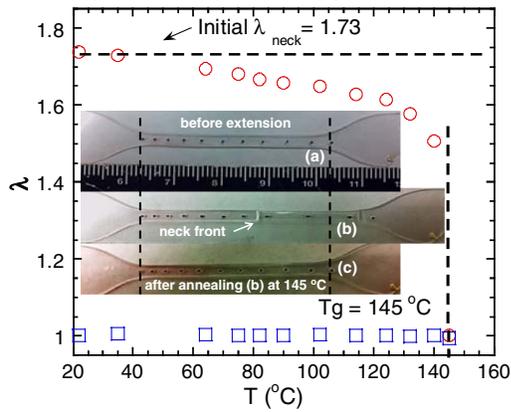
FIG. 2 (color online).   Dimensional retraction upon warming up to the various temperatures including $T_g = 145\,°C$, denoted by the vertical dashed line. The prenecked sample in (b) was prepared by first stretching a PC specimen in (a) at a crosshead speed $V = 10\,\text{mm/min}$ at $45\,°C$ to a natural draw ratio $\lambda_{neck} = 1.73$ and then storing it at $23\,°C$ for 24 h. After annealing at these discrete temperatures for 24 h, the length of the annealed specimens was measured. The circles represent an average over three repeated runs at each temperature. (c) Annealing at T_g for 24 h allows the specimen to restore its original length.

inability of the segments to hop over one another on short time scales. However, after annealing at the increasing temperatures for 24 h, the prenecked PC shows a growing amount of shrinkage as shown in Fig. 2. The dimensional change at temperatures far below T_g is actually rather revealing: it must be caused by the strained chain network.

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 is unsatisfactory [30]. 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 prenecked specimens by stopping short of the onset of the "strain hardening" regime. After days of storage at $23\,°C$ when the prenecked 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 prenecked specimens, the tension builds up 3 orders of magnitude faster as the annealing temperature increases from 35 to $85\,°C$. Upon further analysis, we find that the kinetics obey an Eyring-Arrhenius-like relation: $\tau \sim \exp[(E - A\sigma)/RT]$, where τ is a characteristic time scale extracted from Fig. 3(a), R is the gas constant, and the activation energy E is estimated to be 155 kJ/mol.

The initial negative stress reading occurs because of the thermal expansion of the specimen. (See the Supplemental Material [36] for a detailed description of the setup used to heat the specimen.) The specimen, held at a constant length, 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 nonmonotonic: At 105 and $115\,°C$, the elastic yielding is
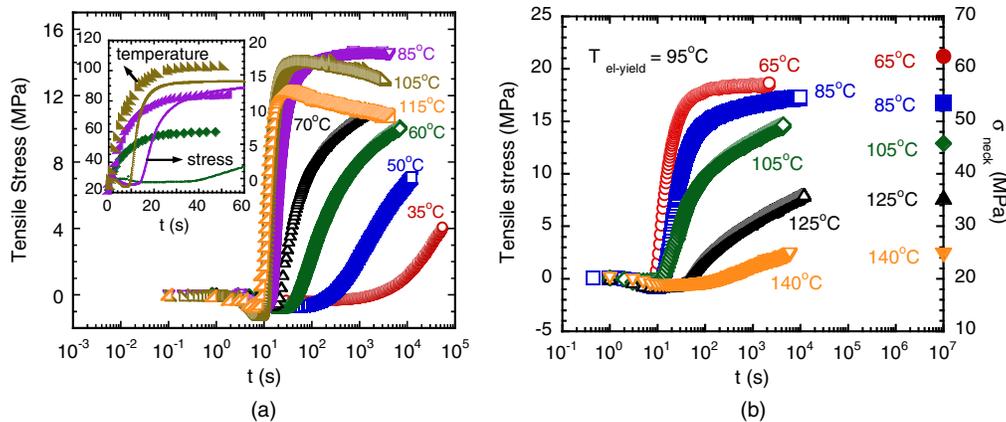

FIG. 3 (color online).   (a) Elastic yielding phenomenon at different annealing temperatures. Cold drawn samples were prepared at $23\,°C$ at constant crosshead speed $V = 6\,\text{mm/min}$. After storage under $23\,°C$ for 24 h, the prenecked sample was placed in an Instron tester and heated up. While holding the clamps in their original positions, the specimen eventually starts to pull on the clamps, reflecting emergence of tension within the specimen. The inset of Fig. 3(a) shows the temperature profiles (symbols in °C) as well as the corresponding stress signals (lines in MPa). (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 $V = 6\,\text{mm/min}$. Before unloading the sample was sprayed with icy water to quench. After storage under $23\,°C$ for 24 h, the prenecked samples were brought to $T_{el-yield} = 95\,°C$ to observe the elasic yielding phenomenon.
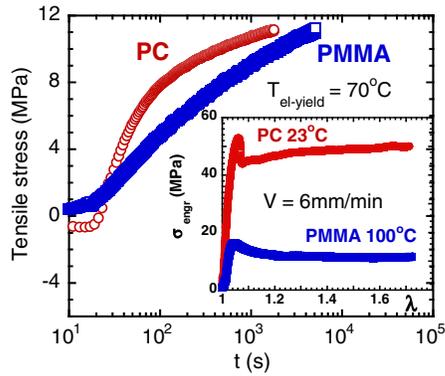
FIG. 4 (color online). Growing tension (i.e., the elastic yielding phenomenon) at the elevated temperature $T_{el\text{-}yield} = 70\,°C$ from a prenecked PMMA glass prepared at $100\,°C$ by uniaxial extension $V = 6\,mm/min$ to $\lambda_{neck} = 1.72$, followed by thermal quenching with icy water before storage under $23\,°C$ for 24 h, along with the data from a prenecked 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 (color online). 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).

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 a considerable and systematic drop in the driving force for elastic yielding with an increasing cold-drawing temperature. The characteristic time τ changes in a way consistent with the Eyring formula $\tau \sim \exp(-A\sigma/RT)$.

To test whether the elastic yielding phenomenon is specific to PC, we "cold draw" another common polymer glass: poly(methyl methacrylate) (PMMA) at $100\,°C$. Figure 4 shows that a "cold" drawn PMMA also exhibits a retractive stress over time at $T_{el\text{-}yield} = 70\,°C$, 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.

Solidlike deformation of polymers can occur both above and below T_g. Below T_g, the stress level is 1 to 2 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 stress 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
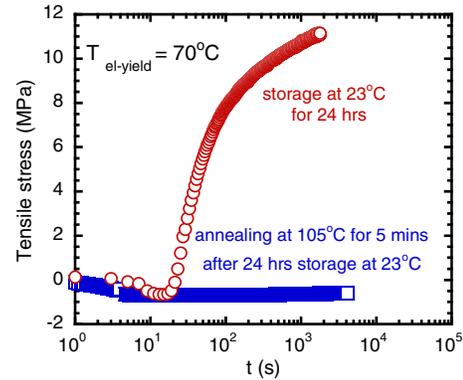
chain conformational change) could account for. In other words, the straining in a glassy state of the chain network may have the efficiency to stretch or bend or twist the covalent bonds in the backbone. Such backbone distortions apparently do not disappear as long as the storage temperature is well 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 intrachain 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 describe 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 and 2 and storing the prenecked specimen at $23\,°C$ for 24 h, we annealed it at $105\,°C$ (still $40\,°C$ below T_g) for 5 min. 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 $T_{el\text{-}yield} = 70\,°C$. Similarly, we show in Fig. S.2 in the Supplemental Material [36] 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 intrachain component of the mechanical stress in tensile deformation of polymer glasses. The backbone distortion [19] 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 $100°$ 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 cold-drawn to neck at a lower temperature shows 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 [37–40].

---

*Corresponding author.
swang@uakron.edu

[1] I. M. Ward, *Mechanical Properties of Solid Polymers* (Wiley-Interscience-John Wiley & Sons Ltd., New York, 1971).

[2] R. N. Haward and R. J. Young, *The Physics of Glassy Polymers* (Chapman & Hall, London, 1997), 2nd ed.

[3] S. Matsuoka, *Relaxation Phenomena in Polymers* (Hanser, Munich, 1992).

[4] H. G. H. van Melick, L. E. Govaert, and H. E. H. Meijer, Polymer **44**, 2493 (2003).

[5] H.-N. Lee and M. D. Ediger, Macromolecules **43**, 5863 (2010).

[6] H. N. Lee, K. Paeng, S. F. Swallen, and M. D. Ediger, Science **323**, 231 (2009).

[7] P. J. Hine, A. Duckett, and D. J. Read, Macromolecules **40**, 2782 (2007).

[8] L. C. A. van Breemen, E. T. J. Klompen, L. E. Govaert, and H. E. H. Meijer, J. Mech. Phys. Solids **59**, 2191 (2011).

[9] E. T. J. Klompen, T. A. P. Engels, L. E. Govaert, and H. E. H. Meijer, Macromolecules **38**, 6997 (2005).

[10] J. M. Brader, T. Voigtmann, M. Fuchs, R. G. Larson, and M. E. Cates, Proc. Natl. Acad. Sci. U.S.A. **106**, 15 186 (2009).

[11] J. M. Brader, M. E. Cates, and M. Fuchs, Phys. Rev. Lett. **101**, 138301 (2008).

[12] S. M. Fielding, R. G. Larson, and M. E. Cates, Phys. Rev. Lett. **108**, 048301 (2012).

[13] K. Chen and K. S. Schweizer, Phys. Rev. Lett. **102**, 038301 (2009).

[14] K. Chen, E. J. Saltzman, and K. S. Schweizer, J. Phys. Condens. Matter **21**, 503101 (2009).

[15] K. Chen, E. J. Saltzman, and K. S. Schweizer, Annu. Rev. Condens. Matter Phys. **1**, 277 (2010).

[16] J. Rottler, J. Phys. Condens. Matter **21**, 463101 (2009).

[17] R. S. Hoy and M. O. Robbins, Phys. Rev. Lett. **99**, 117801 (2007).

[18] R. S. Hoy and M. O. Robbins, Phys. Rev. E **77**, 031801 (2008).

[19] B. Vorselaars, A. V. Lyulin, and M. A. J. Michels, J. Chem. Phys. **130**, 074905 (2009).

[20] R. S. Hoy, J. Polym. Sci., Part B: Polym. Phys. **49**, 979 (2011).

[21] H.-N. Lee, R. A. Riggleman, J. J. de Pablo, and M. D. Ediger, Macromolecules **42**, 4328 (2009).

[22] R. A. Riggleman, H.-N. Lee, M. Ediger, and J. J. de Pablo, Phys. Rev. Lett. **99**, 215501 (2007).

[23] M. Warren and J. Rottler, Phys. Rev. Lett. **104**, 205501 (2010).

[24] M. Warren and J. Rottler, Phys. Rev. E **76**, 031802 (2007).

[25] H. Eyring, J. Chem. Phys. **4**, 283 (1936).

[26] D. J. A. Senden, S. Krop, J. A. W. van Dommelen, and L. E. Govaert, J. Polym. Sci., Part B: Polym. Phys. **50**, 1680 (2012).

[27] G. D. Zartman, S. Cheng, X. Li, F. Lin, M. L. Becker, and S.-Q. Wang, Macromolecules **45**, 6719 (2012).

[28] T. E. Brady and G. S. Y. Yeh, J. Polym. Sci., Polym. Lett. Ed. **10**, 731 (1972).

[29] M. Kochi, T. Sasaki, and H. Kambe, Polym. J. **10**, 169 (1978).

[30] D. G. Legrand, J. Appl. Polym. Sci. **16**, 1367 (1972).

[31] Z. Zhou, A. Chudnovsky, C. P. Bosnyak, and K. Sehanobish, Polym. Eng. Sci. **35**, 304 (1995).

[32] A. Volynskii, T. E. Grokhovskaya, A. I. Kulebyakina, A. V. Bol'shakova, and N. F. Bakeev, Polym. Sci., Ser. A **49**, 1198 (2007).

[33] J. B. Park and D. R. Uhlmann, J. Appl. Phys. **41**, 2928 (1970).

[34] G. Yianakopoulos, J. Vanderschueren, and J. Niezette, IEEE Trans. Electr. Insul. **24**, 429 (1989).

[35] J. T. Bendler, D. G. LeGrand, and W. V. Olszewski, Polymer **43**, 389 (2002).

[36] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.110.065506 for a short description of the sample preparation, instrumentation as well as some additional data.

[37] A. F. Yee, R. J. Bankert, K. L. Ngai, and R. W. Rendell, J. Polym. Sci., Part B: Polym. Phys. **26**, 2463 (1988).

[38] L. S. Loo, R. E. Cohen, and K. K. Gleason, Science **288**, 116 (2000).

[39] F. M. Capaldi, M. C. Boyce, and G. C. Rutledge, Phys. Rev. Lett. **89**, 175505 (2002).

[40] K. Chen and K. S. Schweizer, Europhys. Lett. **79**, 26 006 (2007).