Rapid Communication**Stress-Optical Relationship in Bead-Spring Simulations
for Entangled Polymers under Start-up Shear Flows**Yuichi MASUBUCHI^{*†} and Hiroshi WATANABE^{**}^{*}National Composite Center, Nagoya University, Furocho, Chikusa, Nagoya 464-8603, Japan^{**}Institute for Chemical Research, Kyoto University, Gokasyo, Uji, Kyoto 611-0011, Japan

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Lu et al [ACS Macro Lett. 2014, 3, 569-573; Macromolecules 2015, 48, 4164-4173] performed the Kremer-Grest (KG) bead-spring simulation for entangled polymer melt to report that the stress overshoot under start up shear is not induced by the subchain orientation but by the subchain stretch, even at the shear rates well below the reciprocal Rouse time, $1/\tau_R$. Apart from the contradiction to the tube picture, their result violates the stress-optical rule (SOR), and thus, it contradicts the conventional view in further coarse-grained models that assumes local equilibration of the subchain. In this study, KG simulation was conducted for melts of bead-spring chains each composed of 200 beads. The results obtained under shear at the rates around $1/\tau_R$ were fully consistent with SOR. Namely, the stress overshoot is invoked by the subchain orientation rather than the subchain stretch. Those results are consistent with experiments and tube theories but contradict to the results of Lu et al.

Key Words: Kremer-Grest model / Entangled polymers / Fast shear / Stress optical rule / Local equilibrium

1. INTRODUCTION

Entangled polymer dynamics has been investigated by means of molecular simulations that guarantee uncrossability between polymer chains with excluded volume interactions.¹⁾ The pioneering work by Kremer and Grest²⁾ has demonstrated that the simple bead-spring model shows the entangled polymer dynamics under quiescent state given that the concentration and the molecular weight (number of beads per chain) are sufficiently large. On the basis of their success, the model has been examined under fast flow as well. For example, Kröger and Hess³⁾ reported the crossover between unentangled and entangled dynamics under fast shear. Although quantitative comparison with experimental data has yet to be reported, the Kremer-Grest (KG) simulation has reproduced most of the features experimentally observed for entangled (and unentangled) polymers. The model is thus regarded to be standard and generic, and suitable to test the assumptions and approximations used in the further coarse-grained models such as the tube model.⁴⁾

The recent study by Lu et al⁵⁾ suggested a possible important inconsistency between the KG simulation and the tube theory. They performed the Brownian dynamics

simulation of the KG chain having 500 beads per chain. They applied start-up shear deformations at the flow rates higher than the terminal relaxation frequency but lower than the reciprocal Rouse time, $1/\tau_R$. Owing to the reasonable reproduction of the stress overshoot, they analyzed the origin of the overshoot with respect to the subchain orientation and stretch. (They chose a sequence of 36 beads as the subchain. This choice corresponds to an estimate of the entanglement molecular weight for the KG model.²⁾) In their analysis, the subchain orientation does not exhibit any overshoot whereas the subchain stretch shows an overshoot that coincides with the stress growth. This result contradicts the assumption employed in the tube theory⁶⁾, in which the chain confined in the tube is not stretched at the flow rates lower than $1/\tau_R$.

Lu et al^{5,7)} also demonstrated the failure of the stress-optical rule (SOR)⁸⁾ in their simulation. (As mentioned above, their stress showed the overshoot whereas their subchain orientation grew without any overshoot.) SOR⁸⁾ is the experimentally established linear relationship between stress and optical anisotropy (birefringence), the latter detecting the orientation of the repeating unit. Takahashi et al⁹⁾ and Pearson et al¹⁰⁾ examined rheo-optical behavior of entangled polymer solutions on start up shear at rates around $1/\tau_R$, and found the validity of SOR in the steady state as well as in the transient state where the overshoot was observed for both stress and birefringence. The validity of SOR has been also reported for

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the KG model given that birefringence is calculated from the bond orientation. For example, for the KG chain composed of 250 beads, Yamamoto and Onuki¹¹⁾ reported the validity on start up shear at the rate of $1.68/\tau_R$. Cao¹²⁾ obtained similar results for the bead-spring chain with a bending potential. Although Lu et al⁷⁾ concluded apparent failure of SOR in their KG simulation, all results of earlier studies explained above ensure the validity of SOR. The failure of SOR concluded by Lu et al^{5,7)} might have resulted from insufficient local equilibration within their subchain (sequence of 36 beads).

Expressing concern for the results of by Lu et al,⁵⁾ Masubuchi and Watanabe¹³⁾ performed the coarse-grained multi-chain slip-link simulations to show that the simulation is fully consistent with the experiments¹⁰⁾ and the GLaMM model.¹⁴⁾ This result demonstrates that the entanglement coupling in multi-chain system does not disturb the validity of SOR. Watanabe et al¹⁵⁾ revisited SOR and analyzed the nonlinearities of the subchain orientation and stretch as functions of shear rate $\dot{\gamma}$. According to their analysis, the overshoot of subchain orientation is a nonlinearity of the order of $\dot{\gamma}^3$ and it emerges at lower $\dot{\gamma}$ compared to the subchain stretch (that is a nonlinearity of the order of $\dot{\gamma}^4$). Although these studies have already exhibited the inconsistency of the results from Lu et al^{5,7)} with the established fact, the detail of the problem has not revealed yet.

This paper re-examines the KG model²⁾ under start up shear with respect to the subchain orientation and stretch. It turned out that the KG model is consistent with the tube picture; At shear rates lower than $1/\tau_R$, the stress and subchain orientation were found to be proportional to each other up to the subchain size comparable to the entanglement segment, indicating the validity of SOR in the KG simulation. Details are presented below.

2. MODEL AND SIMULATION

The standard Kremer-Grest (KG) model²⁾ was used. The polymer chain is replaced by the consecutive beads connected with the springs. The inter-beads interaction is the truncated 6-12 Lennard-Jones potential with the energy parameter ϵ and the cutoff radius was $\gamma_c = 2^{1/6}\sigma$ with respect to the bead diameter σ . The spring connecting the beads is the finitely extensible nonlinear elastic (FENE) spring with the spring constant $k = 30 \epsilon/\sigma^2$ and the full-stretched bond length $R_0 = 1.5\sigma$. The monomer density is $0.85\sigma^{-3}$. The position of each bead obeys the Langevin-type equation of motion with the temperature at $k_B T = 10\epsilon$ and the friction constant at $\Gamma = 0.5 \tau^{-1}$. Here, $\tau = \sigma(m/\epsilon)^{1/2}$ is the time unit for Lennard-Jones fluids and m is the bead mass. The code used in this study is house-

made and the consistency with the earlier result has been checked for short chains (not shown).

In the simulation, the melt consisted of 40 linear chains and each chain had 200 beads. The chains were stowed into the cubic box with the periodic boundary condition, and the box dimension was accommodated with respect to the required monomer density. 8 different initial configurations were equilibrated for $10^5 \tau$ that is sufficiently longer than the longest relaxation time. After the equilibration shear flow was applied to each system via the Lees-Edwards periodic boundary condition and the SLLOD algorithm. The time-step for the numerical integration was 0.006τ . The obtained data were ensemble averaged for the 8 independent runs, and time averaged in the time window of $10 \tau^3$.

Apart from the main simulation with $N = 200$, equilibrium simulations with smaller N were carried out for the estimation of the Rouse relaxation time. Because the chain stretch is the issue of discussion, τ_R was determined from the auto-correlation function of the end-to-end vector for various N (≤ 40) for which τ_{ete} is proportional to N^2 . From the results, we found that $\tau_{\text{ete}}/N^2 = 0.9_2 \tau$. Assuming that τ_{ete} corresponds to the (dielectric-based) Rouse relaxation time $\tau_R^{[e]}$, we estimate its value for $N = 200$ as $3.7 \times 10^4 \tau$. In the results below, shear rate $\dot{\gamma}$ and time t are normalized with respect to this $\tau_R^{[e]}$ value. In particular, the shear rate is indicated via $\tau_R^{[e]}$ -based Weissenberg number, $Wi_R^{[e]}$.

3. RESULTS

Figure 1 (a) shows the stress growth at various shear rates. The stress exhibits the overshoot when the shear rate is large. For the examined chain (with $N = 200$) the number of entanglement is rather small so that the overshoot is not apparently observed if $Wi_R^{[e]} < 1$. Figure 1 (b) shows the stress plotted against strain. In harmony with experiments^{9,10)}, the peak is observed around $\gamma \cong 2$ at the smaller strain rates, and the peak position moves toward the larger strain at the larger strain rates. Thus, the obtained stress growth is fully consistent with the earlier studies.

Now we turn our attention to the subchain behavior. Figure 2 shows the orientation and stretch at the shear rate of $Wi_R^{[e]} = 4.0$ obtained for subchains that are defined as sequence of beads connected by the number N_s of bonds. For the orientation (upper panel), the behavior is almost common for the subchains of various size N_s , and the orientation growth is similar to the stress growth; the orientation growth shows an overshoot and the peak is located around $\gamma \cong 2$ (indicated by the vertical dotted line). On the other hand, the stretch (lower

panel) behaves differently. The subchain length remained constant for the small $N_s < 8$, but slightly increased with increasing strain for the larger $N_s (\geq 16)$. The stretch of the subchains with $N_s = 16$ and 32 suggests insufficient local equilibrium in these subchain sizes at the shear rate examined. The results mentioned above are essentially the same for smaller $Wi_R^{[e]}$ values, at which the peak in orientation becomes less apparent in coincidence with the evolution of stress (see Fig. 1). On the other hand, at larger $Wi_R^{[e]}$, the contribution of stretch becomes prominent.

For Gaussian chains, the stress expression is unaffected by the choice of N_s and thus the subchain orientation should be in proportion to N_s . However, for the KG model examined, the proportionality between the subchain orientation and N_s is not strictly valid, due to the non-Gaussianity.

The observations for the subchain stretch and non-Gaussianity may look consistent with the results by Lu et al.^{5,7)} However, the stretch growth does not synchronize with the stress growth. The stress growth does not exhibit clear overshoot and approached its steady state at strains much larger than those for the stress growth. The difference between the subchain orientation and stretch is in harmony with those observed for the tube⁵⁾ and the sliplink¹³⁾ models.

Figure 3 examines the proportionality between the subchain

Fig. 1. Stress growth plotted against (a) time and (b) applied strain at various $Wi_R^{[e]}$ values. For upper panel, $Wi_R^{[e]} = 8.1, 4.0, 2.0, 1.0$ and 0.50 from top to bottom. For lower panel, $Wi_R^{[e]} = 8.1, 4.0, 2.0$ and 1.0 from top to bottom. Vertical broken line in lower panel indicates $\gamma = 2$.

orientation and stress; the subchain orientation is double-logarithmically plotted against stress. The proportionality is well confirmed for small subchains having $N_s \leq 8$, and the experimentally observed SOR corresponds to the proportionality for the case of $N_s = 1$ (i.e., for the monomeric segment). For the larger $N_s (\geq 16)$, the proportionality is not fully satisfied for large stresses (due to the subchain stretch observed in Fig. 2), but this deviation from the proportionality is not significant.

Fig. 2. Subchain orientation (top) and stretch (bottom) plotted against applied strain at $Wi_R^{[e]} = 4.0$ for various subchain sizes N_s ranging from 1 to 32. Vertical broken lines indicate $\gamma = 2$.

Fig. 3. Test of SOR at $Wi_R^{[e]} = 4.0$ for various N_s at 1 (filled triangle), 2 (unfilled triangle), 4 (filled circle), 8 (unfilled circle), 16 (filled square) and 32 (unfilled square). Solid line indicates the slope of unity.

4. DISCUSSION

In this section, we discuss the difference between our simulation and the simulation by Lu et al.^{5,7)} In the previous section, we have demonstrated that the stress overshoot at shear rates around $1/\tau_R$ is induced by the orientation. The subchain stretch occurs at high rates but it does not synchronize with the stress behavior. These results contradict the conclusion of Lu et al.^{5,7)} that the stress overshoot is induced by the subchain stretch.

The critical difference between two studies is the molecular weight (bead number per chain), $N = 200$ in this study and $N = 500$ and 800 in the works by Lu et al.^{5,7)} Yamamoto and Onuki¹¹⁾ reported that some kinks emerge along the chain under shear, and the chain is locally stretched at the kinks (that corresponds to the hooking with the other chains). Since the number of kinks increases with an increase of the chain length N , an accumulation of the local stretch might have occurred in the chain stretch simulated by Lu et al.^{5,7)} Although the full-chain tube models¹⁴⁾ and the slip-link models¹³⁾ take account of the stretch distribution along the primitive path, the effect of the local kink generated *via* the inter-beads interaction is smeared out in the coarse-grained description in those models.

However, the conjecture mentioned above is nothing to explain the violation of SOR in the works by Lu et al.^{5,7)} because the validity of SOR is experimentally well established. Indeed, during preparation of this paper, Cao and Likhtman¹⁷⁾ performed the KG simulation for long chains ($N = 512$) and confirmed the validity of SOR in the simulation. They removed all sources of possible artifacts in the simulation (due to the use of too small simulation box) by using a cuboid cell with sufficiently large dimensions and unequivocally demonstrated the validity of SOR¹⁷⁾, which is in harmony with the results of this study. Thus, there should be a mysterious, technical difference between the simulation by Lu et al.^{5,7)} and those by the other groups, the latter including the simulation reported in this paper and that published by Cao and Likhtman.¹⁷⁾ (There might be a difference in the analysis of subchain orientation/stretch.) It is desired to check all technical details in the simulation and analysis by Lu et al.^{5,7)}

5. COUCLUSIONS

We performed Kremer-Grest simulation for melt chains each composed of 200 beads subjected to start up shear at the rates around $1/\tau_R^{[e]}$. The stress growth behavior, including the overshoot, was fully consistent with earlier results. Similar overshoot was observed for the subchain orientation, and

indeed the stress-optical rule (SOR) was valid. On the other hand, for the subchain stretch, a slight stretch was observed for large subchains even if the flow rate is slower than $1/\tau_R^{[e]}$, possibly because of insufficient local equilibration in those large subchains. However, the stretch growth is minor and does not synchronize with the stress growth. These results are consistent with SOR and with the view in the further coarse-grained models such as tube and slip-link models, but contradict the results/conclusion of Lu et al.^{5,7)} The inconsistency between this and Lu's studies raises a necessity for further investigation of SOR in the bead-spring simulation.

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