Dynamics and Rheology of a Supercooled Polymer Melt

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Molecular dynamics simulations are performed for a polymer melt composed of short chains in quiescent and sheared conditions in supercooled states. In quiescent states, while the self chain motions are excellently described by the Rouse model, the stress relaxation function $G(t)$ exhibits a stretched exponential decay in a relatively early stage and ultimately follows the Rouse function. Transient stress evolution after application of shear obeys the linear growth $\int_0^t dt' G(t')$ for strain less than 0.1 and then saturates into a non-Newtonian viscosity. A glassy component of the stress is much enhanced as compared to the entropic component.

§1. Introduction

In computer simulations of polymer melts, single chain motions have been investigated extensively in quiescent states.1)-4) However, not enough theoretical efforts have been made on the rheological properties of glassy polymers particularly in supercooled states. The stress and dielectric relaxations in glassy polymer melts occur from microscopic to macroscopic time scales in complicated manners.5), 6) Shorter time relaxations arise from rearrangements of jammed atomic configurations as in supercooled simple liquids,8), 7) and the terminal relaxation is governed by subsequent evolution of chain conformations described by the Rouse or reptation dynamics.1), 9) We will first demonstrate that the dynamics of the present short chain system in quiescent supercooled states is well described by the Rouse model and then study linear rheology of the system via very long molecular dynamics simulations.

In a transient regime after application of deformation, the stress-optical relation between birefringence and stress has been reported to be violated as the temperature $T$ is approached the glass transition temperature $T_g$,10)-12) owing to the enhancement of a glassy part of the stress. The origin of this mechanism will be discussed in detail.

§2. Model and simulation

In our model, all the bead particles interact with the Weeks-Chandler-Andersen (WCA) potential,13)

$$U_b(r) = \begin{cases} 4\epsilon \left[ (\sigma/r)^{12} - (\sigma/r)^6 \right] + \epsilon, & r/\sigma \leq 2^{1/6} \\ 0, & r/\sigma > 2^{1/6}. \end{cases} \quad (2.1)$$

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Consecutive beads on each chain are connected by an anharmonic spring of the form, 1), 2), 4)

\[ U_F(r) = -\frac{1}{2}k_c R_0^2 \ln[1 - (r/R_0)^2] \]  

(2.2)

with \( k_c = 30\epsilon/\sigma^2 \) and \( R_0 = 1.5\sigma \), so the bond length cannot exceed \( R_0 \). In a cubic box with length \( L = 10\sigma \) under the periodic boundary condition, we put \( M = 100 \) chains composed of \( N = 10 \) beads. The number density is fixed at a high value of \( n = NM/V = 1/\sigma^3 \), which results in severely jammed configurations at low \( T \). We will measure space and time in units of \( \sigma \) and \( \tau_0 = (m\sigma^2/\epsilon)^{1/2} \) with \( m \) being the mass of a bead. The temperature \( T \) will be measured in units of \( \epsilon/k_B \). Simulations were performed in normal (\( T = 1.0 \)) and supercooled (\( T = 0.4 \) and 0.2) states with and without shear. The bond lengths \( b_j = |R_j - R_{j+1}| \) between consecutive beads on each chain are nearly fixed at 0.96 for any \( T \) and \( \gamma \) in our study.

We took data after long equilibration periods (\( 10^6 \) at \( T = 0.2 \)) to suppress slow equilibration effects in various quantities such as the pressure or the density time correlation functions. At zero shear we imposed the micro-canonical condition with the time step \( \Delta t = 0.005 \). In order to obtain accurate linear viscoelastic behavior, very long simulations of order \( 10^3\tau_R \) were performed, where \( \tau_R \) is the longest Rouse relaxation time. In the literature, 1), 2), 4) simulation times have been typically up to \( \tau_R \) in supercooled states. In the presence of shear we set \( \Delta t = 0.0025 \) and kept the temperature at a constant using the Gaussian constraint thermostat to eliminate viscous heating. After a long equilibration time in a quiescent state for \( t < 0 \), all the particles acquired the average flow velocity \( \dot{\gamma}y \) in the \( x \) direction at \( t = 0 \) and then the Lee-Edwards boundary condition 14), 15) maintained the simple shear flow. Steady sheared states were realized after transient viscoelastic behavior.

§3. Results

As has been confirmed in the literature, 2) - 4) the dynamics in quiescent supercooled states is reasonably well described by the Rouse model, where the relaxation time of the \( p \)-th mode of a chain is expressed as \( \tau_p = \zeta b^2/[12k_B T \sin^2(p\pi/2N)] \) \((p = 1, \cdots, N-1)\). Here, the statistical segment length \( b \) is related to the variance of the end-to-end vector of a chain \( \mathbf{P} = \mathbf{R}_N - \mathbf{R}_1 \) by \( b = (\langle \mathbf{P}^2 \rangle/(N-1))^{1/2} \), which is 1.17, 1.18, 1.19 for \( T = 1.0, 0.4, 0.2 \), respectively. We determined the monomer friction constant \( \zeta \) from the time correlation function of the end-to-end vector

\[ C(t) = \langle \mathbf{P}(t) \cdot \mathbf{P}(0) \rangle = 2N^{-1} \sum_{\ell=0,1,\cdots} \cot^2(\pi(2\ell + 1)/2N) \exp(-t/\tau_{2\ell+1}). \]  

(3.1)

The Rouse relaxation time \( \tau_R (= \tau_1 \cong \zeta b^2 N^2/3\pi^2 k_B T) \) then increases dramatically with lowering \( T \) as \( \tau_R = 250, 1800, \) and \( 6 \times 10^4 \) for \( T = 1.0, 0.4, 0.2 \), respectively. In Fig. 1, we plot the mean square displacements for the center of mass \( \phi_G(t) = \langle ||\mathbf{R}_G(t) - \mathbf{R}_G(0)||^2 \rangle \) and the averaged beads displacements \( \phi_b(t) = \frac{1}{N} \sum_{n=1}^N \langle ||\mathbf{R}_n(t) - \mathbf{R}_G(t) - (\mathbf{R}_n(0) - \mathbf{R}_G(0))||^2 \rangle \), where \( \mathbf{R}_n(t) \) is the position of the \( n \)-th bead at \( t \) and \( \mathbf{R}_G(t) = \frac{1}{N} \sum_{n=1}^N \mathbf{R}_n(t) \). The time scale is normalized in Fig. 1 using \( \tau_R \), and then good agreements of our data with the Rouse model are found for \( t/\tau_R > 10^{-2} \).
Fig. 1. Comparisons of our MD data at $T = 1$ and 0.2 with the Rouse model for the mean square displacements for the center of mass $\phi_G(t) = \langle [R_G(t) - R_G(0)]^2 \rangle$ and the averaged beads displacements $\phi_b(t) = \frac{1}{N} \sum_{n=1}^{N} \langle [(R_n(t) - R_G(t)) - (R_n(0) - R_G(0))]^2 \rangle$. The time scale is normalized using $\tau_R$.

Now let us discuss the linear viscoelastic behavior in supercooled states. In Fig. 2 we show the stress relaxation function,

$$G(t) = \langle \sigma_{xy}^T(t) \sigma_{xy}^T(0) \rangle / V k_B T,$$

where $\sigma_{xy}^T$ is the space integral of the $xy$ component of the total stress tensor over the volume $V = L^3$. At the lowest temperature $T = 0.2$, $G(t)$ exhibits salient features of glassy polymer melts.\(^5,6\) Its initial value is of order 100 (in units of $\epsilon/\sigma^3$) and is very large, and it relaxes to a value $G_0$ about 5 for $t \gtrsim 1$. We then have a slow decay of the form,

$$G(t) \cong G_0 \exp\left[-(t/\tau_s)^\beta\right],$$

where $\tau_s = 90 \sim \tau_\alpha$ (\(\equiv\) structural $\alpha$ relaxation time) and $\beta \simeq 0.5$. The agreement to Eq. (3.3) is excellent for $1 \lesssim t \lesssim 10 \tau_s$. This glassy behavior arises from monomeric structural relaxation. For $t \gtrsim 50 \tau_s$ it approaches the Rouse stress relaxation function,

$$G_R(t) = nk_B T N^{-1} \sum_{p=1}^{N-1} \exp(-2t/\tau_p),$$

which is equal to $T(N-1)/N$ for $t \lesssim \tau_\alpha$ and decays as $TN^{-1} \exp(-2t/\tau_R)$ for $t \gg \tau_R$ in the dimensionless units. Obviously, this final stage behavior arises from relaxation of large scale chain conformations. The crossover between these two regions occurs in a narrow time range in our case. Experimentally, however, the intermediate region, which connects the glassy and polymeric (Rouse or reptation) relaxations, extends over a much wider time range (typically 4 decades\(^5\)), and $G(t)$ there has been fitted
Fig. 2. The stress relaxation function $G(t)$ (thin-solid lines) at $T = 0.2$ in a supercooled state and $T = 1$ in a normal liquid state. It may be fitted to the stretched exponential form (dotted line) at relatively short times and tends to the Rouse relaxation function $G_R(t)$ (bold-dashed lines) at long times.

In addition, with increasing the molecular weight, a rubbery plateau has been observed to develop after the crossover before the terminal decay, whereas it is not apparently seen in our short chain system. In our case, the (zero-frequency) linear viscosity $\eta$ consists of a monomeric part $\Delta \eta$ of order $10 \tau_s$ from the integration in the time region $t \lesssim 10 \tau_s$ and the Rouse viscosity $\eta_R = \int_0^\infty dt G_R(t) \cong 0.808TN^{-1}\tau_R$ from $t \gtrsim \tau_R$. The ratio $\Delta \eta/\eta_R$ is thus of order $1/(TN)$ ($\sim 1$ at $T = 0.2$), whereas we should have $\Delta \eta \ll \eta_R$ for much larger $N$.

In the Rouse model, the space integral of the polymer (entropic) stress $\sigma_{\alpha\beta}^R$ is the sum of $k_BTb_{j\alpha}b_{j\beta}/b^2$ over all the bonds in the system, where $b_{j\alpha}$ are the Cartesian components of the bond vectors $b_j = R_{j+1} - R_j$. We have confirmed that the relaxation function $G_c(t) = \langle \sigma_{xy}^R(t)\sigma_{xy}^R(0)\rangle/Vk_BT$ nearly coincides with $G_R(t) \cong G(t)$ for $t \gtrsim 0.1\tau_R$, whereas it is about a half of $G_R(t)$ for $t \lesssim \tau_s$. We note that the bond vectors have the nearly fixed length $b_0 \cong 0.96$, and a bond orientation tensor $Q_{\alpha\beta}$ may be defined as

$$Q_{\alpha\beta} = (N-1)^{-1}\sum_{j=1}^{N-1} \langle b_{j\alpha}b_{j\beta} \rangle/b_0^2.$$  \hspace{1cm} (3.5)

Then we have $Q_{\alpha\beta} \propto \langle \sigma_{\alpha\beta}^R \rangle$. If the electric polarizability tensor of a bead is uniaxial along the bond vector, the deviation of the dielectric tensor $\Delta \varepsilon_{\alpha\beta}$ is proportional to $Q_{\alpha\beta} - \delta_{\alpha\beta}/3$. In flow birefringence we have a modified stress-optical law,

$$\Delta \varepsilon_{xy} = C\langle \sigma_{xy}^R \rangle/V,$$  \hspace{1cm} (3.6)

where $C$ is a constant. In supercooled states $\langle \sigma_{xy}^R \rangle/V$ can be much smaller than
the total shear stress $\sigma_{xy}$, for instance, in transient states or in oscillatory shear. Therefore, the usual stress-optical law $\Delta \varepsilon_{xy} = C \sigma_{xy}$, which is valid far above $T_g$, breaks down close to $T_g$.

In Fig. 3, we show the stress growth function $\sigma_{xy}(t)/\dot{\gamma}$ after application of shear at $t = 0$ at the lowest temperature $T = 0.2$ for various $\dot{\gamma}$. The curves are the averages of data of eight independent runs. In the initial stage, in which $\dot{\gamma}t \lesssim 0.1$, we can see the linear viscoelastic growth, $\sigma_{xy}(t)/\dot{\gamma} = \int_0^t G(t')dt'$, whereas a nonlinear regime sets in for $\dot{\gamma}t \gtrsim 0.1$, resulting in the non-Newtonian viscosity $\eta(\dot{\gamma})$. As a guide, we also plot the linear growth function $\int_0^t G_R(t')dt'$ from the Rouse model, which is much smaller than the true linear growth for $t \ll \tau_R$. The relevant physical processes are as follows: For $\dot{\gamma}t \lesssim 0.1$ the overall chain conformations are affinely deformed, whereas for $\dot{\gamma}t \lesssim 0.1$ the structural rearrangements among beads belonging to different chains become appreciably induced by shear (as in the case of supercooled simple fluids\cite{7}). Experimentally, a stress overshoot (a rounded maximum of $\sigma_{xy}(t)$) has been observed at $\dot{\gamma}t = 0.05 - 0.1$ for higher molecular weight melts close to $T_g$.\cite{5}

§ 4. Summary

The single chain motions in our nonentangled polymer melt show excellent agreements with the Rouse model in normal and supercooled states. On the other hand, the stress relaxation function $G(t)$ decays with a stretched exponential form in a relatively short time regime and asymptotically obeys the Rouse relaxation in a long time regime in supercooled states. The glass-rubber transition region and the rubbery plateau have not been reproduced because the chain length is too short and the temperature is still too high.
Although not presented in this paper, we have also obtained very early onset of the nonlinear regime of shear.\textsuperscript{20} Strong shear-thinning and anisotropic scattering can be predicted for $\dot{\gamma} \gtrsim \tau_R^{-1}$ or for $\sigma_{xy} \gtrsim nk_BT/N$ in the Rouse case $N < N_e$. In the entangled case $N > N_e$ the threshold shear rate and stress needed for the onset of nonlinearity should be of order $\tau_{\text{rep}}^{-1}$ and $nk_BT/N_e$, respectively, where $\tau_{\text{rep}}$ is the reptation time. Scattering experiments for very weakly sheared melts near $T_g$ are promising. Dynamic heterogeneities are enhanced also in polymer melts at low $T$ in the bond breakage and the monomer diffusivity\textsuperscript{21,22} as in supercooled simple liquids,\textsuperscript{7,8} However, they little affect the center-of-mass motions of chains because their characteristic life time is much shorter than $\tau_R$.

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