Effects of Constraint-Release on Entangled Polymer Dynamics in Primitive Chain Network Simulations

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(Received: December 1, 2019)

For the entangled polymer dynamics, in addition to reptation and contour length fluctuation (CLF), constraint release (CR) has been widely accepted as an essential relaxation mechanism. However, although conceptually established, the nature of CR has not been fully clarified yet. In this study, entangled polymer dynamics were observed via primitive chain network simulations in the melt, and in a matrix where CR is suppressed. The viscoelastic and end-to-end relaxation times, the diffusion constant, and the apparent plateau modulus were obtained as functions of molecular weight. All the obtained results are reasonably consistent with experimental data in the literature. In the results, CR accelerates the relaxation and the diffusion as expected, and the acceleration factor decreases as an increase of the molecular weight. Consequently, the power-law exponent for the molecular weight dependence of the relaxation time is affected by CR. Meanwhile, the plateau modulus is not affected by CR, yet the molecular weight dependence is consistent with the literature. These results explain the time-stress discrepancy, which has been reported as inconsistency between the relaxation time and the modulus.

Key Words: Coarse-graining / Molecular simulation / Entangled polymers / Dynamics / Viscoelasticity

INTRODUCTION

Although the entangled polymer dynamics at equilibrium can be described by the tube theory that incorporates contour length fluctuation (CLF) and constraint release (CR), the consensus on the implementation of these relaxation mechanisms into the tube framework has not been fully established yet. The dominant relaxation mechanism is reptation, in which the polymer diffusion is restricted to the curvilinear direction along the chain backbone. Although this picture explains a lot of phenomena qualitatively, for a quantitative agreement, additional relaxation mechanisms have been proposed. CLF represents the relaxation of the tube along its backbone due to the spring-like dynamics of the test chain in the tube. In contrast, CR represents the tube motion in its lateral directions due to the relaxation of surrounding chains. The effects of CLF are frequently mentioned on the power-law exponents for the molecular weight dependence of the relaxation time and the diffusion coefficient. The reptation theory predicts power-law dependence of the relaxation time $\tau$ and the diffusion coefficient $D$ on the molecular weight $M$ as $\tau \propto M^\alpha$ and $D \propto M^\beta$. Such power-law behaviors have been confirmed experimentally. However, the exponents $\alpha$ and $\beta$ theoretically predicted are not in excellent agreement with experimental ones. The theory gives $\alpha = 3$ and $\beta = -2$, whereas the experimental values are $\alpha \approx 3.4$ and $\beta \approx -2.3$. These discrepancies have been explained by Doi and Frischknecht and Milner on the basis of CLF. In their theory, the relaxation time and the diffusion coefficient for the polymers exhibiting reptation and CLF can be written as follows.

\begin{align}
\tau(Z) &= \tau_r(Z) \left(1 - \frac{A}{\sqrt{Z}}\right)^2. \\
D(Z) &= D_r(Z) \left(1 + \frac{B}{\sqrt{Z}}\right).
\end{align}

Here, $Z$ is the number of entanglement segments per molecule defined as $Z \equiv M/M_e$, where $M_e$ is the entanglement molecular weight. $\tau_r$ and $D_r$ are the predictions from the original reptation theory, and $A$ and $B$ are numerical constants. Eqs 1 and 2 reproduce the power-law behavior in a specific range of $Z$ with apparent exponents consistent with the experimental data.

Although not frequently mentioned, the power-law exponents are affected by CR as well. Graessley proposed a model where the Rouse dynamics of the tube express the CR
relaxation. He assumed that the Rouse-type CR dynamics are independent of reptation and CLF. Consequently, his model predicts that the CR-induced acceleration is molecular weight independent, and the power-law exponents are unaffected by CR. In contrast, Watanabe and Tirrell\(^{14}\) reported that the CR-induced acceleration is molecular weight dependent if the coupling between reptation and CR is introduced. Even though they did not consider CLF, their model predicts \(\alpha \approx 3.4\). Frischknecht and Milner\(^{13}\) reported a similar effect of CR on the diffusion. The molecular weight dependence of the CR-induced acceleration has been suggested experimentally as well. Liu \textit{et al.}\(^{15}\) performed viscoelastic measurements for binary blends composed of long and short chains with well-separated molecular weights. They reported that \(\alpha\) of the short-chain (immersed in the long-chain matrix) is smaller than that for the monodisperse melts. These results demonstrate that the effects of CLF and CR on the power-law exponents have not been fully clarified yet.

Concerning the effects of CLF and CR on the entangled polymer dynamics, there exists another unsolved issue so-called 'time-stress discrepancy'\(^{16}\). Doi\(^{6}\) pointed out that CLF affects the plateau modulus because the fluctuation reduces the number of effective entanglements, as shown below.

\[
G_{N,\text{app}}(Z) = G_{N,\infty} \left(1 - \frac{\alpha}{\sqrt{2}} \right)
\]

Here \(G_{N,\infty}\) is the plateau modulus observed for a melt with infinite molecular weight. Similar molecular weight dependence of the plateau modulus has been reported experimentally\(^{17}\). However, there is a problem with the numerical constant \(A'\), as pointed out by van Ruymbeke \textit{et al.}\(^{16}\). Theoretically, \(A'\) is identical to \(A\) (in eq 1), although reasonable fitting to the experimental data cannot be achieved unless \(A' < A\). This discrepancy between \(A\) and \(A'\) is the so-called time-stress discrepancy. Even for modern molecular theories, in which CLF and CR are taken into account, this problem has not been solved\(^{16,18}\). A possible explanation for this failure is a correlation between CR and CLF, although the mechanism is still unknown.

Attempts have been made using molecular simulations for the contributions of CLF and CR, but the simulations for well-entangled systems are practically challenging. Wang and Larson\(^{19}\) performed Kremer-Grest\(^{20}\) simulation to report that the CR contribution is in harmony with Graessley’s theory\(^7\) if the broad distribution of the disentanglement rate is considered. Stephanou \textit{et al.}\(^{21}\) reported atomistic molecular dynamics simulations for polybutadiene and polyethylene melts. They attempted to quantify the contributions of CR and CLF based on the tube survival probability obtained via the primitive path extraction. However, due to the high computation costs, the effect of molecular weight on CR has not been explored yet.

In this study, multi-chain slip-link simulations were performed for the effect of molecular weight on CR. The simulation is based on the primitive chain network (PCN) model (also referred to as the NAPLES code), in which polymer chains are bundled in pair by slip-links to form a network\(^{1,22-24}\). In this approach, reptation, CLF, and CR are naturally implemented unless artificially switched off. For instance, van Ruymbeke \textit{et al.}\(^{25}\) observed the dynamics of a probe chain, for which the chain ends are fixed in space. For this probe chain, the relaxations induced by reptation and CLF were eliminated, and the relaxation by CR of matrix chains was exclusively evaluated. On the contrary, in the present study, the reptation of matrix chains is switched off and CR for the probe chain is eliminated. The CR-induced acceleration in the viscoelastic relaxation and diffusion and the time-stress discrepancy shall be discussed.

**MODEL AND SIMULATIONS**

In the multi-chain slip-link simulation, an entangled polymer system is represented by a network consisting of nodes, strands, and dangling ends. Each polymer chain corresponds to a path connecting the dangling ends through the strands and the nodes. The strand represents a polymer segment, which is conceptually similar to the primitive path segment in the tube model. From each node, four strands diverge according to the binary assumption of entanglement. Because the node corresponds to entanglement, at each node, a slip-link is located and it allows the bundled polymer chains to slide along their backbone. The state valuables are the node position (slip-link position) \(\{R\}\), the number of Kuhn segments carried by each strand \(\{n\}\), and the number of segments for each polymer chain \(\{Z\}\). The dynamics of \(\{R\}\) is described by a Langevin-type equation of motion according to the force balance among the drag force, elastic tension on the diverging strands, osmotic force, and random force. The development of \(\{n\}\) is described by a rate equation, in which the common force balance with the \(\{R\}\) dynamics is considered. The evolution of \(\{Z\}\) is attained by the creation and destruction of the node (slip-link) at the chain ends. For further details, see earlier publications\(^{1,22-24}\).

For the model, the units of length, energy, and time are chosen as the average length of the strand \(\alpha, kT\), and \(\tau_0 = \frac{\zeta c^2}{6kT}\), respectively. For the unit time, \(\zeta\) is the friction
coefficient of the slip-link. The unit of molecular weight $M_o$ corresponds to the polymer segment carried by the single strand, and $M_o$ is smaller than $M_t$ for the tube models due to the fluctuations around the slip-link\(^{26, 27}\). Consequently, the unit of modulus defined as $G_0 = \rho R T / M_o$ is larger than the plateau modulus, and the number of entanglements per chain $Z_{PCN}$ is also larger than that for the tube models. Note that due to the multi-chain nature, $Z_{PCN}$ has a distribution\(^{28}\), and the value used hereafter is the statistical average.

For the evaluation of the effects of CR, let us consider a test chain in a simulation box entangled with the other chains. If the full-dynamics mentioned above are turned on, the test chain is regarded to be dissolved in a melt, and it exhibits relaxation according to reptation, CLF, and CR. In contrast, the chain dynamics without CR can be observed if the creation and destruction of the node are disallowed for the surrounding chains. Such a matrix without CR (referred to as non-CR matrix hereafter) was prepared from an equilibrated melt. For the dynamics of probe chains embedded in the non-CR matrix, the viscoelastic and dielectric relaxations have been reasonably reproduced for some cases\(^{29}\).

The simulations were performed under periodic boundary conditions with the unit box dimension of $8^3$. The segment density was fixed at 10. For the melt simulations, the code was run for a sufficiently long time, which is more than 10 times longer than the longest relaxation time, and the data were acquired for the latter half of the simulations. The non-CR matrix was created from the equilibrated melt by disallowing the network rearrangement of the chains except one probe chain. The long-time simulation and the data acquisition were performed for the prove chain in the non-CR system as well. The relaxation was evaluated from the auto-correlation functions for the stress and the end-to-end vector under equilibrium. The diffusion constant was obtained from the mean-square distance in the long-time range, where the Einstein diffusion was observed.

**RESULTS**

Figure 1 shows the loss modulus $G''(\omega)$ converted from the stress auto-correlation for the chain with $Z_{PCN} = 40$. For the melt (black), $G''(\omega)$ was calculated from the entire stress, whereas that for the probe chain in the non-CR matrix (red) was obtained from the stress of the probe chain only. The result is consistent with the tube model proposed by Likhtman-McLeish\(^{30}\) for the effect of CR. Namely, $G''(\omega)$ for the non-CR matrix (red) exhibits a slower relaxation than that for the melt (black), demonstrating the CR-induced acceleration. For the non-CR matrix, the slope of $G''(\omega)$ for the high-frequency side of the peak is ca. $-1/2$, which is consistent with the tube theory. Due to the insufficient chain length, the slope of $-1/4$, which is the signature of CLF, is not observed for this specific case. Nevertheless, the slope is gentle for the melt due to the relaxation modes originated from CR. For the melt, the cross-correlation between different chains\(^{27, 30-33}\) also contributes to the broadening of $G''(\omega)$, although it does not affect the relaxation time\(^{29}\). The small discrepancy in the high-$\omega$ region is due to a numerical problem in the data conversion via the fitting to the multi-mode Maxwell function\(^{34}\).

Figure 2 top panel shows the relaxation times for the stress, and the end-to-end vector plotted against $Z_{PCN}$. The relaxation times obtained in the non-CR matrix (triangles) are shorter than those for melts (circles), demonstrating the CR-induced acceleration. Figure 2 bottom panel shows the relaxation times normalized by the prediction of the original reptation theory to demonstrate the molecular-weight dependence of the acceleration. The power-law exponent $\alpha$ for both relaxation times is ca 3.1 for the probe chain in the non-CR matrix, whereas $\alpha \sim 3.4$ for the melt. This result is consistent with the experiment for the stress relaxation reported by Liu et al.\(^{35}\), for which the data are plotted in the right panel for comparison. Note that the CR-induced acceleration is observed for the end-to-end relaxation as well\(^{35}\). This acceleration is experimentally observed as the dielectric relaxation of polyisoprene\(^{77}\), whereas the tube model\(^{30}\) and the single-chain slip-link model\(^{29}\) do not exhibit any acceleration. Note also that the result is consistent with the theory by Watanabe and Tirrell\(^{40}\) who considered the coupling between CR and reptation.

Figure 3 top panel shows the diffusion coefficient $D$ plotted against $Z_{PCN}$. The bottom panel shows the normalized value concerning the reptation theory, with the experimental
data\textsuperscript{40} and the theoretical curves by Frischknecht and Milner\textsuperscript{13}. The results for the melts (black circle) are in good agreement with the experimental data\textsuperscript{40}, as demonstrated in the bottom panel. Being similar to the relaxation time, the diffusion in the melt is faster than that in the non-CR matrix (red triangle), reflecting the CR-induced acceleration. The acceleration factor is molecular weight dependent, similar to the earlier theory\textsuperscript{13}, for which the predictions for CR and non-CR matrices are indicated by solid and broken curves.

Figure 4 shows the apparent plateau modulus as a function of $Z_{PCN}$. Although there have been proposed several methods to determine the plateau modulus from $G(t)$ and $G^*(\omega)$\textsuperscript{35}, those experimental methods are difficult to be applied to the examined range of molecular weight in this study. Instead, the apparent plateau modulus was obtained according to the earlier study for the PCN model\textsuperscript{26}. Namely, $G_{N,app} = G(t_0)$ for $G(t)$ calculated via the Green-Kubo formula. This choice of $G_{N,app}$ is consistent with Doi’s theory\textsuperscript{6} for eq 3, where the molecular weight dependence of the relaxation intensity is induced by the short time fluctuation until $t_0$.

Nevertheless, $G_{N,app}$ increases as an increase of the molecular weight due to the effect of the chain ends, which play a role as defect in the network\textsuperscript{26}. The simulation result for melt (black circle) is consistent with the experiment (cross) and in better agreement than the tube model prediction\textsuperscript{16}, for which the effect of the chain end seems overestimated. Besides, $G_{N,app}$ indicates no significant effect of CR. This insensitivity of $G_{N,app}$ to CR is also consistent with the experimental data for binary blends\textsuperscript{35}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Relaxation times plotted against the entanglement segment number $Z_{PCN}$. Triangles and circles are for the non-CR matrix and the melt, respectively. Filled and unfilled symbols are for the stress and the end-to-end relaxations. In the bottom panel, the relaxation times are divided by $Z_{PCN}^3$, which is the prediction of the reptation theory. The experimental data\textsuperscript{40} for monodisperse (cross) and bidisperse melts (asterisk) are shown for comparison.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Diffusion coefficient $D$ plotted against the entanglement segment number $Z_{PCN}$ for the melt (black circle) and the non-CR matrix (red triangle). In the bottom panel, the diffusion coefficient is normalized with respect to the reptation theory, and compared with the experimental data\textsuperscript{40} (cross) and the theoretical predictions\textsuperscript{13} for CLF only (broken curve) and CLF plus CR (solid curve).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Apparent plateau modulus $G_{N,app}$ plotted against the entanglement segment number $Z_{PCN}$ for the melt (black circle) and the prove chain in the non-CR matrix (red triangle). Experimental data (cross) and the Likhtman-McLeish model (broken curve) for melt, both taken from the literature\textsuperscript{16}, are also shown for comparison.}
\end{figure}
DISCUSSION

Concerning the time-stress discrepancy, molecular weight dependence for the relaxation times (Fig. 2) and the apparent plateau modulus (Fig. 4) suggests a possible explanation related to the CR-induced acceleration. Let us remind that the time-stress discrepancy is caused by the fitting of the viscoelastic relaxation time in melt relying on the CLF contribution (eq 1), and neglecting the effect of CR. This strategy works if the CR-induced acceleration is independent of the molecular weight. However, it is not valid, as shown in Fig. 2, and thus, the comparison between eqs 1 and 3 should be carried out under the non-CR environment for evaluation of Doi’s theory. Such an attempt is made in Fig. 5, where the simulation results of the relaxation times and the apparent plateau modulus are compared with Doi’s CLF theory (eqs 1 and 3). Due to the fluctuations around entanglements in the simulation, the agreement is not excellent. In particular, for the plateau modulus, the molecular weight dependence of Doi’s theory is weaker than that obtained from the simulation.

Nevertheless, the theory with $A = A' = 0.4$ provides a reasonable agreement simultaneously both for the modulus and the relaxation time for the non-CR case (see filled triangles). This result supports Doi’s theory for the effect of CLF and implies that the time-stress discrepancy is due to the CR effect, which is seen only for the relaxation time. Indeed, for the relaxation times in the melt, larger $A$ values are necessary.

Meanwhile, van Ruymbeke et al.16) explained the time-stress discrepancy by introducing a finite relaxation time at the chain ends. In the employed model, the chain end has a finite relaxation time close to $\tau_0$, and this end relaxation may help the consistency between the relaxation time and the plateau modulus for the non-CR case. However, the contribution of CR is the dominant mechanism in the reported simulations.

CONCLUSIONS

A series of PCN simulations were performed for the dynamics of linear polymers in melt and non-CR environment. The longest relaxation time was obtained for viscoelastic and end-to-end relaxations, and the molecular weight dependence was discussed. For both relaxation times, the established power-law relation was confirmed, and the power-law exponent is ca. 3.4 for the melt and 3.1 for the non-CR matrix. This result is entirely consistent with the earlier studies demonstrating the effect of CR on the power-law exponent, as suggested by Watanabe and Tirrell14). The CR-induced acceleration was observed for the diffusion as well as the theory by Frischknecht and Milner13). The apparent plateau modulus was obtained from the viscoelastic relaxation, and the molecular weight dependence is in reasonable agreement with the experiment. Differently from the relaxation times and the diffusion, the plateau modulus is not affected by CR. This discrepancy for the sensitivity to CR between the relaxation time and the plateau modulus is the source of the time-stress discrepancy. The chain dynamics in the non-CR matrix is in harmony with Doi’s CLF theory6), in which the relaxation time and the plateau modulus are consistent with each other.

ACKNOWLEDGEMENT

This study is supported in part by Grant-in-Aid for Scientific Research (A) (17H01152) and for Scientific Research on Innovative Areas (18H04483) from JSPS, Ogasawara foundation, and JST-CREST (JPMJCR1992).
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