Simulations of Startup Planar Elongation of an Entangled Polymer Melt

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(Received : December 6, 2019)

Using the primitive chain network model, we have simulated the startup of steady planar elongation of a moderately entangled polymer melt at several elongation rates. The time dependence of the first normal stress growth coefficient, \( \eta_{\mu} \), was similar to that under startup uniaxial elongation, \( \eta_{\epsilon}^u \), and exhibited significant strain hardening when the Rouse Weissenberg number, \( W_R \), is greater than or equal to 1. Analysis of the chain conformation revealed that planar elongation resulted in the loss of fewer entanglements and in a lower orientation anisotropy compared to uniaxial elongation, and these two effects nearly compensated each other resulting in the qualitative similarity between \( \eta_{\mu} \) and \( \eta_{\epsilon}^u \). The second normal stress growth coefficient, \( \eta_{\mu} \), showed only strain softening and resembled startup shear including the appearance of a stress maximum. Independent of the strain rate, this stress maximum occurred at approximately half the strain at the stress maximum under startup shear. The time dependence of the segment orientation revealed that the molecular origin of the stress maximum can be attributed to the maximum in the corresponding orientation anisotropy, in direct analogy to the behavior under shear.

**Key Words:** Startup of steady planar elongation / Entangled polymer melt / Primitive chain network simulation

1. INTRODUCTION

Several polymer processing operations such as blow molding, fiber spinning, sheet extrusion, and film blowing involve subjecting entangled polymer melts to elongational flows of different types and to different extents. In such operations, the elongational flow characteristics of the polymer often determine its processability. For instance, during film casting, the central portion of the extruded film is subjected to planar elongation. Description of planar elongation requires two normal stress growth coefficients, \( \eta_{\mu} \) and \( \eta_{\epsilon} \), \( \eta_{\mu} \) is available for entangled solutions. Similarly to the experimental uniaxial elongational thinning. For nearly monodisperse polymers, \( \eta_{\mu} \) exhibited strain hardening when the elongation rate, \( \dot{\epsilon} \), approaches and exceeds the reciprocal of a “stretch relaxation time”. For linear polymers, the tube model identifies the stretch relaxation time with the Rouse time of the chain, \( \tau_R \), such that the strain hardening in \( \eta_{\mu} \) occurs when the Rouse Weissenberg number, \( W_R \), \( \equiv \epsilon \tau_R \geq 1 \). In contrast, \( \eta_{\epsilon} \) exhibited strain softening, \( \epsilon \), the connection to shear was not mentioned. For nearly monodisperse polymers, experimental data for the startup of steady planar elongation is available for entangled solutions. Similarly to the polydisperse melts, \( \eta_{\mu} \) of these solutions exhibited strain hardening for \( W_R \geq 1 \). For the investigated elongation rates, \( \eta_{\mu} (t) \) was found to be essentially identical to the uniaxial stress growth coefficient, \( \eta_{\mu}^u \), and this equality was highlighted by explicit comparison of \( \eta_{\mu} \) and \( \eta_{\mu}^u \) at two different elongation rates.

Given the experimental challenges, Kushwaha and Shaqfeh investigated the response of monodisperse polymer melts to planar elongation by simulating a modified version of the primitive chain network (PCN) model. They focused on the steady state viscosity and found qualitative similarity between the simulated planar elongational thinning and the experimental uniaxial elongational thinning. However, they did not discuss the startup of the flow.
On the theoretical side, by solving a modified version of the tumbling-snake model\(^{15}\) using Brownian dynamics, Stephanou and Kroger\(^{16}\) investigated the startup of steady planar elongation and found that while \(\eta_{\text{pp}}\) resembled, but was not identical to, \(\eta_{\text{pc}}\), \(\eta_{\text{pc}}\) resembled the shear stress growth coefficient, \(\eta_{\text{shear}}\), except that no stress undershoot was observed in \(\eta_{\text{pc}}\). However, similarly to the original Doi–Edwards picture\(^{11}\), the model did not incorporate mechanisms such as contour length fluctuations, thermal and convective constraint release, and chain stretch, believed to be necessary for an adequate description of slow and fast flows of entangled polymers\(^{17}\).

Ideally, our investigations should begin by direct comparison of PCN simulations to experimental data. Unfortunately, data for planar elongations of nearly monodisperse polymer melts are not available. Nonetheless, as the PCN model has been successful in describing the startup of shear\(^{38}\), uniaxial\(^{18-21}\), and equibiaxial\(^{22}\) elongations, we proceed with our investigations of planar elongation. In particular, by analyzing the chain conformation of the simulated model chains and using the decoupling approximation to relate the chain conformation derived quantities to the macroscopic stress, we have examined the hitherto poorly understood, molecular origin of the experimentally observed similarity between \(\eta_{\text{pc}}\) and \(\eta_{\text{pp}}\). Similarly, we have investigated the proposed similarity between \(\eta_{\text{pc}}\) and \(\eta_{\text{shear}}\) and its molecular origin.

### 2. MODEL

In the PCN model\(^{14}\), polymers are modeled as primitive chains consisting of subchains representing entanglement segments. To model entanglements, the primitive chains are connected at several junctions using slip-links to form a four functional pseudo network of subchains in three-dimensional space. The motion of the slip-links is described by a Langevin-type equation that accounts for force balance and includes subchain tension, an osmotic force, and a random Brownian force. The sliding motion of polymer chains is implemented by allowing the monomers to slide along the primitive chains. When the number of subchain monomers at the chain ends falls outside specified ranges, the corresponding slip-links between chains are either created or destroyed. Therefore, the number of slip-links in a chain fluctuates with time. Finite extensibility is implemented using the FENE-P approximation\(^{19}\) (refer Equation (2) in Results and Discussion) for the elastic force of a subchain. The molecular mechanisms believed to be important for entangled dynamics such as reptation, contour length fluctuations, thermal and convective constraint release, are included in the PCN model.

Similarly to our earlier work\(^{22}\), we have used the average number of subchains per chain under equilibrium, \(Z_0 \approx 23\) in the simulations. Past work\(^{23}\) using the PCN model has indicated that for polystyrene the appropriate value for the average molecular weight of the subchain, \(M_k \approx 1.1 \times 10^4\), which is comparable to but smaller than its experimentally determined entanglement molecular weight. Therefore, the \(Z_0\) used here corresponds to a molecular weight of \(2.5 \times 10^4\). The number of Kuhn segments in a subchain, \(n_0 = M_k / M_k = 15\) for polystyrene melts as the molecular weight of their Kuhn segments, \(M_k = 700^{24}\). The maximum stretch was determined from \(n_0\). The viscoelastic Rouse relaxation time, \(\tau_k = Z_0 \tau_0 / 2\pi^2\), where \(\tau_0\) is the unit time in the simulations. The simulations were performed using periodic boundary conditions. For the planar case, a \(4 \times 256 \times 32\) simulation box was deformed till it reached a size of \(256 \times 4 \times 32\), corresponding to a maximum Hencky strain of approximately 4.2, while for the uniaxial case, a \(4 \times 44.7 \times 44.7\) box was deformed to a size of \(500 \times 4 \times 4\) and corresponded to a maximum Hencky strain of approximately 4.8.

### 3. RESULTS AND DISCUSSION

Figure 1 exhibits the simulated \(\eta_{\text{pp}}/4\), \(\eta_{\text{pp}}/2\) and \(\eta_{\text{pp}}/3\) at several \(W_iR\). For \(W_iR \gtrsim 1\), \(\eta_{\text{pp}}^*\) exhibited significant strain hardening consistent with available experimental data on polydisperse melts\(^{39}\) and monodisperse solutions\(^{25}\). As can be seen from Fig. 1, \(\eta_{\text{pp}}^*\) is close, but not identical, to \(\eta_{\text{pc}}^*\). The similarity observed is qualitatively consistent with the
experimental data for entangled solutions\(^2\) and the theoretical predictions of tumbling-snake model for melts\(^6\). Note that experiments on entangled solutions\(^2\) indicated that \(\eta^1\) and \(\eta^2\) were essentially identical. Our simulations and the predictions of the tumbling-snake model\(^6\) suggest that while \(\eta^1\) and \(\eta^2\) are indeed close for entangled melts, they are not identical.

At all of the investigated \(W_R\), \(\eta^1\) exhibited strain softening, \textit{i.e.}, did not exceed the corresponding linear value. The occurrence of strain softening is consistent with experimental data on polydisperse melts\(^8\). With increasing \(W_R\), \(\eta^1\) exhibited a maximum at progressively earlier times and qualitatively resembled \(\eta^1_{\text{shear}}\). In Fig. 2, the \(W_R\) dependence of the strain at the maximum in \(\eta^1_{\text{shear}}\), \(\varepsilon_{\max}\) and the experimentally observed \(W_R\) dependence of the strain at the maximum in \(\eta^1_{\text{shear}}\), \(\gamma_{\max}\) for nearly monodisperse melts of two polymers\(^{25, 26}\) are exhibited.

The figure suggests that both \(\varepsilon_{\max}\) and \(\gamma_{\max}\) exhibit qualitatively similar \(W_R\) dependence. For \(W_R << 1\), both \(\varepsilon_{\max}\) and \(\gamma_{\max}\) are weakly dependent on \(W_R\). Upon increasing \(W_R\), \(\varepsilon_{\max}\) and \(\gamma_{\max}\) progressively begin to increase, and the increase becomes sharper upon approaching \(W_R \approx 1\). Figure 2 also suggests that \(\varepsilon_{\max} \approx \gamma_{\max}/2\). It is germane to note that no clear stress overshoot is visible in the experimental data\(^6\). While definite conclusions cannot be drawn from the limited experimental data that is available, sample polydispersity could be a reason.

Figure 1 also indicates that the \(\eta^2\) (\(t\)) has not reached steady state for the maximum strain \(\approx 4\) reached in the current simulation. These results are consistent with experimental data for polydisperse melts\(^8\), where the steady state has not been attained even for strain \(\approx 6\). In addition, our results are also consistent with the predictions of the tumbling-snake model\(^6\), which suggests that \(\eta^2\) (\(t\)) reaches steady state at a larger strain \(\approx 7-8\). As there are indications that the steady state has not been reached in our simulations, especially for \(\eta^2\), we have refrained from a direct comparison of our results to that of Kushwaha and Shaqfeh\(^{13}\).

To understand the macroscopic response in terms of the molecular response, we used a decoupling approximation\(^{27}\). Within this approximation, the tensile stress \(\sigma\) can be written as,

\[
\sigma = \left(\frac{Z}{X}\right) f_{\text{FENE}} S. \tag{1}
\]

Here \(Z\) is the instantaneous average of the number of entanglement segments in one chain and \(Z_0\) is its equilibrium value. As the PCN model approximates the nonlinear elastic response of the chain using the FENE-P equation, the finitely extensible nonlinear elastic (FENE) factor, \(f_{\text{FENE}}\) is defined as

\[
f_{\text{FENE}} = \frac{1}{1-\lambda^2} \text{ with } \lambda = \lambda/\lambda_{\max}, \tag{2}
\]

where \(\lambda\) is defined using the root mean squared stretch, \(\lambda\), normalized by the maximum possible stretch of the entangled subchain, \(\lambda_{\max}\). The \(S\) indicates the orientation anisotropy and analogously to the two normal stress differences, the first and second orientation anisotropies, \(S_{p1}\) and \(S_{p2}\), can be defined as,

\[
S_{p1} = \langle u_1^2 \rangle - \langle u_2^2 \rangle; \quad S_{p2} = \langle u_2^2 \rangle - \langle u_3^2 \rangle. \tag{3}
\]

Here \(u_i\), is the segment unit vector in direction \(i (= x, y, z)\) where, \(x\) is the elongation direction, \(y\) is the neutral direction, and \(z\) is the compression direction. The \(\langle \cdot \rangle \) denotes averaging over all of the entanglement segments in all of the chains. The corresponding \(S\) for uniaxial elongation, \(S_u\), can be defined using

\[
S_u = \langle u_1^2 \rangle - \frac{1}{2} \langle u_2^2 + u_3^2 \rangle, \tag{4}
\]

where, \(x\) the elongation direction and, \(y\) and \(z\) are the compression directions. Equations (1) – (4) relate the stress to measures of chain deformation that can be directly calculated from the conformations of the simulated chains. Below, we have attempted to use the chain quantities suggested by Equation (1) to understand the macroscopic stress response. Figure 3 compares the \(\lambda^2\) under planar and uniaxial
elongations and indicates that the time dependence of \( \lambda_2^2 \) is quantitatively similar for both planar and uniaxial elongations. This suggests that the difference in the geometry of the deformation between planar and uniaxial elongations had little effect on the time development of \( \lambda_2^2 \). Combined with Equation (2), the similarity of the time dependence of \( \lambda_2^2 \) for both planar and uniaxial elongations imply that the time dependence of the FENE is also very similar for these two deformations. Therefore, from Equation (1), any difference between \( \eta_{p1} \) and \( \eta_u \) must arise from the difference in the time dependence of \( Z/Z_0 \) and the corresponding orientation anisotropy, \( S_{p1} \). The time dependence of \( Z/Z_0 \) shown in Fig. 4 indicates that, under planar elongations, \( Z \) remains at its equilibrium value \( Z_0 \) for a length of time that varies with \( W_{R} \) before exhibiting a decrease. Interestingly, this behavior is similar to that observed in simulations of startup shear using the PCN model where the model was successful in describing experimental data \(^{18}\). In contrast, under uniaxial elongations, \( Z/Z_0 \) begins to decrease at significantly earlier times, nearly at the inception of the flow. At all times, including at the steady state, the \( Z/Z_0 \) under planar elongations is larger than that under uniaxial elongations. This suggests that, at any \( W_{R} \), the flow induced loss of entanglements is less significant for planar than for uniaxial elongations.

From Fig. 5, it can be seen that \( S_{p1} \) increases monotonically with time. The increase is initially rapid, becomes more gradual at longer times, and finally, appears to almost saturate. While the increase in \( S_{p1} \) and \( S_u \) with time appear to be qualitatively similar, \( S_{p1} < S_u \) at all times accessible to the simulation. This suggests that the orienting effect of planar elongation is weaker than that of uniaxial elongation. The similarity between \( \eta_{p1} \) and \( \eta_u \) (see Fig. 1) suggests that these opposite effects nearly compensate each other and result in the \( \eta_{p1} \) and \( \eta_u \) being quantitatively close to each other.

On the other hand, at all of the investigated \( W_{R} \), the time dependence of \( S_{p2} \) was exhibited non-monotonic with a maximum at intermediate times. The \( W_{R} \) dependence of the strain at the maximum in \( S_{p2} \), \( \epsilon_{\text{max}} \), is exhibited in Fig. 2. For \( W_{R} \leq 1 \), \( \epsilon_{\text{max}} = \epsilon_{\text{max}} \) and this allows us to suggest that the non-monotonicity of \( S_{p2} \) is origin of the overshoot seen in \( \eta_{p2} \). For \( W_{R} > 1 \), while \( \epsilon_{\text{max}} \) did not vary significantly, \( \epsilon_{\text{max}} \) progressively increased due to effect of the progressively larger values of \( \lambda_2^2 \). Incidentally, the explanation proposed above for the maximum in \( \eta_{p2} \) is essentially identical to that for the shear stress overshoot \(^{27-29}\), suggesting a similarity even at the level of the molecular response.
4. CONCLUSION

We have simulated a moderately entangled polymer melt ($Z_0 = 23$) under the startup of steady planar elongation at different elongation rates using the PCN model\(^{16}\). Similarly to $\eta_\text{sel}$, $\eta_\text{un}$ exhibited significant strain hardening for $Wi_k \gtrsim 1$. The time dependence of $\eta_\text{un}$ was qualitatively similar to that of $\eta_\text{sel}$ for all of the $Wi_k$ investigated. In order to relate the macroscopic response to the deformation of the chain, we calculated the measures of chain deformation suggested by a decoupling approximation. We found that the time dependence of $\lambda^2$ and consequently, $f_{\text{FENE}}$ were nearly identical for both planar and uniaxial elongations. Interestingly, the time dependence of $Z/Z_0$ under startup planar elongations closely resembled that under shear. For all of the investigated $Wi_k$ and at all times, the $Z/Z_0$ under planar elongations was larger than that for uniaxial elongations but $S_{\text{pl}} < S_{\text{un}}$. These two effects appear to cancel each other to yield similar qualitative time dependence for both $\eta_\text{un}$ and $\eta_\text{sel}$.

In contrast to $\eta_\text{un}$, but similarly to startup shear\(^{26,27}\), $\eta_\text{sel}$ showed strain softening, and a stress overshoot for all of the investigated $Wi_k$. The dependence on $Wi_k$ of $\epsilon_{\text{max}}$ was qualitatively similar to that of $\gamma_{\text{max}}$ and nearly satisfied the relation $\epsilon_{\text{max}} \approx \gamma_{\text{max}}/2$ independent of $Wi_k$. For $Wi_k \lesssim 1$, as $\epsilon_{\text{max}} \approx \epsilon'_{\text{max}}$ the origin of the maximum in $\eta_\text{sel}$ can be directly attributed to the maximum in $\lambda^2$. In addition, combining our results with past experiments\(^8\), simulations\(^{13}\) and theory\(^{16}\) strongly suggests that for uniaxial elongations but $\gamma_{\text{un}} < \gamma_{\text{sel}}$. This reason for this difference is presently unclear and will be the subject of future investigations.

In summary, we have subjected a monodisperse entangled melt to planar elongations and found similarities to both uniaxial elongation and shear not only in the macroscopic stress response but also in the molecular response. Given these intriguing similarities and although the relevant experimental data is not yet available, further exploration of planar elongational flow using simulations and theory and their comparison to uniaxial and shear flows appears worth pursuing.

ACKNOWLEDGEMENTS

SKS is grateful to Prof. J. Takimoto of Yamagata University and Prof. H. Watanabe of Kyoto University for illuminating discussions. SKS was supported by the Grant-in-Aid for Scientific Research (C) (19K03761) from JSPS and by the Collaborative Research Program of Institute for Chemical Research, Kyoto University (2019-51)

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