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From elastic deformation to terminal flow of a monodisperse entangled melt in uniaxial extension

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Synopsis

Using a well-entangled monodisperse styrene-butadiene random-copolymer (SBR) melt as a model system, we illustrate generic features of uniaxial extension behavior that may be shared by all well-entangled thermoplastic and elastomeric materials. Depending on the imposed extensional rate, the same sample may behave like a viscous liquid or an elastic “solid.” Analogous to the recently revealed shear inhomogeneity, the SBR melt inevitably undergoes cohesive failure in the form of sample breakage whenever the Weissenberg number is much greater than unity, making it challenging to reach steady state. In the elastic deformation regime where the external deformation rate is faster than Rouse relaxation rate, the sample undergoes a finite amount of uniform stretching before yielding occurs in a period much shorter than the terminal relaxation time. Steady flow can be achieved only in the terminal regime where entangled chains utilize directed molecular diffusion to achieve rearrangement and enable uniform flow. © 2008 The Society of Rheology. [DOI: 10.1122/1.2995858]

I. INTRODUCTION

Extensional rheology of entangled polymer melts is a subject of extensive research over the past several decades because many industrially important processes, such as fiber and melt spinning, film blowing, and blow molding, are controlled by extensional flow properties. Entangled liquids under study are often molten thermoplastics (e.g., polyethylene, polypropylene and polystyrene) [for recent work, see [Bach *et al.* \(2003a, 2003b\)](#); [Rasmussen *et al.* \(2005\)](#); [Münstedt *et al.* \(2005\)](#); [Nielsen *et al.* \(2006\)](#)]. Rubber polymers such as polybutadiene and polyisoprene have also been investigated extensively [[Vinogradov *et al.* \(1975\)](#); [Vinogradov \(1975\)](#); [Malkin and Petrie \(1997\)](#)].

Systematic experimental efforts to explore extensional flow behavior started more than three decades ago [[Meissner \(1971\)](#); [Laun and Münstedt \(1976, 1978\)](#); [Ide and White \(1977\)](#); [Petrie \(1979\)](#); [Münstedt and Laun \(1981\)](#); [Meissner \(1985a, 1985b\)](#); [Laun and Schuch \(1989\)](#)] and have continued in recent years [[Yao *et al.* \(1998\)](#); [Schweizer \(2000\)](#); [McKinley and Sridhar \(2002\)](#); [Bhattercharjee *et al.* \(2002, 2003\)](#); [Heindl *et al.* \(2004\)](#); [Sentmanat *et al.* \(2005\)](#)]. Since one principal aim of rheology is to search for suitable constitutive relationships such as a mathematical expression relating stress to flow rate in steady state, experimental efforts have been directed toward obtaining material properties such as steady-state extensional viscosity at various applied extensional rates and relax-

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ation moduli at different step extensions. With this objective, many papers [McKinley and Hassager (1999); Bach *et al.* (2003a, 2003b), Rasmussen *et al.* (2005); Nielsen *et al.* (2006)] focused on comparing experimental data with the latest molecular-level theoretical description based on the Doi–Edwards tube theory (1988).

On the theoretical side, substantial efforts have been devoted to developing a molecular level understanding. Today, the Doi–Edwards (DE) tube theory (1988) is regarded as the standard model to depict not only linear viscoelastic properties but also nonlinear flow behavior of well entangled polymers, although several difficulties have also been recognized. First, several sets of data [Osaki (1993); Ravindranath and Wang (2007)] are in discord with the DE theory, including the large step shear experiments of Osaki and Kurata (1980) predating a subsequent paper [Osaki *et al.* (1982)] that positively supported the DE theory. Second, the original prediction by Doi and Edwards (1979) of a nonmonotonic constitutive relation between steady-state shear stress and rate was thought to be a theoretical artifact because there was no experimental evidence for shear flow instability. Subsequent theoretical efforts [Marrucci (1996); Ianniruberto and Marrucci (2001)] attempted to remove this nonmonotonic character from the theory [see Graham *et al.* (2003) for a review of the current theoretical status]. Recent observations of shear banding upon startup shear of well entangled polymer solutions [Tapadia and Wang (2006); Boukany and Wang (2007); Ravindranath and Wang (2008a, 2008b)] suggest that the experimentally observed shear banding may not be due to the nonmonotonic relationship between shear stress and rate in the original DE theory [Doi and Edwards (1979)]. On the other hand, the original suggestion of a necking instability in uniaxial extension of well-entangled polymers [Doi and Edwards (1979)] was never taken seriously in the sense that to our knowledge no experimental study was ever carried out to demonstrate such necking behavior in the past. Basically, in the Doi–Edwards calculation (1979), the tensile stress σ monotonically increases to a limiting value at a high stretching ratio λ , which automatically implies that the engineering stress σ_{engr} (i.e., the total force) has a maximum because $\sigma_{\text{engr}} = \sigma/\lambda$. The Maxwell model also by definition describes in the terminal flow regime a maximum in the engineering stress σ_{engr} . The emergence of such a maximum in σ_{engr} in terminal flow has not been interpreted as indicating a necking instability.

The Doi–Edwards theory, a single-chain mean-field treatment of chain dynamics and deformation, encountered another challenge nearly two decades ago [Lodge (1989)]. According to Lodge, it is difficult for the DE theory to describe elastic recoil because the retraction of the primitive chain in the Edwards tube would not return its center-of-mass (CM) to the initial position. According to Lodge, the chain must retract under the action of the elastic retraction force without meeting any resistance within the tube model, and such a retraction would not move its CM back to its original location, making it impossible to describe elastic recoil. The remarkable reality is that a specimen such as our entangled melt is able to undergo considerable stretching (as much as quadrupling its original length) and still able to exhibit full elastic recoil after fast stretching so that the CM of each chain presumably does return to its initial position.

Failure to achieve steady uniform-extensional flow has been reported by Vinogradov *et al.* (1975) and Vinogradov (1975). In an excellent review, Malkin and Petrie (1997) identified different modes of failure for different extensional rates relative to the molecular relaxation rate and updated our understanding from a phenomenological basis. This thorough review relieves us from having to summarize all previous literature results in detail. To avoid confusion regarding nomenclature, we wish to indicate that the present study also covered phenomena in the first three zones described in Malkin and Petrie (1997): (1) flow zone, (2) transition zone, and (3) rubbery zone. We correspondingly call

them terminal flow, viscoelastic (crossover) and elastic deformation regimes, respectively. In Malkin and Petrie (1997), phrases of “failure,” “yielding,” and “necking,” are used to describe the flow zone; breaking was used to describe the transition zone; and rupture for the breakup in the rubbery zone. However, we would like to reserve rupture to mean brittle failure in the glassy zone that is not studied here and refer the cohesive failure due to breakup of the entanglement network in both elastic deformation and crossover regimes as yielding. Note that Malkin and Petrie (1997) used the phrase cohesive to describe brittle failure, although Joshi and Denn (2003) have clearly referred to the rubbery zone as involving cohesive failure. Another important difference between Malkin and Petrie (1997) and the present work is that the former focused on characterizing the true stress at the point of specimen breaking, whereas we suggest the tensile force maximum to coincide with the point of yielding and observe scaling behavior consistent with that observed for simple shear [Wang *et al.* (2007a); Ravindranath and Wang (2008c); Boukany and Wang (2008a)].

Built on the phenomenological foundation of Malkin and Petrie (1997), Joshi and Denn (2004) reviewed the state of art concerning any theoretical depiction of the various failure modes, including their own proposal [Joshi and Denn (2003)] on the mechanism for “rupture.” It was clear to them that the failure phenomena reviewed by Malkin and Petrie (1997) were cohesive in origin and therefore could not be depicted by the Doi–Edwards tube theory. They described the failure as the point when “the frictional force on an entangled chain can no longer balance the tension in the chain.” This is the first molecular argument that envisioned a structural breakdown of an entangled melt undergoing continual elastic deformation. Unfortunately, it does not describe the recent experimental data [Wang *et al.* (2007b)] that found scaling behavior in the elastic deformation regime: the tensile force showing the same maximum value at the same Hencky strain independent of the chain length at the same value of the product of the extensional rate and Rouse relaxation time. Moreover, the theoretical account of Joshi and Denn (2003) cannot depict elastic yielding after a large step extension, which was first anticipated based on new theoretical understanding [Wang *et al.* (2007a)] and, subsequently reported by Wang *et al.* (2007b), where a stretched filament was observed to fail (i.e., lose its integrity) from a resting state of uniform extension instead of remaining uniform during relaxation.

The emerging evidence of shear inhomogeneity during startup simple shear of entangled polymer solutions and melts [Tapadia and Wang (2006); Hu *et al.* (2007); Ravindranath and Wang (2008a, 2008b)] raises a parallel question of whether uniaxial extension would become nonuniform due to yielding during sudden constant-rate stretching. In other words, if the same physics dictate both shear and extensional deformation behaviors of well-entangled polymers, then we should also anticipate yield-like behavior in uniaxial extension, leading to nonuniform stretching. The purpose of the present study is to explore with experiments whether steady state is feasible to reach in fast uniform uniaxial extension for well-entangled polymers without encountering cohesive failure. The symptom of nonuniform extension as a signature of yielding may not be so obvious in previous studies of thermoplastics since the Weissenberg number Wi is typically not very high at experimental temperatures that are typically above 100 °C, and experiments may have been terminated before occurrence of any visible sample failure such as nonuniformity. The present rubber polymer [styrene-butadiene rubber (SBR)] offers a model system for room-temperature experiments where very high Wi can be achieved.

In this paper, we study the rheological responses of a monodisperse entangled polymer melt by subjecting it to uniaxial extensional deformation at rates corresponding to the Weissenberg number Wi ranging from below unity to higher than Z , the number of

entanglements per chain. Our experiments reveal that steady extensional flow can be established only in the terminal flow regime with $Wi < 1$ based on the protocol involving separating the two ends of a specimen of a fixed length at a constant speed. In both the viscoelastic elongation ($1 < Wi < Z$) and elastic extension ($Wi > Z$) regimes, the stretched sample suffers cohesive failure leading to nonuniform extension. Such a material instability encountered in the nonlinear regime appears analogous to the shear banding observed in entangled polymer solutions and melts [Tapadia and Wang (2006); Boukany and Wang (2007, 2008a, 2008b); Ravindranath and Wang (2008a, 2008b)].

II. EXPERIMENT

A. Apparatus

The pioneering experimental studies of Laun and Münstedt (1978) on elongational flow behavior of polymeric liquids were challenging to carry out because the early Instron-type apparatus typically operated in such a way that it was difficult to maintain a constant rate of extension, although the Russian school [Vinogradov *et al.* (1975)] seemed to have overcome the difficulty without using the Meissner apparatus invented at the end of 1960s [Meissner (1971)]. For example, in a standard Instron-type setup, to keep the Hencky strain rate $\dot{\epsilon} = V/L$ constant means that the speed of the crosshead has to increase in proportion to the exponentially growing length L of the specimen. After the commercialization of Meissner extensional rheometer, there has been an option to examine a specimen over a fixed length [Meissner *et al.* (1981); Meissner and Hostettler (1994)].

The invention of Sentmanat extensional rheometer (SER) fixture [Sentmanat (2004, 2005)] makes it even more convenient to apply a fixed value of $\dot{\epsilon}$ during uniaxial extension. This capability, although simple to accomplish, greatly improved the experimental method for extensional flow studies of materials that can retain their integrity over the experimental time scales. Note that the SER setup is conceptually close to the Meissner type device because both apply a constant speed on the ends of a fixed specimen length.

Our experiments were all carried out using a SER mounted onto an Anton Paar MCR 301 rotational rheometer. A constant rate of extensional strain $\dot{\epsilon} = V/L$ is accomplished by stretching a filament between two counter-rotating drums of diameter D (separated by a distance L), where V is related to the angular velocity Ω of the drum by $V = D\Omega$. The tensile force F can be calculated from the measured torque T_q according to $FD = T_q$. The SER makes it rather straightforward to perform step extension experiments that were challenging to carry out previously as pointed out by Barroso and Maia (2002) and Barroso *et al.* (2003).

B. Materials

One ideal polymer for the present study of melt extensional flow behavior is styrene-butadiene rubber (SBR). We have recently made a preliminary investigation of extensional deformation behavior for four different molecular weights and observed universal scaling behavior [Wang *et al.* (2007b)]. The present study only focuses on one such monodisperse SBR (100 K) whose M_w and M_w/M_n are 95 kg/mol and 1.05, respectively. There are $Z = 24$ entanglements per chain in this sample. The terminal relaxation time can be taken as the reciprocal of the crossover frequency where the storage and loss moduli G' and G'' are equal, as shown in Fig. 1, and is found to be around $\tau = 25$ s. We can estimate the Rouse relaxation time as $\tau_R \sim \tau/Z = 1.0$ s [Wang *et al.* (2007b)]. For the extension tests, we prepare the specimens by extruding cylindrical filaments from an

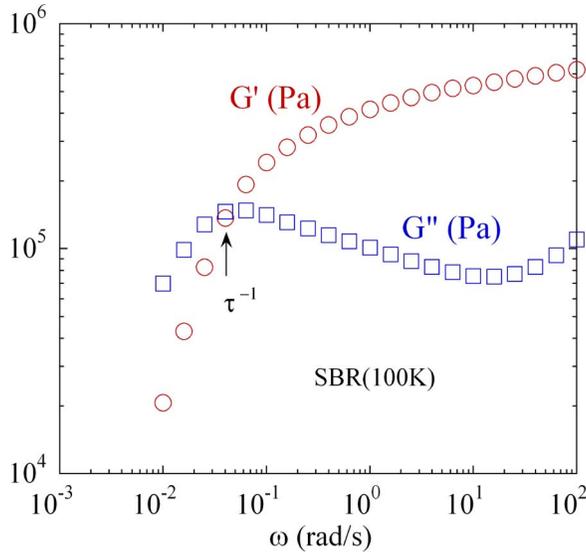


FIG. 1. Small amplitude oscillatory shear measurement of storage and loss moduli at room temperature (23 °C), where the terminal relaxation time τ of this monodisperse SBR is indicated.

automatic Monsanto capillary rheometer. A typical radius r_0 of a filament is around 1 mm. Note that all experiments were carried out at room temperature around 23 °C.

III. RESULTS AND DISCUSSION

A. Terminal flow regime: $Wi = \dot{\epsilon}\tau < 1$

To determine the linear viscoelastic behavior of the SBR melt, small amplitude oscillatory shear measurements were carried out using MCR 301 rheometer as shown in Fig. 1. To produce fluid-like response in extension of this sample, we need to apply an extension rate lower than 0.04 s^{-1} .

Figure 2(a) shows that at $\dot{\epsilon} = 0.004 \text{ s}^{-1}$ the elongational (Cauchy) stress $\sigma(t) = T_q / \pi r^2 D = F / \pi r^2$ approaches a steady-state value at long times where the time dependence of the filament radius $r = r_0 \exp(-\epsilon/2)$ with $\epsilon = \dot{\epsilon}t$ was also verified by video monitoring. Plotted in Fig. 2(a) are additional data for $\dot{\epsilon} = 0.008$ and 0.016 s^{-1} , as well as the terminal stress growth in simple shear at $\dot{\gamma} = 0.005 \text{ s}^{-1}$. In this terminal flow regime, steady state is possible as shown by the leveling-off of the true tensile stress σ . It is equally revealing to represent these data in terms of the tensile force F in its normalized form, i.e., the (Piola–Kirchhoff) engineering stress $\sigma_{\text{engr}} = F / \pi r_0^2$ as shown in Fig. 2(b). The initial increase of σ_{engr} indicates solid-like deformation up to a point around the terminal relaxation time $\tau \sim 25 \text{ s}$ when flow becomes possible due to directed molecular diffusion. The maximum in σ_{engr} coincides with the moment when flow takes place through rearrangement of the initial entanglement network by molecular diffusion. In other words, σ_{engr} could not further grow because more chain deformation is prohibited as the chain diffusion rearranges irreversibly the state of polymer entanglement. Because this flow takes place by individual molecular motion, it is able to occur evenly throughout the sample. Thus, in the terminal flow regime, it is possible to observe the diffusion-driven structural rearrangements as signified by the peak in σ_{engr} without encountering nonuniform extension. The subsequent decrease of σ_{engr} arises from the fact that the number of deformed chains contributing to the measurement of the total tensile force is

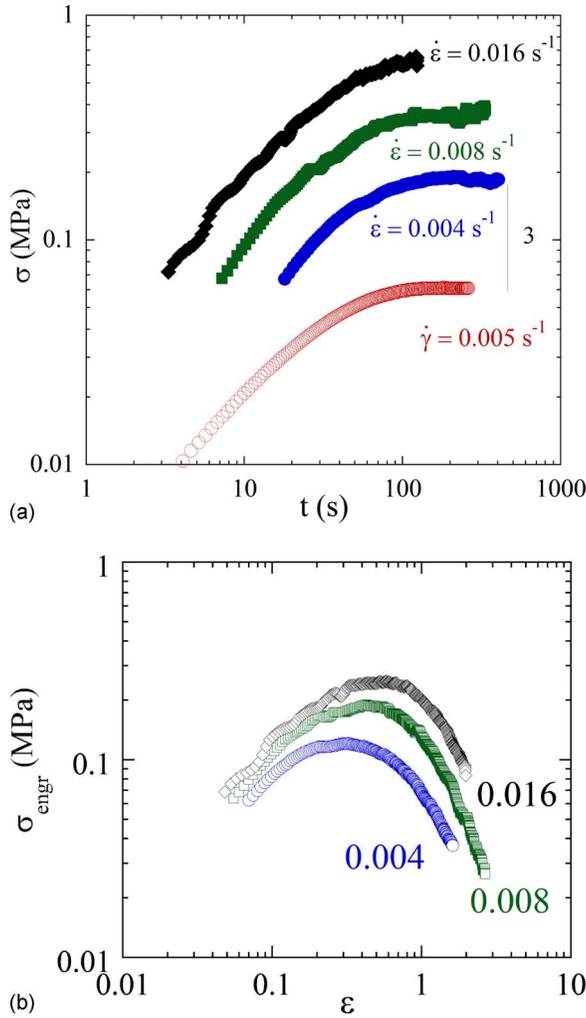


FIG. 2. (a) Tensile (Cauchy) stress growth for three constant rates of extension along with shear stress growth of the same sample in the terminal flow regime that is nearly a factor of three lower. Note that the rates are different, 0.004 vs 0.005 s⁻¹ (b) The same data represented in terms of the Piola–Kirchhoff (engineering) stress σ_{engr} as a function of the elapsed Hencky strain $\epsilon = \dot{\epsilon}t$. The maximum is indicative of disintegration of the original entanglement network due to molecular diffusion.

shrinking with the dwindling cross-sectional area of the filament. It is important to emphasize that this maximum of σ_{engr} is a sign of “equilibrium yielding.”

B. Elastic deformation regime: $\dot{\epsilon} \tau_R > 1$

1. Yielding in continuous extension

When the Weissenberg number $Wi = \dot{\epsilon} \tau \gg 1$, molecular diffusion is too slow. A large amount of stretching, given by $l/l_0 = \exp[Wi(t/\tau)]$, can take place in a time $t < \tau$. Since the entanglement network is not infinitely extendable, yielding is expected to occur. In the case of elastic deformation defined by $\dot{\epsilon} \tau_R \geq 1$, i.e., $Wi > Z$ (with $\tau \sim \tau_R Z$), we may consider a test chain to be “frozen” into its entanglement with others since the experimental time scale is shorter than the Rouse relaxation time τ_R . Prior to disintegration of

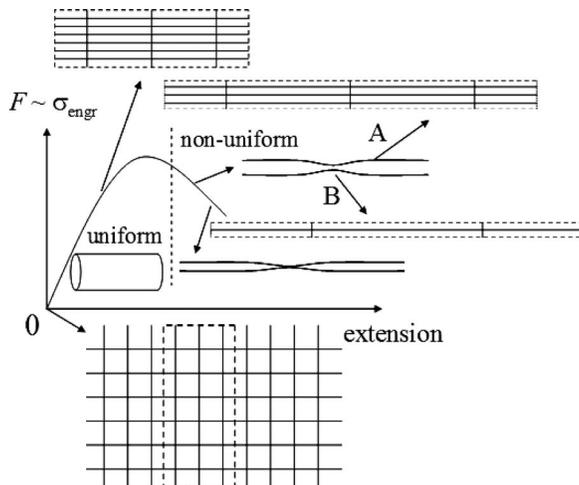


FIG. 3. Depiction of a startup uniaxial extension of entangled melts in the elastic deformation limit at different stages before and after the yield point (the tensile force maximum) when, after the vertical dashed line, nonuniform extension occurs. Before the yield point, a noncross-linked melt is like a permanent network as depicted. Here, the number of extended strands per unit cross-sectional area has increased at the expense of those wiggling strands not shown such that the chain density remains constant. As depicted, the total number of load-bearing strands is the same up to the yield point. The decrease of the tensile force F with further extension is due to loss of load bearing strands across the sample thickness. This disintegration of the entanglement network eventually reaches a point where uniform extension cannot be sustained and the sample nucleates a weak segment where uneven stretching is caused by the localized yielding of the entanglement network, leading to failure of the sample.

the entanglement network, it is the total tensile force that directly measures the elastic retraction force produced by each load-bearing strand between entanglements. Yielding of the network stems from the interchain sliding when further stretching the strand is no longer possible as the elastic retraction force grows to be as high as the intermolecular gripping force. Consequently, the tensile force F ceases to increase. Sufficient interchain sliding leads to chain disentanglement and a drop in F . Thus, the tensile force maximum could be a revealing feature in elastic extension of entangled polymers as depicted in Fig. 3, a signature of cohesive failure or yielding. As depicted in Fig. 3, this yielding might result in localized failure.

Indeed, a family of uniaxial extension experiments reveals maxima in Fig. 4 of the engineering stress σ_{engr} as a function of Hencky strain ε for four different rates from 4.8 to 0.8 s^{-1} . The sample undergoes complete uniform extension until just beyond the tensile force maximum at time t_{max} : following the force maximum the specimen subsequently suffers uneven extension and failure. This is of course not anticipated by considering affine deformation of a Gaussian chain network that can be depicted by a neo-Hookean model as shown by the dashed line in Fig. 4. In such a neo-Hookean model, the tensile force grows without bound, let alone the true stress, because there is no built-in cohesive failure mechanism. The Doi-Edwards model also predicts a maximum in σ_{engr} as shown in Fig. 4, because it found the true tensile stress to approach a constant value over time in the elastic deformation limit. Doi-Edwards (1979) suggested that necking would take place during continual extension, an elastic mechanical instability. However, we think the experimentally observed force maximum is the symptom of a cohesive failure.

There are some scaling characteristics associated with the force maximum. One scal-

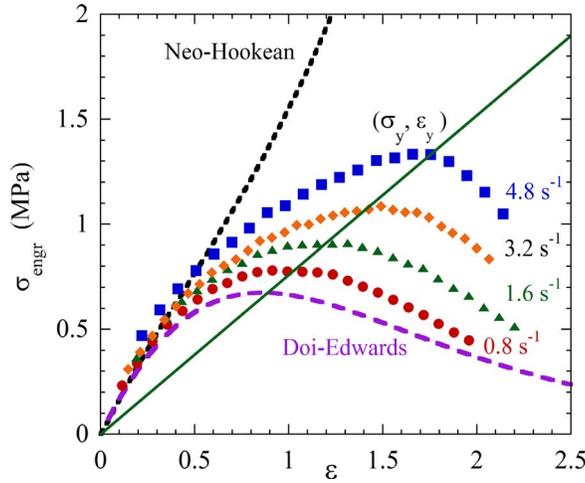


FIG. 4. The tensile force represented in terms of σ_{engr} as a function of the Hencky strain ϵ at different constant rates of extension ($1/s$) as labeled in the elastic deformation regime of $\dot{\epsilon}\tau_R > 1$, where the continuous dashed line denotes the calculation from the classical rubber elasticity theory, and the smooth line is based on the Doi-Edwards model from Eq. (10) of McKinley and Hassager (1990).

ing law is evident from Fig. 4: $\sigma_y = E_{\text{coh}}\epsilon_y$, which is similar to a linear relationship associated with stress overshoot in startup simple shear of the same sample, i.e., $\sigma_y = G_{\text{coh}}\gamma_y$, as shown in Fig. 5 [Boukany and Wang (2008a)], where approximately $E_{\text{coh}} = 3G_{\text{coh}}$. This correlation links the force maximum to a cohesive breakdown since startup shear has been proposed by us to cause yielding. Equally remarkable is a common scaling exponent $1/3$ found [Wang *et al.* (2007b)] for both uniaxial extension: $\epsilon_y \sim \dot{\epsilon}^{1/3}$ and startup shear: $\gamma_y \sim \dot{\gamma}^{1/3}$ [Ravindranath and Wang (2008c); Boukany and Wang (2008a)].

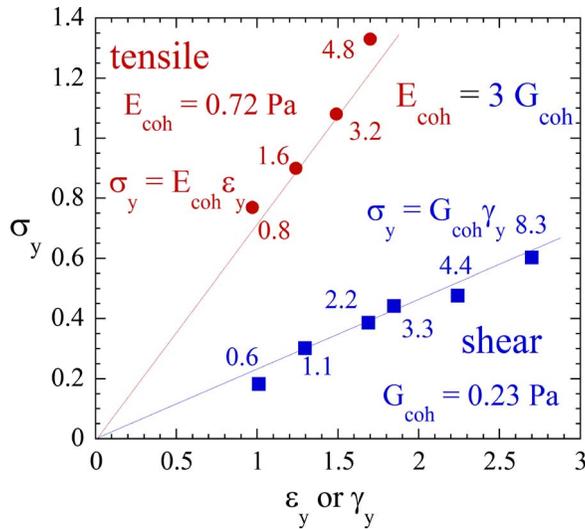


FIG. 5. The Piola–Kirchhoff yield stress σ_y , read from Fig. 3 as a function of the strain at the yield point, ϵ_y , along with a similar linear relationship found for the same sample in startup simple shear. Note the yield tensile modulus E_y relating σ_y to ϵ_y is essentially three times G_y found for simple shear from Boukany and Wang (2008a).

The striking commonality between shear and extension indicates that the maximum of the tensile force has the same physical significance as that of the shear force: signifying yielding. In passing, we note that a phantom Gaussian chain network behaves as $\sigma(\lambda) \sim (\lambda - 1/\lambda^2)$ for a stretching ratio λ according to the rubber elasticity theory, and only in the small tensile strain limit $\varepsilon' = \Delta x/L_0 \ll 1$ does such a formula produce an exact linear relation of $\sigma \sim \varepsilon$ because $\sigma(\lambda) \sim \varepsilon' = \varepsilon$ to the leading order where the Hencky strain $\varepsilon = \ln \lambda = \ln(1 + \varepsilon') = \varepsilon'$ for $\varepsilon' \ll 1$. On the other hand, we remark that the difference between $3\varepsilon = 3 \ln \lambda$ and $(\lambda - 1/\lambda^2)$ is numerically insignificant up to $\varepsilon = 1.8$ or $\lambda = 6$, although ε and λ are defined with respect to the different frames of reference. Thus, the observed scaling behavior is fully consistent with the perception that the sample is undergoing elastic extension.

2. Elastic yielding: The case of step extension

In the elastic deformation regime, the cohesive breakdown produces filament failure during stretching. Such yielding behavior can even occur in quiescence for a stretched filament. Specifically, a rapidly stretched sample undergoes failure over various times as shown in Figs. 6(a) and 6(b). This case of elastic yielding during sample relaxation was actually first predicted theoretically by Wang *et al.* (2007a) and can be understood in terms of a force imbalance between the elastic retraction force (arising from the imposed chain deformation) and cohesive force due to chain entanglement. Currently, a detailed explanation is missing of why the elastic yielding could not take place homogeneously, i.e., why the failure is localized. Apparently for the same reason, a shear-strained sample was unable to undergo quiescent relaxation [Wang *et al.* (2006); Ravindranath and Wang (2007); Boukany and Wang (2008b)]. It is important to note that such cohesive failure can occur involving a step extension of $\varepsilon = 1.2$ [squares in Fig. 6(a)] that is well before the force maximum. Moreover, the stretched sample remained uniform after extension over a period of time (~ 20 s) much longer than the Rouse relaxation time $\tau_R \sim 1$ s. These two features make it difficult to interpret the failure as an elastic instability. Finally, we mention that the same was observed in simple shear where the sample failure occurred in the form of significantly delayed macroscopic motions [Boukany and Wang (2008b)].

C. Viscoelastic regime: $\tau_R^{-1} > \dot{\varepsilon} > \tau^{-1}$

Having explored the responses in the “viscous” terminal flow and “elastic” deformation regimes in the preceding subsections, we proceed to study the crossover regime with $\tau_R^{-1} > \dot{\varepsilon} > \tau^{-1}$. We shall term this regime the “viscoelastic” elongation regime. Expressing in terms of the transient viscosity $\eta_e^+(t)$ for three extension rates of 0.04, 0.08, and 0.4 s⁻¹ in the viscoelastic regime, along with the data from the terminal regime, we have Fig. 7(a). Overlapping of all the data at short times reflects the fact that the sample deforms solid-like regardless of the imposed rate at any time $t \ll \tau$: at initial times $\sigma \sim E\varepsilon$, so that with $\varepsilon = \dot{\varepsilon}t$, $\eta_e^+(t) = \sigma/\dot{\varepsilon} \sim Et$, which explains the initial linear increase indicated in Fig. 7(a). Unfortunately, at the end of each of these three tests, we did not reach steady state [i.e., $\eta_e^+(t)$ was still changing] before the sample failed in contrast to the three data sets involving terminal flow. It is interesting to show that extension in the elastic deformation regime distinguishes itself from the other two regimes when expressed in terms of $\eta_e^+(t)$ as shown in Fig. 7(a). This figure is similar to the recent data on linear polystyrene melts of Bach *et al.* (2003b). It is also reminiscent of the earlier work on LDPE by Münstedt and Laun (1979). However, unlike LDPE, this upward deviation may not imply true strain hardening and may arise from expressing the elastic deformation in terms of the

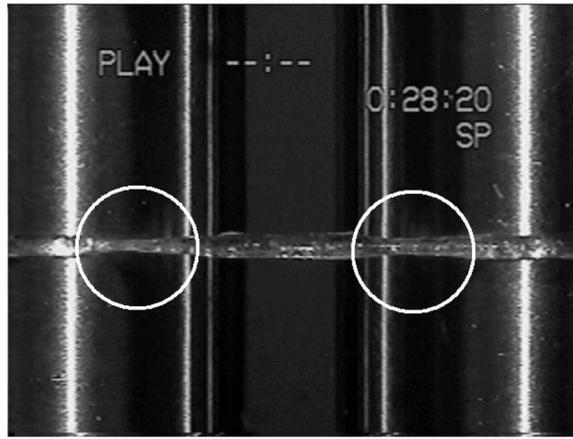
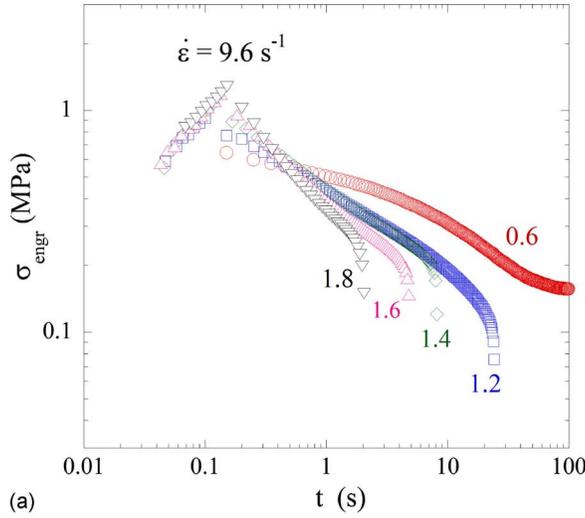


FIG. 6. (a) Step extensions at various amplitudes produced by a high rate of 9.6 s^{-1} . The sharp drop of the force signal stems from the material failure. Cohesion survives only for the lowest applied strain of 0.6. At a high Hencky strain of 1.8, the sample suffers breakage within 2 s. (b) A photo showing the delayed uneven stretching 4 s after a step extension of 1.3 produced with a rate of 9.6 s^{-1} , where the two thinner sections are circled.

transient viscosity: Since $\sigma_{\text{engr}} \sim E\epsilon$ in the elastic deformation limit, the true stress $\sigma = \sigma_{\text{engr}} \exp(\epsilon)$ rises exponentially leading to $\eta_e^+(t) = \sigma / \dot{\epsilon} \sim \exp(\dot{\epsilon}t)Et$, i.e., deviating upward from the linear dependence.

The same data of Fig. 7(a) shows nonmonotonic behavior in Fig. 7(b) when expressed in terms of the engineering stress σ_{engr} , where the maximum again reflects cohesive disintegration of the initial entanglement network. However, in contrast to the situation in the terminal flow regime, the filament suffers breakage beyond the maximum at each rate in this crossover regime. Such sample failure prevented the transient elongational viscosity from reaching a constant value with respect to time as shown in Fig. 7(a). It is noted that the strain at the force maximum is systematically lower at a lower applied rate. In the purely elastic deformation regime, the strain at the force maximum ϵ_y actually increases with the Hencky rate $\dot{\epsilon}$ as $\epsilon_y \sim \dot{\epsilon}^{1/3}$ [Wang *et al.* (2007b)].

In summary, we present all data obtained in the three different regimes in Fig. 8: the

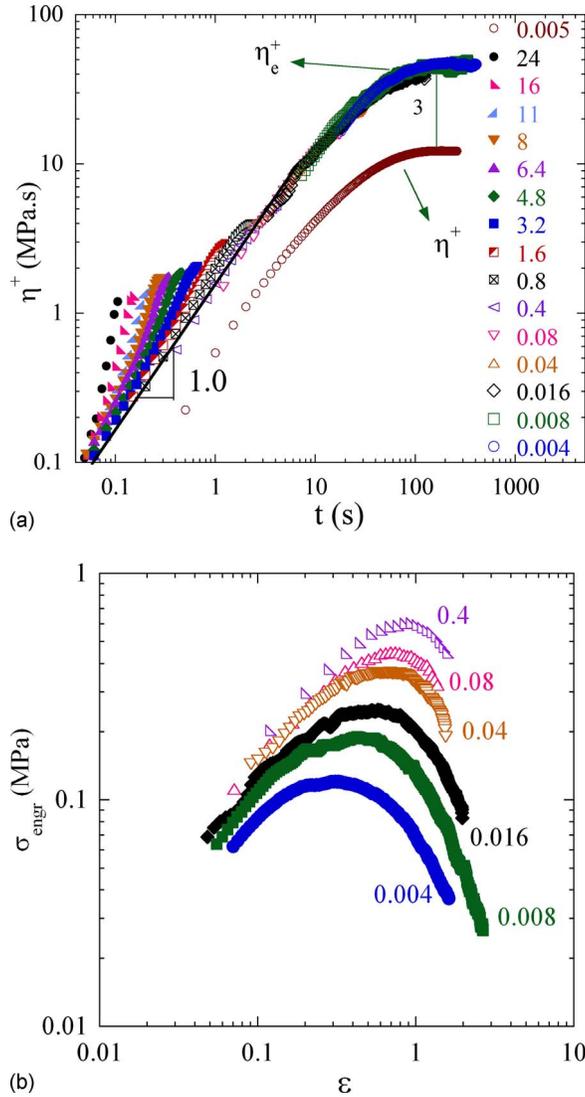


FIG. 7. (a) The transient elongational viscosity at several rates in the viscoelastic regime as well as the terminal flow regime. Also plotted for comparison are $\eta_e^+(t)$ at extensional rates from 0.8 to 24 s^{-1} in the elastic deformation regime and the shear viscosity η^+ obtained in the terminal flow regime. (b) The same data represented in terms of the engineering stress σ_{engr} as a function of the elapsed Hencky strain $\varepsilon = \dot{\varepsilon}t$. The maxima also occur in this crossover regime, indicative of disintegration of the original entanglement network.

engineering stress σ_{engr} normalized by the Hencky strain rate $\dot{\varepsilon}$, i.e., η_{engr} , has a common upper bound when expressed as a function of time. All data deviate downward from the limiting line of slope one that arises from the initial solid-like response. Here every maximum signifies the onset of disintegration of the initial entanglement network, which takes place on increasingly shorter time scales as the applied rate increases. However, only in the terminal flow regime (filled symbols), does the disintegration occur smoothly and homogeneously all the way to steady state. For well entangled polymers, uniaxial extension produces cohesive breakage when the extensional rate exceeds the overall molecular relaxation rate. Figure 8 is reminiscent of a conventional transient shear vis-

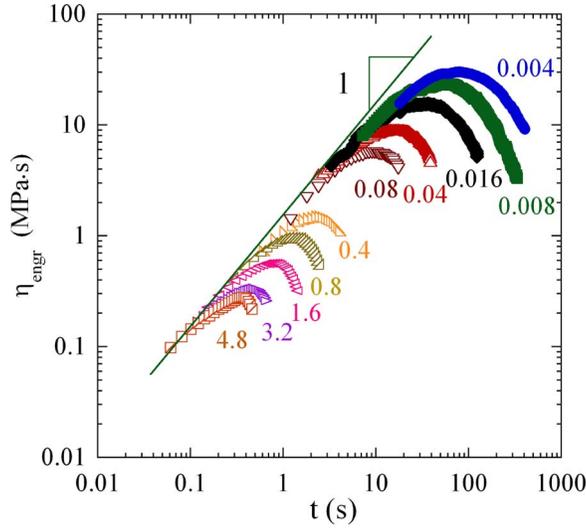


FIG. 8. Piola–Kirchhoff viscosity $\eta_{\text{engr}} = \sigma_{\text{engr}} / \dot{\epsilon}$ as a function of time at all different rates ranging from terminal flow to elastic deformation regimes, where a maximum is visible in each of the ten continuous extension experiments.

cosity plot for startup shear. The reason why $\eta_{\text{engr}} = \sigma_{\text{engr}} / \dot{\epsilon}$ is so much lower in the elastic deformation regime is that σ_{engr} increases with the rate $\dot{\epsilon}$ more weakly than linearly.

D. Flow: Irrecoverable deformation

An effective way to demonstrate whether a sample has undergone flow is to perform a strain recovery experiment. Meissner (1971) carried out a pioneering study of elastic recoil to quantify strain recovery. The meaning of the force maximum and the nature of the crossover regime can be better understood through a family of strain recovery experiments. Using different values of $\dot{\epsilon}$ and letting the stretched sample go free after different levels of extension ϵ , either before or after the force maximum, we examined post-stretched samples to determine whether their final radii r_f are smaller than their original radii r_0 or not. In a typical strain recovery experiment, we interrupt the extension at different strains by going to the stress-free condition and remove the sample immediately from the drums to allow tension-free recovery. Fortunately, the sample does not stick to the drums during stretching so that when it goes to the stress-free state it is able to recoil freely. The value of the filament radius r_f after full recovery is then measured with a micrometer screw gauge. The recoverable strain ϵ_{rec} can be calculated according to $\epsilon_{\text{rec}} = \epsilon - 2 \ln(r_0/r_f)$. We found the following results in Fig. 9: For $\dot{\epsilon}\tau_R \geq 1$, $r_f = r_0$, i.e., we have 100% strain recovery. In other words, $\epsilon_{\text{rec}} = \epsilon$, as long as $\epsilon \leq \epsilon_y$ (i.e., up to the force maximum). For $\dot{\epsilon}\tau_R < 1$, complete strain recovery is also possible for strains that take less than τ_R to reach. Outside these two conditions, the recoverable strain is always less than 100%, implying that irreversible deformation has taken place. In other words, all other data points stay below the diagonal line of perfect strain recovery in Fig. 9.

Thus, these measurements explicitly indicate occurrence of flow beyond the force maximum for $\dot{\epsilon}\tau_R \geq 1$. It is essential to point out that flow actually occurred before any nonuniform extension became visibly detectable. The measurements in filled symbols in Fig. 9 were made without any sign of sample nonuniformity. With further stretching, cohesive failure eventually gives rise to nonuniform extension.

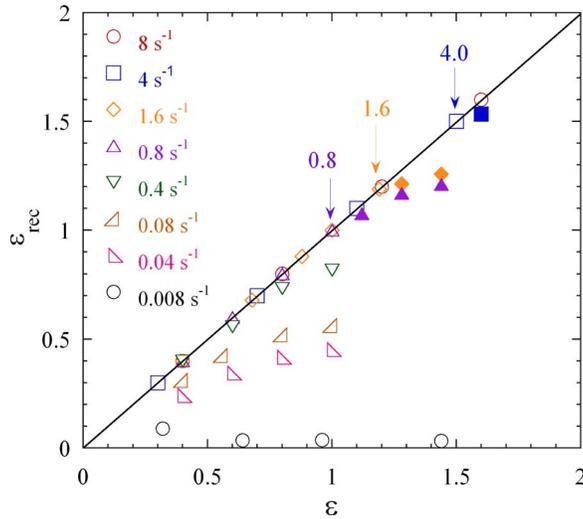


FIG. 9. Recoverable strain ε_{rec} vs the applied strain ε for eight different rates at different stages of uniaxial stretching, where the vertical arrows indicate the respective locations (i.e., ε_y) of the yield point at three rates of 0.8, 1.6, and 4.0 s^{-1} (in the elastic regime), beyond which the recovered strains are denoted with filled symbols.

E. Contrasting with filament stretching rheometer studies

We have shown in both Secs. III B and III C that it is difficult to attain steady uniform stretching during continual uniaxial extension because of cohesive failure. As long as the extension is carried out outside the terminal flow regime, SER appears to cause yielding in the form of nonuniform stretching. Recently, several studies [Bach *et al.* (2003a, 2003b), Rasmussen *et al.* (2005); Nielsen *et al.* (2006)] have adopted a method based on a filament stretching rheometer (FSR) [Tirtaamadja and Sridhar (1993)]. In this protocol, the cross-sectional area of the sample is monitored and fed back to the controller that adjusts the end-stretching speed to insure an exponential local areal decrease. This approach of avoiding an eventual breakup by slowing down the global stretching rate permits the local extensional flow to be studied. Actually, such a procedure explicitly disguises the symptom of yield-like behavior in fast stretching of an initially uniform sample because occurrence of any impending failure is simply treated as part of the local rheological testing.

A SER device or a Meissner extensional rheometer applies a constant speed on both ends of a specimen that are separated by a fixed distance. This protocol presumably allows a constant and uniform extensional rate to be imposed externally. In the FSR device, the local rate has contributions from both the external world and the internal retraction process that is elastic in nature and leads to yielding. Consequently, the late-stage stretching does not appear to involve an externally imposed constant rate when yielding starts to occur (which is inevitable). It thus remains an interesting issue whether such a test can be taken as a constant rate experiment and be used for comparison with any theoretical treatment of constant-rate uniaxial extension.

IV. CONCLUSIONS

We have carried out uniaxial extension experiments on a monodisperse SBR melt at Weissenberg numbers ranging from $1 < Wi$ to $Wi > 100$. The total tensile force (or the engineering stress σ_{enfr}) always shows a maximum in all regimes including terminal

($\dot{\epsilon}\tau < 1$), viscoelastic ($1 < \dot{\epsilon}\tau_R < 1$) and elastic deformation ($\dot{\epsilon}\tau_R > 1$). In the terminal flow regime, σ_{enfr} first rises due to elastic deformation and then ceases to increase as flow starts to take place through molecular diffusion and the cross-sectional area decreases. Clearly, no nonuniform extension ensues after this maximum. Beyond the terminal flow regime, e.g., in the elastic deformation regime, a maximum in σ_{enfr} always emerges during startup continual stretching. We have correlated this force maximum with cohesive failure or yielding. Because the entangled polymer cannot extend infinitely, it has to disintegrate (or yield) in time at high values of Wi . The yield point is found to show scaling characteristics analogous to those found in simple shear of the same polymer [Boukany and Wang (2008a)]. For reasons that are still unclear, such yielding always seems to evolve into localized failures along the stretched filament, making it impossible to reach steady uniform extensional flow. This localized yielding is also reminiscent of shear banding that arises from sudden startup shear [Tapadia and Wang (2006); Boukany and Wang (2007, 2008b); Ravindranath and Wang (2008a, 2008b)]. Finally, elastic yielding can also occur in quiescence in a suddenly stretched specimen, confirming that cohesion of entangled polymer is actually finite as found previously in nonquiescent relaxation after a large step shear [Wang *et al.* (2006); Ravindranath and Wang (2007)]. It remains unknown whether all or part of these features hold true for most (well-entangled) molten thermoplastics and elastomers and whether less entangled polymer melts would behave differently.

In closing, we admit that there is still a general debate in the community about whether the observed inhomogeneity in both simple shear and uniaxial extension originates from a material instability, i.e., cohesive failure, as we have suggested for both modes of deformation [Wang *et al.* (2007a)]. In the case of uniaxial extension, the original Doi–Edwards tube theory (1979) suggested an elastic necking instability. In simple shear, the same paper anticipated a hydrodynamic instability. Both are rather different from our suggestion of a material instability related to the cohesive failure of the chain entanglement network. In the present case of uniaxial extension, for example, we did not observe stable necking that is expected from an elastic instability. Instead, we observed failure in the form of the filament breakup.

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