Stress Undershoot of Entangled Polymers under Fast Startup Shear Flows in Primitive Chain Network Simulations

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(Received : November 14, 2017)

In this study, viscosity growth of entangled polymers under startup of fast shear flows was investigated by means of primitive chain network simulations. In particular, we focused on the undershoot following the well-known overshoot. The simulations reasonably reproduced the viscosity growth data reported in the literature for polystyrene melts. To investigate the origin of the observed undershoot, stress was decomposed into orientational and stretch contributions through a decoupling approximation. The decoupled results show a tiny undershoot in both orientation and stretch. Molecular tumbling was also monitored, both for single molecules and in terms of an average end-to-end orientation angle. Results appear to confirm that tumbling causes the viscosity undershoot, consistently with the suggestion of Costanzo et al. [Macromolecules, 2016, 49, 3915].

Key Words: Nonlinear viscoelasticity / Viscosity / Molecular simulations

1. INTRODUCTION

One of the open issues in the nonlinear viscoelasticity of entangled polymers is the origin of the stress undershoot in startup of fast shear flows. It is well established that the shear stress shows an overshoot when the applied shear rate is larger than the reciprocal longest relaxation time. The origin of the overshoot has been unequivocally attributed to the tube segment orientation by using both birefringence experiments and molecular simulations. Frequently, after the overshoot the stress monotonically decreases to the steady-state value. However, some experimental data at very high shear rates show a stress undershoot following the overshoot, just before reaching the steady state. In the past, such undershoot was not taken too seriously because it could not be clearly distinguished from possible experimental artifacts. In recent times, however, due to the significant improvement of the experimental techniques, the undershoot has been recognized as a real phenomenon, possibly useful for testing nonlinear molecular models of polymer dynamics.

As an explanation of the undershoot phenomenon, Costanzo et al. proposed the tumbling motion of entangled polymers, an unexpected molecular mechanism just discovered in the nonequilibrium molecular dynamics simulations of Nafar Sefiddashti et al.. Inspired by the damped oscillations shown in the end-to-end vector autocorrelation function, as observed by Nafar Sefiddashti et al. at the steady state of fast shear flows, Costanzo et al. introduced a damped oscillating tumbling function into the equation for the chain stretch dynamics, while leaving unaltered the equation for the orientation dynamics. Such a simplified approach, however, has been recently questioned in a second paper by Nafar Sefiddashti et al., who analyzed nonequilibrium molecular dynamics simulations also under transient startup of fast shear flows, revealing undershoots. Their analysis suggests that the undershoot is most probably linked to tube segment orientation, rather than to chain stretch.

For completeness, we mention that Stephanou et al. reported another explanation of the undershoot based on the molecular model originally proposed by Curtiss and Bird. In that approach the important parameter is the link tension coefficient, which describes the effect of rotation in the orientational relaxation. However, the Curtiss and Bird theory does not include chain stretch, and is therefore unable to describe very fast flows.

In this study, the undershoot phenomenon in fast shear startup is investigated by means of primitive chain network simulations. The simulation method has been shown capable of predicting linear viscoelasticity, as well as several
Here, we first confirm the ability of the simulation algorithm in reasonably describing the experimental data reported by Costanzo et al.\(^7\) in the linear viscoelastic range and in shear startup, stress undershoot included. Then, by decoupling the stress into the orientational and stretch contributions, we investigate the origin of the undershoot. Next, with a similar aim, we also examine the tumbling motion of the entangled molecules and the creation/destruction kinetics of entanglements.

### 2. SIMULATION MODEL

Because the simulation model is the same as that used in the earlier studies\(^4, 18, 19\), readers who are familiar with the methodology can skip this section. The molecular model employed in this study is the multi-chain slip-link model known as primitive chain network model\(^12\). In the model, an entangled polymeric liquid is replaced by a network consisting of nodes, strands and dangling ends. Each polymer chain in the system is represented by a path from a dangling end through the consecutive network strands to another dangling end. Each network node has four diverging strands, corresponding to the assumption of binary chain entanglements. Each network node is made up of a slip-link binding together the two entangled chains, yet allowing the sliding motion of the chains along their respective backbones. Slip-links are created and destroyed at the dangling ends according to the number of monomers in the dangling ends. Slip-links are created and destroyed at the dangling ends according to the number of monomers in the dangling ends. When a sufficient number of Kuhn segments protrude from the slip-link at the chain end, a new slip-link is created on the dangling end by hooking another network strand in the surroundings. Vice versa, when the Kuhn segment number becomes lower than a minimum value, the slip-link is removed and the coupled chain at the network node is released. The state variables are then: (i) the position in space of slip-links (network nodes), (ii) the number of monomers in each network strand, and (iii) the number of slip-links along each polymer chain. The slip-link position obeys a Langevin-type equation of motion, in which the drag force, the tension in each diverging strands, the osmotic force suppressing density fluctuations, and a random thermal force, sum up to zero. A second Langevin-type equation with a similar set of forces rules the evolution of the Kuhn segment number in each network strand, thus mimicking reptation and fluctuation mechanisms. The number of slip-links in each chain, as well as that in the simulation box as a whole, fluctuates over time owing to the creation/destruction hooking/unhooking mechanisms mentioned above.

The materials simulated in the present study are two polystyrene melts with molecular weight 185 k and 133 k, respectively, for which the linear viscoelasticity and the viscosity growth under startup shear are available in the literature\(^7\). Consistently with earlier studies\(^15, 16, 18-21\), the unit molecular weight \(M_0\) was set at 11 k. The unit modulus \(G_0\) was thus obtained according to the relation \(G_0 = \rho RT/M_0\) as 0.32MPa, where \(\rho\) is density and \(T\) is temperature. The unit of time \(\tau_0\) was obtained by fitting simulation results to linear viscoelastic data as shown in Fig. 1 below, and found to be \(\tau_0 = 1.1 \times 10^{-2}\) s. To account for finite extensibility of network strands, the maximum stretch ratio was set at 4.0 at equilibrium\(^18-21\). Reduction of friction\(^19\) was not needed in the present work, which is limited to shear flows.

Simulations used periodic boundary conditions with box dimension of \((10a)^3\), where \(a\) is the unit length corresponding to the equilibrium average strand length. The linear viscoelastic response was obtained from the Green-Kubo relation of the equilibrium stress autocorrelation function. The linear relaxation modulus thus obtained was converted to the complex modulus via a multi-mode Maxwell fit. Simulations of shear flows adopted Lees-Edwards boundary conditions with the SLLOD algorithm. At each shear rate, 8 independent simulation runs with different initial network configurations were performed to improve statistics.

### 3. RESULTS AND DISCUSSION

#### Linear viscoelasticity

Figure 1 shows the linear viscoelasticity for the 133 k and 185 k polystyrene melts. As reported earlier, the linear viscoelastic response is nearly quantitatively reproduced for both systems with the same set of parameters reported above (\(M_0 = 11\) k and \(\tau_0 = 1.1 \times 10^{-2}\) s). Shear flow calculations were then performed without further tuning of the parameters.

![Fig. 1 Linear viscoelasticity of polystyrene melts with the molecular weights of 133 k and 185 k at the reference temperature of 160°C. Symbols are experimental data^7 and lines are simulation results.](image)
Viscosity growth curve

Figure 2 shows the viscosity growth in startup shear flows for several shear rates for the two polymers of Fig. 1. Although the qualitative agreement between simulations and data is satisfactory, quantitative discrepancies are observed both at low and high shear rates. At low shear rates, the simulation somewhat underestimates the data. This tendency is clearly demonstrated for $M = 133$ k (top panel), as shown, for example, by the first set of data (and corresponding predictions) just below the linear viscoelastic curve. This discrepancy at low shear rates for $M = 133$ k is only partly due to the difference in the zero shear viscosity (see uppermost data and simulation curve in the upper panel of Fig. 2). Indeed, a similar (if smaller) discrepancy is observed for $M = 185$ k (bottom panel), although the linear viscoelasticity is better captured in this case.

At high shear rates, Fig. 2 shows that the overshoot is underestimated, whereas the steady-state viscosity is overestimated. The underestimation of the steady shear viscosity at low shear rates, and the overestimation at high shear rates, imply a shear-rate dependence of the steady shear viscosity weaker than that experimentally observed. Similar discrepancies were reported for the full-chain tube model known as GLaMM\textsuperscript{22}, for which a remedy was suggested by tuning the chain retraction parameter. In our case, no improvement of the model appears feasible at present.

We now consider the main issue of this study, which is the undershoot at high shear rates. Although undershoots are barely seen in Fig. 2 where logarithmic scales are used, they are more clearly visible in Fig. 3 where the viscosity is reported in a linear scale (for the 185 k melt, and the highest shear rates only). For clarity, horizontal lines show the steady-state values predicted by the simulations. In Fig. 3 the quantitative discrepancies between data and predictions are again visible. However, the magnitude of the undershoots is similar to that observed in the experimental data. We then proceed to analyze the possible reasons for the presence of such undershoots.

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**Fig. 2** Viscosity growth in startup shear flow for the 133 k (top) and 185 k (bottom) polystyrene melts at 160 °C. Symbols are data\textsuperscript{7} and curves are simulation results. The linear viscosity growth is shown by unfilled circles (data) and bold solid curves (simulations), at the top in both figures. Shear rates (in s\textsuperscript{-1}) are 31.6, 17.8, 10.0, 5.62, 3.16, 1.78 from bottom to top for the case of 133 k (top panel), and 56.2, 31.6, 17.8, 10.0, 5.62, 3.16, 1.78, 1.0, 0.562 from bottom to top for 185 k (bottom panel).

**Fig. 3** Viscosity growth (linear scale) in fast startup shear flows of the 185 k polystyrene melt. Symbols are data\textsuperscript{7} and curves are simulation results. Shear rates (in s\textsuperscript{-1}) are 31.6, 17.8 and 10.0, from bottom to top. Horizontal lines indicate the steady-state values from the simulations.
Decoupling stress

In nondimensional units, the shear stress $\sigma_{xy}/G_0$ is obtained from the simulations through the following formula

$$\frac{\sigma_{xy}}{G_0} = 3 \frac{Z}{Z_0} f_{\text{FENE}} \langle r_x r_y \rangle / n,$$

where $Z$ is the entanglement density (and $Z_0$ its equilibrium value), $r$ the end-to-end vector of a network strand, $n$ the corresponding number of Kuhn segments (normalized to the average equilibrium value), and the angular bracket $\langle ... \rangle$ indicates the current average over the network strands in the simulation box. In the non-Gaussian factor $f_{\text{FENE}}$, $r_{\text{max}}$ is the fully extended length of the network strand. It should be noted that Eq. (1) already contains a decoupling approximation in computing the non-Gaussian factor through a separate average. Such approximation, known as FENE-P, is needed in our numerical calculations. Indeed, the hooking/unhooking dynamics at chain ends, as well as the random forces, generate sudden changes in both length and monomer number of the network strands, which prove incompatible with adopting individual FENE corrections\(^\text{(18)}\).

We now wish to rewrite Eq. (1) in a further approximated form where the average strand orientation $S_{xy}$ is decoupled from the average square strand stretch $\lambda^2$:

$$\frac{\sigma_{xy}}{G_0} \approx 3 \frac{Z}{Z_0} f_{\text{FENE}} \lambda^2 S_{xy}.$$

Here, by introducing the unit vector $u = r / |r|$ specifying the orientation of the strand, $S_{xy}$ and $\lambda$ are calculated as:

$$S_{xy} = \frac{(nu_x u_y)}{(n)}, \quad \lambda^2 = \frac{(r_x^2)}{(n)}.$$

In Eq. (3), the individual strand orientation $u_x, u_y$, and square stretch $r_x^2/n$ are weighted with the number of monomers in that strand.

For the case of $M = 185$ k and $\dot{\gamma} = 31.6$ s\(^{-1}\), Fig. 4 shows the evolution of the shear stress (both from Eqs. 1 and 2), as well as that of the four contributions appearing on the right-hand-side of Eq. 2. In the decoupled form, the stress is overestimated from the region of the overshoot onwards, but the undershoot is still present (see panel a). Also, the stretch and the orientation (panels c and e, respectively) exhibit the undershoot, although not exactly at the same time. The ratio $Z / Z_0$ appears not to be involved in the stress undershoot because, after the decrease following the stress overshoot due to chain retraction (convective constraint release), $Z / Z_0$ soon reaches its steady-state value (see panel b).

The results of the Brownian simulations reported here, showing undershoots both in the stretch and in the orientation, fall somewhere in between the suggestion of Costanzo et al.\(^\text{(7)}\) and that of Nafar Sefiddashti et al.\(^\text{(10)}\). Indeed, the former attributed the undershoot exclusively to chain stretch, whereas the latter observed the undershoot in the orientation only, though both the orientation and the stretch were estimated in their NEMD simulations through an arbitrary subdivision of the chain into network strands with an equal number of monomers.

Molecular tumbling

A possible explanation for the stress undershoot is the tumbling motion of the entangled molecules, as suggested by Costanzo et al.\(^\text{(7)}\). To explore tumbling, we define the angle $\theta$ as the angle that the projected end-to-end vector of the molecule onto the $xy$ shear plane forms with the shear direction $x$ (see Fig. 5).
The individual behavior of entangled molecules is analyzed in Fig. 6, showing the time evolution of $\sin \theta$ and $\cos \theta$ for three molecules. Both functions exhibit an oscillatory behavior that reflects the tumbling motion. During the tumbling cycle, molecules stay aligned to the shear direction for a long time, and suddenly flip direction by a quick rotation: the plateaus in $\cos \theta$ represent the long-lived aligned conformations, and the spikes in $\sin \theta$ correspond to the quick rotations. Such flow-induced rotations are generally clockwise, as clearly shown in the time domain $500 < t / \tau_0 < 1700$ of Fig. 6(c). Indeed, when $\cos \theta$ jumps up from $-1$ to $+1$, $\sin \theta$ shows a positive spike from $0$ to $1$, whereas, when $\cos \theta$ jumps down from $+1$ to $-1$, $\sin \theta$ exhibits a negative spike from $0$ to $-1$. However, Fig. 6 also shows that in many cases $\sin \theta$ spikes are uncorrelated with $\cos \theta$ jumps, indicating strong clockwise, as well as counterclockwise, fluctuations.

In order to investigate the initial coherence during shear startup of the tumbling cycles of the different molecules (implicitly assumed by Costanzo et al.), the time evolution of the average value (over $10^5$ chains) of $\sin^2 \theta$ is reported in Fig. 4(f). At equilibrium, it is $\langle \sin^2 \theta \rangle = 0.5$, and upon shear startup it decreases because of molecular orientation to the shear direction. However, before reaching the steady-state value, also $\langle \sin^2 \theta \rangle$ exhibits a visible undershoot. The presence of the undershoot in $\langle \sin^2 \theta \rangle$ appears to confirm a degree of coherence in the tumbling motion of the molecules before the steady state is achieved (when coherence is completely lost), consistently with the assumption of an oscillatory damped behavior proposed by Costanzo et al.

**Entanglement kinetics**

Nafar Sefiddashti et al. suggested that the entanglement destruction/reformation kinetics could also be a possible explanation for the stress undershoot. The results of our simulations for what concerns the creation/destruction kinetics of entanglements are reported in Fig. 7, again for the case of $M = 185$ k at $\dot{\gamma} = 31.6$ s$^{-1}$. At $t = 0$, i.e. at equilibrium, the creation and destruction rates are obviously the same. As a fast flow starts (faster than the reciprocal Rouse time), the
destruction rate increases, and the creation rate decreases. This behavior is due to the entanglements moving towards, and dropping off, the chain ends. As a consequence, the entanglement density decreases. However, the creation/destruction rates soon approach one another after the stress overshoot, but sometime before the stress undershoot, so that a steady-state value of $Z / Z_0$ is established before that of the stress, as is apparent by comparing Fig. 4(b) to Fig. 4(a). The increase of the creation rate, implying a faster randomization of the tube segments, could induce an increase of $S_r$. However, since such increase of the creation rate occurs before both stress and orientation undershoots are observed, the entanglements kinetics does not appear to play a role in the undershoot phenomenon itself, at least to within the validity of the model adopted here.

4. CONCLUSIONS

The viscosity growth during startup of shear flows of entangled polystyrene melts was analyzed by means of the primitive chain network simulations. At the highest shear rates, a viscosity undershoot following the overshoot was found, in agreement with the experiments. The origin of such undershoot was investigated by decoupling the stress into its orientational and stretch components, as well as by analyzing the molecular tumbling motion and the entanglement creation/destruction kinetics. It was found that both the orientation and the chain stretch exhibit an undershoot, though not exactly at the same time. By examining the orientation angle of the end-to-end vector, tumbling is observed, and the average value of the absolute value of such angle was also found to exhibit an undershoot. The creation/destruction rates of entanglements do not appear to affect the undershoot phenomenon. All together, these results lend support to the idea of a tumbling-induced oscillatory damped behavior affecting chain stretch, as proposed by Costanzo et al., although the appearance of an undershoot also in the orientation partially confirms the conclusions reached by Nafar Sefiddashti et al.

ACKNOWLEDGEMENT

This work is supported in part by Grant-in-Aid for Scientific Research (A) (17H01152) from JSPS and by Council for Science, Technology and Innovation, Cross-ministerial Strategic Innovation Promotion Program, “Structural Materials for Innovation” from JST.

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