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# Exploring stress overshoot phenomenon upon startup deformation of entangled linear polymeric liquids

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## Synopsis

This work explores the picture associated with stress overshoot during sudden continual (i.e., startup) external deformation of entangled polymeric liquids and proposes a specific scaling form to depict the intermolecular interactions responsible for chain deformation. Following a previously proposed idea that the stress overshoot in startup deformation is a signature of yielding, we search for ingredients that should go into the description of the force imbalance at the yield point and show that the expression for the intermolecular locking force  $f_{\text{iml}}$ , derived from the characteristics associated with the yield point, can be tested against experiment. New rate-switching experiments support the proposed formula for  $f_{\text{iml}}$ .

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## I. INTRODUCTION

Nonlinear rheological behavior of entangled polymeric liquids has been extensively studied for decades [Ferry (1980)]. The modern era began with the advent of the Doi-Edwards (DE) tube model [Doi and Edwards (1988)] based on de Gennes' reptation picture [de Gennes (1971)]. This tube model for the first time offered a quantitative depiction of linear viscoelastic properties and has thus been greeted with broad enthusiasm [Graessley (1980, 1982); Kremer and Grest (1990); Lodge *et al.* (1990); Watanabe (1999); McLeish (2002)]. According to the recent consensus, the latest version of the tube model has also captured the essential physics concerning nonlinear responses of entangled polymers to external deformation.

However, one notable difficulty facing the DE theory is its inability to determine whether or not simple shear flow is constitutively stable at all rates. Historically, a polymer-like material known as wormlike micellar solutions was first taken as an example [Callaghan *et al.* (1996)] to show that some entangled living-polymers are capable of undergoing shear banding [Olmsted (2008)]. In the next 10 years, no experimental observations of bulk shear banding were ever found for non-living and non-associating polymers, making it questionable whether the anticipated flow instability in original paper of Doi and Edwards (1979) would truly exist. To explain the seeming absence of shear banding, the convective constraint release (CCR) concept [Marrucci (1996)] was applied by Graham *et al.* (2003) to build a full tube theory where no constitutive insta-

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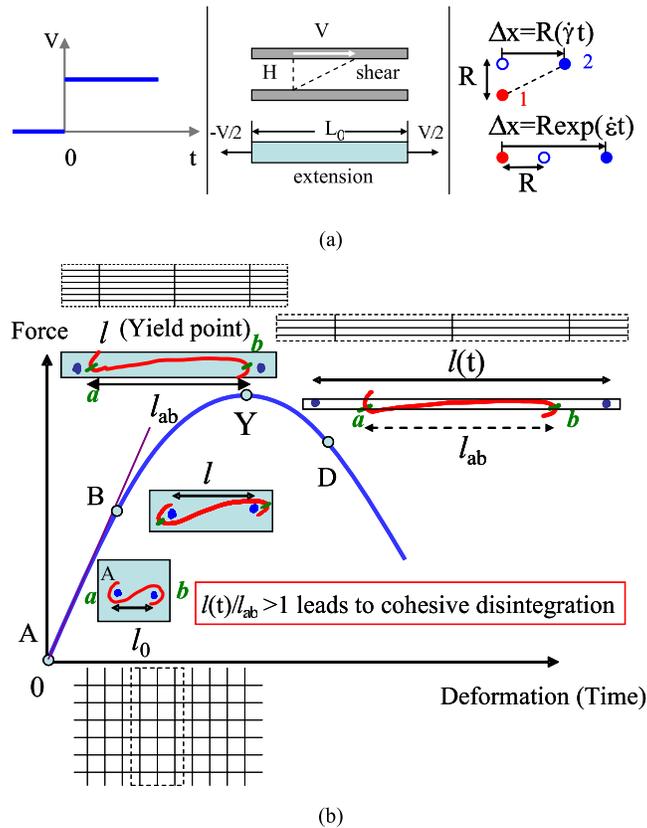
bility would appear. During this period, wormlike micellar solutions remained the only entangled liquid known to show shear banding [Britton and Callaghan (1997); Britton *et al.* (1999); Salmon *et al.* (2003a, 2003b); Bécú *et al.* (2004)].

Assuming that the type of constitutive instability envisioned by Doi and Edwards (1979) would not occur for covalently bonded polymer chains, encouraging agreement has been obtained between the latest tube-based theoretical calculations [Graham *et al.* (2003); Auhl *et al.* (2008)] and standard rheometric experiments involving startup shear [Menezes and Graessley (1982); Bercea *et al.* (1993); Pattamaprom and Larson (2001); Auhl *et al.* (2008)]. It is against this background that the recent particle-tracking velocimetric (PTV) observations of shear banding caught us unprepared during either a startup shear [Tapadia and Wang (2006); Boukany and Wang (2007); Ravindranath and Wang (2008a)] or large amplitude oscillatory shear [Ravindranath and Wang (2008b)]. In experimental reality, there could be finite size effects. But Ravindranath and Wang (2008c) showed that edge effects were not the source of an entanglement-disentanglement transition [Tapadia and Wang (2004)].

Despite well-known shortcomings of the DE theory, the most widely known agreement between theory [Doi (1980)] and experiment [Osaki *et al.* (1982)], involving mechanical relaxation from large step strain, has built enough confidence that a valid theoretical framework has been achieved within the tube model. It thus came as a bigger surprise that this quantitative agreement actually involved an unforeseen complication: the stress relaxation was found to be accompanied by macroscopic motions [Wang *et al.* (2006); Ravindranath and Wang (2007); Boukany *et al.* (2009a)], making it invalid to compare experiment with the theoretically perceived quiescent dynamics. It was admitted by Osaki (1993) that there were more cases of disagreement [e.g., Osaki and Kurata (1980)] than apparent agreement [e.g., Osaki *et al.* (1982)] between experiment and the tube theory.

Moreover, recent step strain experiments [Wang *et al.* (2007a); Wang and Wang (2008); Boukany *et al.* (2009a)] on well-entangled polymer melts indicate that macroscopic motions emerge *not* immediately after shear cessation *but long* after, much longer than the Rouse relaxation time  $\tau_R$  that governs chain retraction in a tube model [Doi and Edwards (1988)]. Therefore, chain retraction as the only available mechanism within the tube model cannot explain the findings. It also seems clear that chain retraction process in the tube model does not involve movement of a test chain's center of mass (CM), let alone anticipating delayed non-quiescent relaxation processes.

These difficulties call upon us to search for new theoretical treatments. Conversely, the new PTV-based experimental observations have helped us identify key ingredients in any theoretical depiction of mechanical responses of entangled polymers to sudden large deformations [Wang *et al.* (2007b)]. These new theoretical insights have provided us a unifying platform for discussion of both shear and extensional deformations of entangled polymers. Specifically, we discovered through step strain experiments that an entangled polymeric liquid possesses a finite cohesion: a small strain does not result in any discernible failure, whereas a sudden strain of sufficient magnitude causes a stretched filament to fail in uniaxial extension [Wang *et al.* (2007a); Wang and Wang (2008)] and produces macroscopic motions in the sample interior [Ravindranath and Wang (2007); Boukany *et al.* (2009a)] after step shear, both suggestive of a structural or cohesive collapse. More recent efforts verified that non-quiescent relaxation still takes place in the absence of any failure at the meniscus [Li and Wang (2009)].



**FIG. 1.** (a) Schematic representation of startup deformation in either simple shear or uniaxial extension, where a velocity of  $V$  is applied to the boundaries instantly at time  $t=0$  as plotted. Consider the centers of mass (CM) of two nearby chains initially separated by a distance comparable to their coil size  $R$ . Over time during startup deformation,  $CM_2$  (denoted by the dot) moves away relative to  $CM_1$  as depicted for both simple shear and uniaxial extension. (b) Conceptual depiction of a plausible cohesive failure process during uniaxial extension at a sufficiently high rate (the same mental picture applies to simple shear where strands stretch at an angle). Starting from point A up to point B, affine deformation occurs, where the blue spots (representing all surrounding strands) make no relative motion to the (red) test strand. From B to the yield point (Y), appreciable molecular sliding may take place. At rates below that  $1/\tau_R$ , the molecular deformation beyond B may no longer be affine, and the blue spots move farther apart than the distance between the two segments  $a$  and  $b$ ; at rates above  $1/\tau_R$ , the cartoon with blues spots inside the “hairpins” may still apply. Y is the yield point, beyond which further network deformation is no longer possible, the CMs of the two chains are separated farther than depicted by the formulas in (a) due to mutual sliding. At point D, sufficient relative motion has taken place among strands that irreversible change in the state of chain entanglement can lead to structural (i.e., cohesive) failure of the entanglement network. A great challenge in the future is to answer the questions of whether and why this failure should be localized and whether the subsequent flow is inhomogeneous or not. In contrast, up to Y, the response of the system to the external deformation is essentially elastic and homogeneous, allowing nearly complete strain recovery. In other words, if there were six load bearing strands at the beginning of deformation, the six strands are still present up to the yield point Y. Cohesive failure occurs as the number of load bearing strands reduces as depicted for the point of extension at D, leading to a declining total force.

**II. THEORETICAL PICTURE FOR YIELDING OF ENTANGLED POLYMERS**

Let us picture a standard startup deformation in Fig. 1(a) on a viscoelastic liquid with a dominant internal relaxation time  $\tau$ , where the external boundary suddenly displaces with a velocity  $V$  at  $t=0$ . The time it takes to make a shear strain of 1 or to double the initial length  $L_0$  in extension is  $t_1 = H/V = 1/\dot{\gamma}$  or  $L_0/V = 1/\dot{\epsilon}$ . If  $t_1 \ll \tau$ , which is readily

realizable in experiment by choosing a sufficiently high  $V$ , this “liquid” should respond like a solid. In other words, when the Weissenberg number  $Wi = \dot{\gamma}\tau$  or  $\dot{\epsilon}\tau \gg 1$ , a great deal of strain could take place in a time much shorter than  $\tau$ .

For entangled polymeric liquids, chain entanglement can be perceived as the condition that chains have no chance to pass around one another until thermal agitation causes them to diffuse past each other on a time scale often taken to be the terminal relaxation time  $\tau$  or known as the reptation time in the tube model. Thus, initially, the CM relationship between two chains (separated by a distance comparable to the coil size  $R$ ) can be approximately depicted by the formulas in Fig. 1(a). This early quasi-elastic deformation ceases to continue when the chains are forced to *pass around* each other leading to disentanglement. This transition from elastic deformation to plastic flow must occur under the condition of  $\dot{\gamma}\tau \gg 1$  (or  $\dot{\epsilon}\tau \gg 1$ ) since no “solid” is capable of sustaining a diverging amount of elastic deformation without breaking up. Accompanying this structural transformation or yielding is typically a stress overshoot. In other words, during startup deformation, the initial monotonic rise in the measured force is actually phenomenological evidence for elastic deformation. After the disentanglement beyond the yield point, the measured stress begins to decline, producing the so-called overshoot [Huppler *et al.* (1967); Crawley and Graessley (1977)].

Some other materials undergo such perceived yielding as well, for example, amorphous glasses, gels and dense (colloidal) dispersions, associative and solutions, to name a few. Phenomenologically, yield-like behavior occurs upon startup rapid deformation as stress overshoot emerges. Transient “solids” are eventually forced to flow due to the ever growing external deformation. Since each system is governed by physics specific to its microstructure and since we are interested in exploring the molecular process involved in yielding of entangled polymeric liquids, we cannot profit further by speaking only generically and phenomenologically.

For an entangled melt, a bowl of “elastic” noodles comes to mind as a mental picture. Upon external deformation, a test chain deforms due to inter-chain interactions. During continuing deformation, *intermolecular locking forces*  $f_{\text{iml}}$  [Wang *et al.* (2007b)] arise from the non-crossability among chains on time scales shorter than the terminal relaxation (i.e., reptation) time  $\tau$ . In quiescence, there is a cohesive force or entanglement force  $f_{\text{ent}}$  due to the intertwining of all chains. We can evaluate  $f_{\text{ent}}$  by envisioning strands between neighboring entanglement points. The force required to cause such a strand to disengage from the entanglement network is related to the work involved in the disengagement, comparable to  $1 k_{\text{B}}T$ . Thus, we envisage a cohesion force

$$f_{\text{ent}} \sim k_{\text{B}}T/l_{\text{ent}}, \quad (1)$$

that is intermolecular in origin [Wang *et al.* (2007b)], where  $l_{\text{ent}}$  is the entanglement spacing or the coil size of an entangling strand.

Before the yield point, the experimentally measured force is the elastic retraction force  $f_{\text{retract}}$  that is produced in each chain due to chain deformation. This force  $f_{\text{retract}}$  is intra-chain in origin, given by [Wang *et al.* (2007b)]

$$f_{\text{retract}}(\gamma) \approx (k_{\text{B}}T/l_{\text{ent}})\gamma, \quad (2)$$

where the molecular strain  $\gamma$  is the external strain  $\dot{\gamma}t$  in the limit of affine deformation and grows monotonically with the continuing external deformation.

We know experimentally that the measured stress slows down to eventually display a maximum, implying deformation of the entanglement network, as well as  $f_{\text{retract}}$  ceases growing. Since this overshoot character is rather universal at different rates in the elastic deformation regime [Ravindranath and Wang (2008d); Boukany *et al.* (2009b)], there

must be a universal route leading to the yield point, beyond which the force decreases with further external deformation. To reiterate, the shear stress initially increases linearly with time during affine deformation, corresponding to a level of stiffness comparable to the elastic plateau modulus, followed by weaker growth in time as sketched in Fig. 1(b).

Chain deformation ceases increase and, correspondingly, the measured force reaches a maximum when the retraction force  $f_{\text{retract}}$  reaches the same magnitude as that of the intermolecular locking force  $f_{\text{iml}}$ . Beyond this yield point, the externally imposed deformation would cause the “test chain” to slide past the other surrounding chains in the network that are collectively represented by the blue spots in Fig. 1(b). This intermolecular sliding as depicted in Fig. 1(b) must eventually cause load bearing strands to disengage from the network. In other words, beyond the yield point, chains are brought to pass around one another, resulting in chain disentanglement. Parallel superposition of oscillatory shear frequency sweep measurement reveals [Boukany and Wang (2009a)] that residual chain entanglement only exists on time scales shorter than the reciprocal deformation rate.

We have found [Wang *et al.* (2007b); Ravindranath and Wang (2008d); Boukany *et al.* (2009b)] that the force maximum, or the yield stress  $\sigma_y$  corresponding to point Y in Fig. 1(b), scales with the corresponding time at the force maximum  $t_y$  as  $\sigma_y \sim (\tau_R/t_y)^{1/2}$  in the elastic deformation limit. The purpose of this work is to further explore the origin of this scaling behavior at the yield point and search for a specific form for  $f_{\text{iml}}$  that is consistent with and inspired by additional experiments.

Finally, before exploring how characterization of the intermolecular locking force  $f_{\text{iml}}$  is related to the scaling laws observed at the force maximum, we would like to clarify any connection or lack of connection between the present discussion and the CCR concept advocated by Marrucci (1996). At long times, startup deformation depicted in Fig. 1(a) eventually produces a state of steady shear flow. The CCR idea was explored to describe steady state shear. It provides us with a phenomenological rationale for why the shear thinning is nearly as steep for monodisperse entangled polymers as the viscosity being reciprocally proportional to shear rate  $\dot{\gamma}$ , i.e., why there appears a shear stress plateau in the steady state stress versus shear rate plot. The CCR concept envisions that when steady state flow takes place chains pass around one another on a time scale comparable to the reciprocal shear rate. It does not concern itself with the phenomenon of yielding that precedes the eventual steady shear flow. More importantly, it cannot address the phenomenon of elastic yielding [Wang *et al.* (2007b)], i.e., yielding after shear cessation from a large step strain—one might call it ECR, i.e., constraint release driven by elastic restoring forces, not CCR. In short, the convective CR idea by definition tries to account for how flow is eventually possible in an entangled polymeric liquid, whereas the present discussion concerns about how this liquid transitions from initial elastic deformation to final plastic deformation, i.e., flow.

### III. EXPERIMENTAL

In order to explore the characteristics of yielding behavior, we resort to one previously made and studied entangled solution [Ravindranath and Wang (2008c, 2008d)] that consists of 10 wt % high molecular weight 1,4-polybutadiene (PBD) and 90 wt % low molecular weight 1,4-PBD. The linear viscoelastic properties of this sample were reported by Ravindranath and Wang (2008c). The sample was prepared by first dissolving the desired wt % of PBD of  $M_w = 1.052 \times 10^6$  g/mol in large excess of toluene. To this solution, a proper amount of low molecular weight PBD of  $M_w = 15$  kg/mol was added and intimately mixed. Most of the toluene was evaporated slowly under a hood at room

temperature over a period of 2 weeks and the remaining was removed under vacuum condition until the residual toluene is less than 0.5%, at which time the sample no longer gives toluene smell. The low molecular weight PBD does not evaporate. Since  $T_g$  of 1,4-PBD is  $-100$  °C, any residual toluene of this level is not rheologically noticeable and thus of no consequence. The experiments were carried out at room temperature using an Advanced Rheometric Expansion System rotational rheometer.

#### IV. PHENOMENOLOGICAL CONJECTURE ON INTERMOLECULAR FORCES

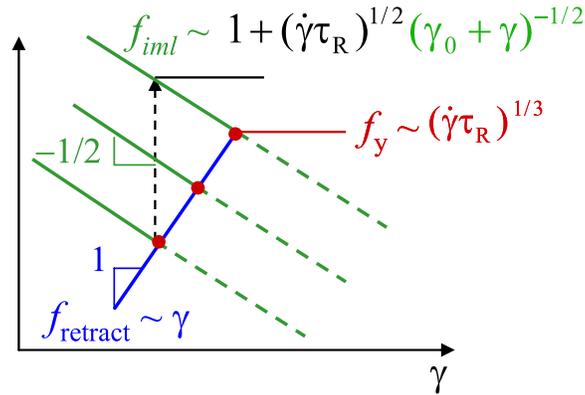
The relation  $\sigma_y \sim (\tau_R/t_y)^{1/2}$  caused us to suggest previously [Wang *et al.* (2007b)] that  $f_{iml}(t, \dot{\gamma}$  or  $\dot{\epsilon}) \sim (\tau_R/t_y)^{1/2}$ , such that the yield point is the point when the rising  $f_{retract}$  meets a declining  $f_{iml}$  as shown in Fig. 13 of Wang *et al.* (2007b). In other words, it was explicitly postulated that due to molecular relaxation  $f_{iml}$  would automatically decrease in time after startup deformation, leading to force imbalance. This conjecture arose from the conceptual convenience that such a declining force would naturally produce force imbalance. It turns out that multiple functional forms of  $f_{iml}(t, \dot{\gamma}$  or  $\dot{\epsilon})$  satisfy the observed scaling behavior. For example, alternatively,  $f_{iml}/f_{ent} \sim (\dot{\gamma}\tau_R)^{1/3}$  or  $(\dot{\epsilon}\tau_R)^{1/3}$  is also consistent with the observed scaling law of  $\sigma_y \sim (\tau_R/t_y)^{1/2}$  upon equating  $f_{iml} \sim \dot{\gamma}^{1/3}$  with  $f_{retract} \sim \dot{\gamma}$  of Eq. (2) at the yield point. Now we realize that there is no conceptual difficulty to visualize occurrence of yield for a time-independent  $f_{iml}$ . Basically, when the value of  $f_{iml}$  is matched by the elastic retraction force  $f_{retract}$  chain deformation stops growing, and the subsequent disintegration must occur through mutual molecular passing-by, i.e., a test (red) chain attains relative movement with the surrounding chains (represented by the blue spots) as illustrated in Fig. 1(b).

In reality, it is more reasonable to envision  $f_{iml}$  to also depend on the level of chain deformation and topological states of chain entanglement. As the chains become more aligned in the direction of displacement, the effectiveness of intermolecular interactions to grip any given test chain tends to decrease. If chains assume a less entangled state due to external deformation, a subject to be discussed elsewhere [Wang and Wang (2009)],  $f_{iml}$  should also be weaker. On the other hand, the ability of other chains (represented by the blue dots in Fig. 1) to grip a test chain and to deform it effectively during shear is clearly related to how quickly chain relaxation takes place. The faster the shear rate, the less relaxation can occur to cause deterioration of  $f_{iml}$ . Therefore,  $f_{iml}$  must be an increasing function of the deformation rate. Based on these considerations, we propose, by neglecting in the first-order approximation any topological effect that we do not know how to depict yet, a simplest functional form for  $f_{iml}$  that could be tested against and verified by experiment,

$$f_{iml} \sim f_{ent}(\dot{\gamma}\tau_R)^\beta(\gamma_0 + \gamma)^{-\alpha} \quad \text{or} \quad f_{iml} \sim f_{ent}(\dot{\epsilon}\tau_R)^\beta(\varepsilon_0 + \varepsilon)^{-\alpha}, \quad (3)$$

where the exponents  $\alpha$  and  $\beta$  remain to be determined by comparison with experiment,  $\gamma_0$  or  $\varepsilon_0$  is a positive parameter introduced as a mathematical device to render the right-hand-side of Eq. (3) finite in the limit of vanishing  $\gamma$  or  $\varepsilon$ . This parameter can best be regarded as related to the maximum available intermolecular interactions at the onset of deformation (when  $\gamma \ll \gamma_0$ ). Here  $\gamma$  or  $\varepsilon$  is the molecular strain (in simple shear or uniaxial extension) equal to  $\dot{\gamma}t$  or  $\dot{\epsilon}t$  under the condition of affine deformation. According to the recent data [Boukany *et al.* (2009b)] on the scaling behavior of various systems, Eq. (3) can be expected to apply in the elastic deformation regime.

In the limit of elastic deformation, i.e., with  $\dot{\gamma}\tau_R$  or  $\dot{\epsilon}\tau_R > 1$ , we know from experiment [Wang and Wang (2008); Ravindranath and Wang (2008d); Boukany *et al.* (2009b)] that the magnitude of the stress maximum  $\sigma_y$  scales as  $\sigma_y \sim (\tau_R/t_y)^{1/2}$  and  $\sigma_y \sim \gamma_y$ . The linear



**FIG. 2.** Graphic depiction of the yielding condition of Eq. (5), where the growing elastic retraction force eventually meets the values of the intermolecular locking force  $f_{iml}$  for three rates, on double-log scales.

relationship  $\sigma_y = G_{coh} \gamma_y$  obtained at different rates can be understood to reflect the fact that at the stress maximum the system has reached the same structural yielding point, corresponding to a common “cohesive” modulus  $G_{coh}$ . The origin of  $\sigma_y \sim (\tau_R/t)^{1/2}$  may be associated with the character of the intermolecular locking force  $f_{iml}$  at the yield point of  $\gamma_y$ , such that

$$(\dot{\gamma}\tau_R)^\beta (\gamma_0 + \gamma_y)^{-\alpha} \sim (\tau_R/t_y)^{1/2}. \tag{4}$$

At sufficiently high rates,  $\gamma_y \gg \gamma_0$  so that Eq. (4) becomes  $(\dot{\gamma}\tau_R)^\beta (\dot{\gamma}t_y)^{-\alpha} \sim (\tau_R/t_y)^{1/2}$ . For this relation to hold true, we must have  $\alpha = \beta = \frac{1}{2}$  in Eq. (3).

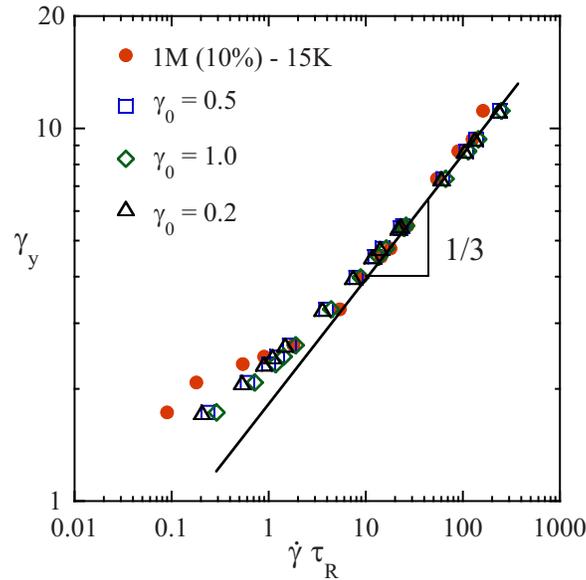
The measured force no longer increases when no further chain deformation is possible under the condition that  $f_{retract}$  has grown to meet the driving force  $f_{iml}$ . This is illustrated in Fig. 2. In other words, the yield points at the red dots are where  $f_{retract}$  grows to equal  $f_{iml}$ . Equating these forces at the yield point allows us to write

$$(\dot{\gamma}\tau_R)^{1/2} (\gamma_0 + \gamma_y)^{-1/2} \sim \gamma_y, \tag{5}$$

which gives an approximate scaling relationship of  $\gamma_y \sim (\dot{\gamma}\tau_R)^{1/3}$  between the strain at the yield point  $\gamma_y$  and the applied rate  $\dot{\gamma}$ . This equation describes the scaling behavior observed experimentally rather well without any adjustable parameters in the sense that any value of  $\gamma_0 < 1.0$  in Eq. (5) hardly influences the fitting as shown in Fig. 3. Here the experimental data are based on startup shear at various rates of the 10% PBD solution depicted in Sec. III whose scaling characteristics at the yield point have been discussed in detail elsewhere [Ravindranath and Wang (2008d)]. The comparison in Fig. 3 between the experimental data and scaling description of Eq. (5) reveals that the rate dependence of the intermolecular locking force in Eq. (5) comes in the form of the dimensionless Rouse–Weissenberg number  $\dot{\gamma}\tau_R$ .

**V. EXPERIMENTAL RESULTS AND DISCUSSION**

With  $\beta = \alpha = \frac{1}{2}$ , the expression of Eq. (3) indeed produces the character of  $f_{iml} \sim (\dot{\gamma}\tau_R)^{1/2} (\gamma_0 + \gamma)^{-1/2}$  approaching  $(\tau_R/t)^{1/2}$  at high strains with  $\gamma_0 \ll \gamma$  and  $\gamma_0 + \gamma \sim \dot{\gamma}t$ . In other words, the seemingly decreasing  $f_{iml} \sim (\tau_R/t)^{1/2}$  with time noted in Wang *et al.*



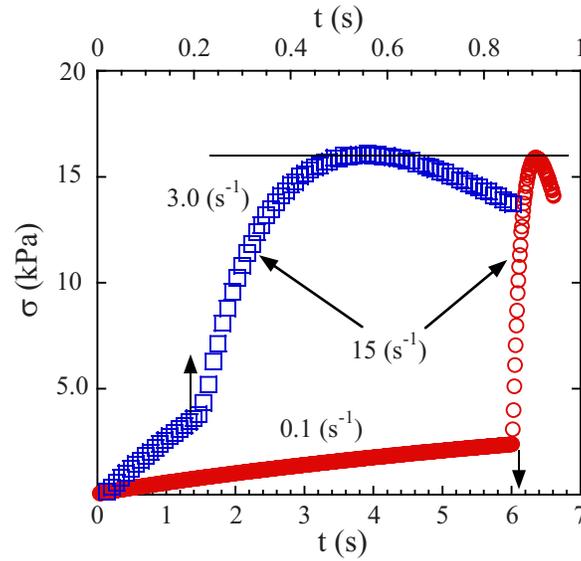
**FIG. 3.** Comparison between experimental data in filled circles with the expression of yielding criterion, i.e., Eq. (3), in open symbols for three values of the parameter  $\gamma_0$ .

(2007b) appears to arise from its dependence on chain deformation, i.e., the factor of  $(\gamma_0 + \gamma)^{-1/2}$ , and does not explicitly reflect any explicit decay associated with local chain relaxation dynamics.

In this section, we would like to discuss experiments that verify and confirm the characteristics of  $f_{\text{iml}}$  discussed in the preceding section. Specifically, we carry out rate-switching experiments to determine whether  $f_{\text{iml}}$  would actually explicitly decline with time. The present work only describes the yielding behavior in simple shear and omits a parallel set of data from rate-switching experiments on uniaxial extensional deformation.

The sample under study is a well-entangled solution of 10% 1,4-PBD, which has been investigated previously [Ravindranath and Wang (2008c, 2008d)]. We explore any time dependence of  $f_{\text{iml}}$  by examining the force maximum character produced by a high rate of  $15 \text{ s}^{-1}$  following a startup shear at various much lower rates from  $0.1$  to  $3.0 \text{ s}^{-1}$ . Figure 4 compares the arrivals at the shear stress maximum upon switching at the same elapsed strain of  $0.6$  from a preceding startup shear at either  $3.0$  or  $0.1 \text{ s}^{-1}$ . Because of the difference in the preceding rate by a factor of  $30$ , the second experiment waited a much longer time before switching to the rate of  $15 \text{ s}^{-1}$ . Any decline of  $f_{\text{iml}}$  with time would have resulted in a lower stress maximum for the  $0.1$  to  $15 \text{ s}^{-1}$  rate-switching experiment. The horizontal line in Fig. 4 indicates that this did not happen.

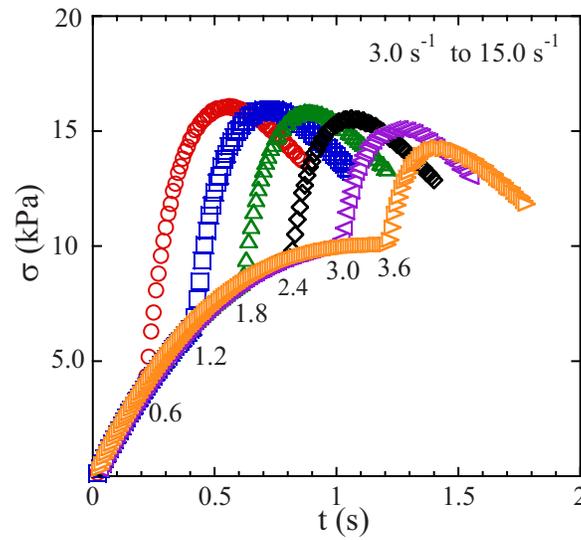
The rate-switching experiments also offer us an opportunity to gain some insight into any structural change during startup shear. Figure 5 shows a sequence of discrete rate-switching experiments. The lack of any appreciable decline of the stress maximum at the various stages of switching along the stress growth curve associated with the startup shear at  $3.0 \text{ s}^{-1}$  is consistent with two separate observations: (i) the particle-tracking velocimetric observations reveal homogeneous elastic deformation up to the yield point (i.e., the stress maximum) [Tapadia and Wang (2006); Boukany and Wang (2007); Ravindranath and Wang (2008a)]; (ii) complete strain recovery was observed in this elastic deformation regime up to the yield point [Wang and Wang (2008); Ravindranath and



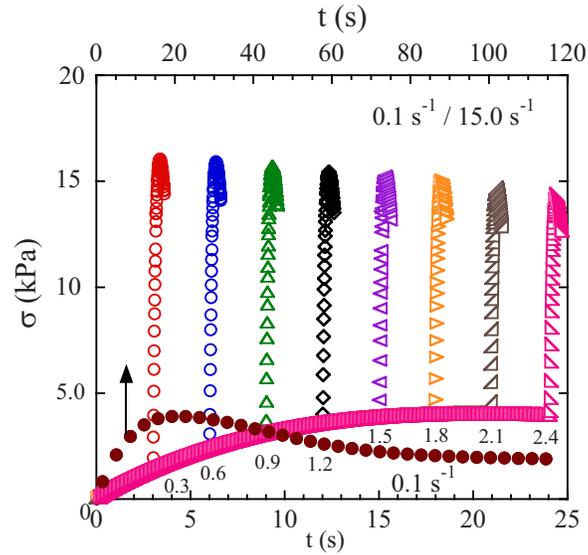
**FIG. 4.** Shear stress growth in two rate-switching experiments from a rate of either 0.1 or 3.0 to 15 s<sup>-1</sup>, where the switching occurs after a strain of 0.6. The switch from 3.0 to 15 in squares needs to be read from the top X axis.

Wang (2008d)]. In other words, our rate-switching experiments support the idea that the state of chain entanglement is preserved up to the yield point and there is little decline of  $f_{iml}$  with time.

The slight drop (seen in Figs. 5 and 6) of the peak stress with the increasing strain  $\gamma_s$ , at which the switching occurs, reflects a greater amount of strain experienced by the system. The circles in Fig. 7 show this slight decrease with the strain at switching,  $\gamma_s$ .

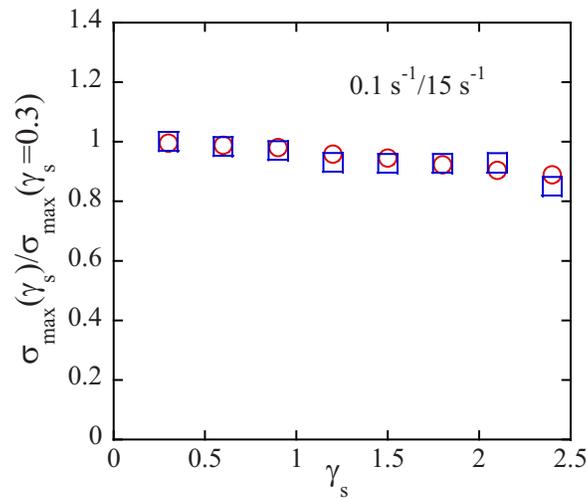


**FIG. 5.** Stress growth at different stages of rate-switching from 3.0 to 15 s<sup>-1</sup>, where the numbers from 0.6 to 3.6 denote the shear strains when switching was made.



**FIG. 6.** Double X plots of the rate-switching from 0.1 to 15 s<sup>-1</sup>, where the stress overshoot at 0.1 s<sup>-1</sup> was plotted against the top X axis.

Inserting the total strain elapsed at the peak stresses from the data in Fig. 6 into the formula of Eq. (3) with  $\alpha=\beta=\frac{1}{2}$  and  $\gamma_0$  taken to be 0.5, we can also predict the small decrease in the peak stress as shown in the squares. The agreement observed in Fig. 7 shows that the depiction of the intermolecular interactions by Eq. (3) may have captured the essential scaling behavior of this intermolecular gripping force. As indicated in Fig. 2 and in Eq. (5), this force sets the upper boundary for the extent of chain deformation and level of elastic retraction force produced at a given rate of deformation.



**FIG. 7.** Normalized stress maxima as a function of the switching strain in the switching experiment from 0.1 to 15 s<sup>-1</sup>.

## VI. SUMMARY

We have presented a conceptual picture to depict yielding of well-entangled polymeric liquids undergoing rapid (continuous) external deformation as shown in Figs. 1(a) and 1(b). Based on the characteristics associated with the stress overshoot during startup deformation, we proposed an explicit scaling form, i.e., Eq. (3), to depict the intermolecular interactions that cause the individual chain deformation during external straining. We were able to determine that the exponents in Eq. (3) are both equal to  $\frac{1}{2}$ . In terms of this intermolecular locking force  $f_{\text{iml}}$ , we can visualize how the entanglement network reaches the brink of failure during sudden rapid deformation as the elastic retraction force  $f_{\text{retract}}$  in each strand grows to match the declining  $f_{\text{iml}}$ , as shown in Fig. 2. Here  $f_{\text{iml}}$  declines because of the reducing effectiveness to grip a test chain with increasing chain deformation. In our theoretical depiction of the yield-like behavior of entangled polymers, this intermolecular locking force occupies a central position. The same concept is required to explain how yielding occurs at polymer/wall interface to produce wall slip [Boukany and Wang (2009b)]. A step strain is a truncated startup deformation experiment. Upon shear cessation,  $f_{\text{iml}}$  turns off, leaving the residual elastic retraction force  $f_{\text{retract}}$  to fight against the cohesion due to chain entanglement, which is represented by  $f_{\text{ent}}$  of Eq. (1) [Wang *et al.* (2007b)]. Elastic yielding could occur either at the interface [Boukany and Wang (2009b)] or bulk [Boukany *et al.* (2009a)] when  $f_{\text{retract}}$  of Eq. (2) is greater than  $f_{\text{ent}}$ , i.e., in a step strain with  $\gamma > 1$ .

We note that there is currently no direct, explicit evidence for chain scission as the mechanism of yielding. However, we have not been able to rule it out with experimental proof although several observations go against chain scission as the origin of shear inhomogeneity. For example, an entangled polymer would undergo homogeneous deformation (i.e., without failure) up to the force maximum during startup deformation. Yet the same sample would suffer internal failure (evidenced by recoil motions) if the same startup is terminated well before the force maximum. This character, found for both shear and extensional deformation, that the entanglement network would be intact during deformation up to the yield point and yet could not maintain its integrity for a step strain of lower amplitude, is inconsistent with a chain scission mechanism. Future work may yield direct evidence for or against chain scission mechanism for yielding in sudden deformation of linear polymer melts.

In closing, we also remark that chain disengagement during yielding takes place through chain ends in linear polymers. Polymers with long chain branching (LCB) is expected to resist cohesive breakdown after a step strain (what we call *elastic yielding*). The quiescent cohesion is clearly strengthened by LCB: it requires all chain ends on the main backbone to pull off before a polymer with LCB can disengage from the network. In other words, an event of elastic yielding after step strain in entangled LCB polymers would obviously require much higher amplitude of step strain than required for linear polymers. The cohesive strength is expected to depend on the detail architectural structure of LCB polymers. On the other hand, how LCB enhances  $f_{\text{iml}}$  and delays the yield point to much higher strains is another matter. Here the role of the branching point remains elusive. However, it is intuitively obvious that a LCB polymer would also resist pulling-out more effectively than linear chains. There is actually some evidence that LCB prevents ductile yielding all together in uniaxial extension: low density polyethylene tends to undergo brittle failure during sudden rapid stretching instead of necking.

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## References

- Auhl, D., J. Ramirez, A. E. Likhtman, P. Chambon, and C. Fernyhough, "Linear and nonlinear shear flow behavior of monodisperse polyisoprene melts with a large range of molecular weights," *J. Rheol.* **52**, 801–836 (2008).
- Bécu, L., S. Manneville, and A. Colin, "Spatiotemporal dynamics of wormlike micelles under shear," *Phys. Rev. Lett.* **93**, 018301 (2004).
- Bercea, M., C. Peiti, B. Simionescu, and P. Navard, "Shear rheology of semidilute poly(methyl methacrylate) solutions," *Macromolecules* **26**, 7095–7096 (1993).
- Boukany, P. E., and S. Q. Wang, "Correlation between velocity profile and molecular weight distribution in sheared entangled polymer solutions," *J. Rheol.* **51**, 217–233 (2007).
- Boukany, P. E., and S. Q. Wang, "Nature of steady flow in entangled fluids revealed by superimposed small amplitude oscillatory shear," *J. Rheol.*, to be published (2009a).
- Boukany, P. E., and S. Q. Wang, "Exploring origin of interfacial yielding of entangled melts during or after shear," *Macromolecules* **42**, 2222–2228 (2009b).
- Boukany, P. E., S. Q. Wang, and X. Wang, "Step shear of entangled linear polymer melts: New experimental evidence for elastic yielding," *Macromolecules* **42**, 6261–6269 (2009a).
- Boukany, P. E., S. Q. Wang, and X. Wang, "Universal scaling behavior in startup shear of entangled linear polymer melts," *J. Rheol.* **53**, 617–629 (2009b).
- Britton, M. M., and P. T. Callaghan, "Two-phase shear band structures at uniform stress," *Phys. Rev. Lett.* **78**, 4930–4933 (1997).
- Britton, M. M., R. W. Mair, R. K. Lambert, and P. T. Callaghan, "Transition to shear banding in pipe and Couette flow of wormlike micellar solutions," *J. Rheol.* **43**, 897–909 (1999).
- Callaghan, P. T., M. E. Cates, C. J. Rofe, and J. B. A. F. Smeulders, "A study of the 'spurt effect' in wormlike micelles using nuclear magnetic resonance microscopy," *J. Phys. II* **6**, 375–393 (1996).
- Crawley, R. L., and W. W. Graessley, "Geometry effects on stress transient data obtained by cone and plate flow," *Trans. Soc. Rheol.* **21**, 19–49 (1977).
- de Gennes, P. G., "Reptation of a polymer chain in the presence of fixed obstacles," *J. Chem. Phys.* **55**, 572–579 (1971).
- Doi, M., "Molecular rheology of concentrated polymer systems. I," *J. Polym. Sci., Polym. Phys. Ed.* **18**, 1005–1020 (1980).
- Doi, M., and S. F. Edwards, "Dynamics of concentrated polymer systems Part 4.—Rheological properties," *J. Chem. Soc., Faraday Trans.* **2**, 38–54 (1979).
- Doi, M., and S. F. Edwards, *The Theory of Polymer Dynamics*, 2nd ed. (Clarendon, Oxford, 1988).
- Ferry, J. D., *Viscoelastic Properties of Polymers*, 3rd ed. (Wiley, New York, 1980).
- Graessley, W. W., "Some phenomenological consequences of the Doi-Edwards theory of viscoelasticity," *J. Polym. Sci., Polym. Phys. Ed.* **18**, 27–34 (1980).
- Graessley, W. W., "Entangled linear, branched and network polymer systems—molecular theories," *Adv. Polym. Sci.* **47**, 68–117 (1982).
- Graham, R. S., A. E. Likhtman, T. C. B. McLeish, and S. T. Milner, "Microscopic theory of linear, entangled polymer chains under rapid deformation including chain stretch and convective constraint release," *J. Rheol.* **47**, 1171–1200 (2003).
- Huppler, J. D., I. F. MacDonald, E. Ashare, T. W. Spriggs, R. B. Bird, and L. A. Holmes, "Rheological properties of three solutions. Part II. Relaxation and growth of shear and normal stresses," *Trans. Soc. Rheol.* **11**, 181–204 (1967).

- Kremer, K., and G. S. Grest, "Dynamics of entangled linear polymer melts: A molecular-dynamics simulation," *J. Chem. Phys.* **92**, 5057–5086 (1990).
- Li, X., and S. Q. Wang, "Elastic yielding after step shear and during LAOS in absence of edge failure," *J. Rheol.*, under review (2009).
- Lodge, T. P., N. A. Rotstein, and S. Prager, "Dynamics of entangled polymer liquids: Do linear chains reptate?," *Adv. Chem. Phys.* **79**, 1–132 (1990).
- Marrucci, G., "Dynamics of entanglements: A nonlinear model consistent with the Cox–Merz rule," *J. Non-Newtonian Fluid Mech.* **62**, 279–289 (1996).
- McLeish, T. C. B., "Tube theory of entangled polymer dynamics," *Adv. Phys.* **51**, 1379–1527 (2002).
- Menezes, E. V., and W. W. Graessley, "Nonlinear rheological behavior of polymer systems for several shear-flow histories," *J. Polym. Sci., Polym. Phys. Ed.* **20**, 1817–1833 (1982).
- Olmsted, P. D., "Perspectives on shear banding in complex fluids," *Rheol. Acta* **47**, 283–300 (2008).
- Osaki, K., "On the damping function of shear relaxation modulus for entangled polymers," *Rheol. Acta* **32**, 429–437 (1993).
- Osaki, K., and M. Kurata, "Experimental appraisal of the Doi-Edwards theory for polymer rheology based on the data for polystyrene solutions," *Macromolecules* **13**, 671–676 (1980).
- Osaki, K., K. Nishizawa, and M. Kurata, "Material time constant characterizing the nonlinear viscoelasticity of entangled polymeric systems," *Macromolecules* **15**, 1068–1071 (1982).
- Pattamaprom, C., and R. G. Larson, "Constraint release effects in monodisperse and bidisperse polystyrenes in fast transient shearing flows," *Macromolecules* **34**, 5229–5237 (2001).
- Ravindranath, S., and S. Q. Wang, "What are the origins of stress relaxation behaviors in step shear of entangled polymer solutions?," *Macromolecules* **40**, 8031–8039 (2007).
- Ravindranath, S., and S. Q. Wang, "Banding in simple steady shear of entangled polymer solutions," *Macromolecules* **41**, 2663–2670 (2008a).
- Ravindranath, S., and S. Q. Wang, "Particle-tracking velocimetric investigation of large amplitude oscillatory shear behavior of entangled polymer solutions," *J. Rheol.* **52**, 341–358 (2008b).
- Ravindranath, S., and S. Q. Wang, "Steady state measurements in stress plateau region of entangled polymer solutions: Controlled-rate and controlled-stress modes," *J. Rheol.* **52**, 957–980 (2008c).
- Ravindranath, S., and S. Q. Wang, "Universal scaling characteristics of stress overshoot in startup shear of entangled polymer solutions," *J. Rheol.* **52**, 681–695 (2008d).
- Salmon, J. B., A. Colin, S. Manneville, and F. Molino, "Velocity profiles in shear-banding wormlike micelles," *Phys. Rev. Lett.* **90**, 228303 (2003a).
- Salmon, J. B., S. Manneville, and A. Colin, "Shear banding in a lyotropic lamellar phase. I. Time-averaged velocity profiles," *Phys. Rev. E* **68**, 051503 (2003b).
- Tapadia, P., and S. Q. Wang, "Nonlinear flow behavior of entangled polymer solutions: Yieldlike entanglement-disentanglement transition," *Macromolecules* **37**, 9083–9095 (2004).
- Tapadia, P., and S. Q. Wang, "Direct visualization of continuous simple shear in non-Newtonian polymeric fluids," *Phys. Rev. Lett.* **96**, 016001 (2006).
- Wang, S. Q., S. Ravindranath, P. E. Boukany, M. Olechnowicz, R. P. Quirk, A. Halasa, and J. Mays, "Non-quiescent relaxation in entangled polymeric liquids after step shear," *Phys. Rev. Lett.* **97**, 187801 (2006).
- Wang, S. Q., S. Ravindranath, Y. Y. Wang, and P. E. Boukany, "New theoretical considerations in polymer rheology: Elastic breakdown of chain entanglement network," *J. Chem. Phys.* **127**, 064903 (2007b), wherein Ref. 34 is *Macromolecules* **40**, 8684 (2007), Ref. 40 is *Macromolecules* **41**, 2663 (2009), Ref. 43 is *Macromolecules* **40**, 8031 (2007), Ref. 44 is *Phys. Rev. Lett.* **99**, 237801 (2007), Ref. 52 is *J. Rheol.* **52**, 681 (2008), Ref. 53 is *J. Rheol.* **52**, 1275 (2008), and Ref. 61 is *Macromolecules* **42**, 2222 (2009).
- Wang, Y. Y., P. E. Boukany, S. Q. Wang, and X. Wang, "Elastic breakup in uniaxial extension of entangled polymer melts," *Phys. Rev. Lett.* **99**, 237801 (2007a).
- Wang, Y. Y., and S. Q. Wang, "From elastic deformation to terminal flow of a monodisperse entangled melt in uniaxial extension," *J. Rheol.* **52**, 1275–1290 (2008).
- Wang, Y. Y., and S. Q. Wang, "Probing state of chain entanglement in polymer solutions during startup shear and step strain relaxation," *J. Rheol.*, under review (2009).
- Watanabe, H., "Viscoelasticity and dynamics of entangled polymers," *Prog. Polym. Sci.* **24**, 1253–1403 (1999).

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