Note

Re-Examination of the Effect of the Stretch/Orientation-Induced Reduction of Friction under Equi-Biaxial Elongational Flow via Primitive Chain Network Simulation Using Two Definitions of Orientation Anisotropy

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In this study, we examined the effect of the stretch/orientation-induced reduction of friction (SORF) between under uniaxial and equi-biaxial elongational flows using the primitive chain network (PCN) simulation with two definitions of orientation anisotropy under equi-biaxial elongational flow. We used two types of the orientation parameter S (S_1 and $S_{1/2}$) under equi-biaxial elongational flow, giving rise to different values 1 and 1/2 of S , as the limiting values for S_1 and $S_{1/2}$ along the elongational direction, respectively. We calculated the steady-state elongational viscosity of monodisperse polystyrene melts to observe the SORF, which should be effected at large strain rate by PCN simulation. Furthermore, we attempted molecular level analysis utilizing decoupling approximation. The difference between S_1 and $S_{1/2}$ was the critical strain rate of the SORF effect when using $S_{1/2}$. The friction decreased at the critical strain rate, which was comparable with the inverse of the Rouse relaxation time under uniaxial and equi-biaxial elongational viscosities. On the other hand, the friction under equi-biaxial elongational flow using S_1 decreased at earlier than that.

Key Words: Biaxial elongational flow / Orientation / Reduction of friction / Simulation

1. INTRODUCTION

Many molecular theories of entangled polymer liquids based on the tube model by Doi and Edwards¹⁾ have been proposed for understanding of entangled molecular behavior. Many modifications of the tube model has been made for more precise prediction of polymer liquid behavior²⁻⁴⁾.

Nevertheless, molecular behavior under fast elongational flow has not been fully explained. It has been known that linear monodisperse polystyrene (PS) concentrated solutions exhibit the increase of steady-state elongational viscosity as increasing the strain rate ($\dot{\epsilon}$) when the strain rate is higher than the inverse Rouse time⁵⁻⁷⁾, though PS melts show a decrease of the steady-state elongational viscosity^{8,9)}. Yaoita *et al.*¹⁰⁾ focused on a flow-induced change of the monomeric friction coefficient ζ which was proposed by Ianniruberto *et al.*¹¹⁾ to solve the issue under the fast uniaxial elongation. They made the hypothesis that the monomeric friction coefficient ζ was changed by the extent of stretch and orientation of polymeric chains under high strain rates (stretch/orientation-induced reduction of monomeric friction: SORF). They

evaluated how the SORF in the primitive chain network (PCN) simulation including finite extensible nonlinear elasticity (FENE)^{12, 13)} affects the elongational flow behavior. They mentioned that the entangled subchains become rapidly close to fully orientation and stretch limit, hence ζ significantly decreases and then the steady-state elongational viscosity exhibits the monotonic thinning under fast elongation for melts. Conversely, for solutions, the solvent governs an average orientational anisotropy of the polymer chains and remains it small, and a change of the friction ζ cannot be seen in the available range of the simulation, differing from the polymer melts. This in solutions leads to an increase of the viscosities as the strain rate increased. They determined the magnitude of SORF from the deformation stress decay after cessation of the fast uniaxial elongational flow for PS melts and solutions¹⁴⁾. The equation proposed by Yaoita *et al.*¹⁰⁾ to express the SORF effect is as,

$$\frac{\zeta(F'_{SO})}{\zeta(0)} = f_{FENE} \frac{1}{(1+\beta)^\gamma} \left[\beta + \frac{1}{2} \left\{ 1 - \tanh \alpha (F'_{SO} - F'^*_{SO}) \right\} \right]^\gamma, \quad (1)$$

$$F'_{SO} = F_{SO} f_{FENE}, \quad (2)$$

$$F_{SO} = \tilde{\lambda}^2 \bar{S}. \quad (3)$$

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where F_{SO} is the so-called stretch-orientation order parameter, ζ is the segmental friction, and $\zeta(0)$ is the equilibrium value. f_{FENE} is the finitely extensible nonlinear elastic factor defined as

$$f_{FENE} = \frac{1}{1-\tilde{\lambda}^2} \text{ with } \tilde{\lambda} = \lambda/\lambda_{\max}, \quad (4)$$

where $\tilde{\lambda}$ is the average stretch ratio normalized by the maximum stretch of entangled subchains ($\lambda_{\max}$). $\tilde{\lambda}^2$ is the ensemble average for all the segments of the entangled polymer chain. In Eq. 1, friction coefficient parameters, α ($= 20$), β ($= 5 \times 10^{-9}$), γ ($= 0.15$) and the threshold value for the onset of friction reduction F'^*_{SO} ($= 0.14$) are determined via fitting of the experimental data¹⁰. $\bar{S}$ is the average orientational anisotropy of the components defined as

$$\bar{S} = \phi_p S, \quad (5)$$

where ϕ_p is the polymer volume fraction and is unity for polymer melts. S is the polymer anisotropy of the subchain orientation vector $\mathbf{u}$ obtained from the eigenvalues of the orientation tensor $\langle \mathbf{u}\mathbf{u} \rangle$ where $\mathbf{u}$ denotes the unit bond vector and $\langle \dots \rangle$ denotes the ensemble average.

It is noteworthy that, the stretch-orientation order parameter F_{SO} proposed by Yaoita *et al.*¹⁰ was determined from the uniaxial stress at the cessation of elongational flow. The deformation stress, with the decoupling approximation¹⁵, can be written as

$$\sigma = 3G_0 f_{FENE} \tilde{\lambda}^2 S. \quad (6)$$

where G_0 is the unit modulus, f_{FENE} is the FENE factor, $\tilde{\lambda}^2$ the polymer stretch averaged for all the segments of an entangled polymer chain, and S the orientation anisotropy. Note that Eq. 6 is compatible with the stress-optical rule (SOR)¹⁶ given that $f_{FENE} \sim \tilde{\lambda}^2 \sim 1$ under marginal flows. The possible reduction of entanglement due to convective constraint release is allowable because the orientation anisotropy of the segment that determined by SOR is proportional to the orientation anisotropy of the segment determined by the stress. According to Eq. 6, the first normal stress difference, which corresponds to the uniaxial stress, can be written as

$$\sigma_{xx} - \sigma_{yy} = 3G_0 f_{FENE} \tilde{\lambda}^2 S_{xx-yy} \quad (7)$$

Here, S_{xx-yy} is the orientational anisotropy defined under uniaxial deformation, and according to the stress-optical rule it should be written as

$$S_{xx-yy} = \langle u_x^2 \rangle - \langle u_y^2 \rangle \quad (8)$$

Yaoita *et al.*¹⁰ utilized this orientational measure as their orientational order parameter, and obtained $F'_{SO} = f_{FENE} \tilde{\lambda}^2 S_{xx-yy}$ from the experimentally observed $\sigma_{xx} - \sigma_{yy}$ at the flow cessation.

Following Yaoita *et al.*¹⁰, one may extend SORF to the other type of deformations by considering an appropriate orientational order parameter. For equi-biaxial elongational flows, a possible formula is written as follows.

$$S_{1/2} = (\langle u_y^2 \rangle + \langle u_z^2 \rangle) / 2 - \langle u_x^2 \rangle \quad (9)$$

This formula is rationalized according to the usual form of equi-biaxial stress. However, in this form, the maximum value of $S_{1/2}$ is 1/2, which might inappropriately restrict the activation of SORF. According to such an idea, in our previous work¹⁷, we used the other form to set the maximum value of unity as

$$S_1 = (\langle u_y^2 \rangle + \langle u_z^2 \rangle) - 2 \langle u_x^2 \rangle \quad (10)$$

with S_1 , we simulated steady-state viscosities under equi-biaxial and uniaxial flows at various strain rates to study the effect of SORF¹⁷. When we used the definition of the polymer anisotropy S_1 (Eq. 10) under equi-biaxial deformation, the onset of the SORF effect occurred at smaller strain rate than that of uniaxial deformation. Yaoita *et al.*¹⁰ assumed that the friction coefficient of the Kuhn segment remains isotropic even under fast flow and can be characterized by the scalar factor, ζ . That scalar quantity should be expressed regarding the scalar invariants of the tensor $\langle \mathbf{u}\mathbf{u} \rangle$. There are two orientation parameters, $S_{yy-xx} = \langle u_y^2 \rangle - \langle u_x^2 \rangle$ and $S_{zz-xx} = \langle u_z^2 \rangle - \langle u_x^2 \rangle$ for equi-biaxial flow, which affects to the stress. S_{yy-xx} and S_{zz-xx} are the same value. It is assumed that friction reduction may depend on not the average of orientation tensors but two orientation parameters for equi-biaxial elongational flow, it also depend on the $S_{1/2}$ value. We reviewed from these points the effect of two orientational anisotropy of polymer parameters (Eq. 9 and Eq. 10) on the SORF effect under equi-biaxial elongational flow and the resulting elongational flow behavior in this study, also compared with that of uniaxial deformation.

2. MODEL

We denote the primary aspect of the primitive chain

network (PCN) model¹²⁾ because detailed description can be referred elsewhere^{10, 17-19)}. The polymer chains are connected through quasi-crosslinked points referred to as slip-links in 3-dimensional spaces. Consecutive strands (subchains) including two nodes which connect chains forming a group with other chains. Two subchains are linked to a slip-link so that four subchains diverge from each node. The motion of nodes (slip-links) is described by a Langevin-type equation of motion considering the force balance, subchain tension, osmotic force suppressing the density fluctuation, and random Brownian force. FENE is adopted as an elastic force with FENE-P approximation¹³⁾. The number of slip-links Z fluctuates due to hooking and un-hooking processes between chains. The known molecular mechanisms for entangled polymers are considered: reptation^{20, 21)}, contour length fluctuation²²⁾, thermal²³⁻²⁵⁾ and convective²⁾ constraint release. In addition to these mechanisms, SORF is implemented according to Eqs. 1-5, where the orientational anisotropy is either Eq. 9 or 10. The parameters in Eq. 1 are assumed to be the same with those obtained from the stress relaxation under uniaxial deformations due to the absence of experimental data for equi-biaxial deformations.

3. RESULTS

Figure 1 shows the steady-state elongational viscosity η_E divided by linear viscosity $\eta_{E(0)}$, the average orientation $\bar{S}$, square of normalized stretch by the maximum stretch $\bar{\lambda}^2$, FENE factor f_{FENE} , reduced segment number Z/Z_0 and reduced friction to the equilibrium value $\zeta(F_{SO})/\zeta(0)$ as a function of Weissenberg number Wi defined with the Rouse relaxation time at equilibrium τ_R^0 , $Wi_R \equiv \dot{\epsilon}\tau_R^0$, for equi-biaxial and uniaxial elongational flow of monodisperse melt in the steady-state, from top to bottom. The results with the definition of equi-biaxial orientation anisotropy $S_{1/2}$ (Eq. 9) as bold red curves, and thin blue curves are S_1 (Eq. 10) which we reported before¹⁷⁾. Thin black curves are for uniaxial flow. Solid curves are with SORF and dotted are without SORF.

Although we used same Wi_R to compare uniaxial and equi-biaxial elongational viscosities, to be exact, when we compare them, we should use strain invariants because the strain rate is different. We will discuss this matter in other work.

At $Wi_R < 0.1$, the steady-state elongational viscosity ratio η/η_0 (1st panel) for uniaxial flow is almost flat, and η/η_0 for equi-biaxial flow decreases as increasing Wi_R , independent of the use of $S_{1/2}$ and S_1 . In this region, it is clear that η/η_0 (1st panel) is dominated by the orientation (2nd panel) because the

squared reduced stretch and f_{FENE} remain unchanged in this area (3rd and 4th panels) for both flows. Although the orientational anisotropy of both flows are already induced, even at this low Wi_R range, the growth rates of orientation anisotropy S (S_1 and $S_{1/2}$) are weaker than that of uniaxial flow. In addition to this, the decreases of Z/Z_0 under equi-biaxial flows (S_1 and $S_{1/2}$) are somewhat steeper. These induce the decrease of η/η_0 of equi-biaxial flows (S_1 and $S_{1/2}$). Thus, under the uniaxial elongational flow, steeply increasing of S (2nd panel) and gradual decrease of Z/Z_0 (5th panel) comparing with equi-biaxial flow corresponds to the constant value of η/η_0 (1st panel) in this area.

At $0.1 < Wi_R < 1$, decrease rates of all η/η_0 curves become mild, and the curves almost level off. This mainly

Fig. 1 Steady-state values for the reduced viscosity, orientation, squared reduced stretch, FENE factor, reduced segment number and reduced friction from top to bottom. The viscosity, segment number and friction are reduced with respect to the equilibrium values. The stretch $\bar{\lambda}^2$ is normalized by the maximum stretch. Blue thin curves and black thin curves are for equi-biaxial and uniaxial deformations, respectively. Red bold curves are for equi-biaxial deformations with definition of Eq. 9. Blue thin curves are for equi-biaxial deformations with definition of Eq. 10. Solid and dotted curves are for the results with and without SORF.

results from competing behavior of the chain stretch and orientation anisotropy. The stretch growth (3rd panel) contributes to suppressing the decrease of η/η_0 under uniaxial and equi-biaxial flows despite the moderate growth of orientation anisotropy S (2nd panel). In both cases of uniaxial and equi-biaxial ($S_{1/2}$), the stretch/orientation order parameter F_{SO} does not reach the threshold value F_{SO}^* (0.14) (Eq. 1), and friction reduction of uniaxial and equi-biaxial ($S_{1/2}$) does not occur in this range (6th panel). Contrary to this, for the equi-biaxial (S_1) case, $\zeta/\zeta(0)$ (6th panel) sharply decreases at around 0.5 of $\dot{W}_R$, if SORF is considered. The developed and saturated orientation anisotropy of S_1 (Eq. 10) and the increase of stretch growth exceed the threshold value F_{SO}^* (0.14) (Eq. 1), then a friction decrease is induced at the point, while $\zeta/\zeta(0)$ of uniaxial and equi-biaxial flow ($S_{1/2}$) using Eq. 9 maintain unity.

At $\dot{W}_R \geq 1$, if we consider SORF, F_{SO} reach the threshold value F_{SO}^* (0.14) (Eq. 1), and friction reduction of uniaxial and equi-biaxial ($S_{1/2}$) occur in this range (6th panel). This friction reduction suppresses the growths of the stretch (3rd panel) and FENE factor (4th panel) for uniaxial and equi-biaxial ($S_{1/2}$) elongational flow, both steady-state viscosities decrease as seen for equi-biaxial flow ($S_{1/2}$). If we do not consider SORF, the growth of stretch and FENE increase with increasing $\dot{W}_R$ for both flows and the steady-state viscosities increase. The simulation results which was obtained by taking account of $\zeta/\zeta(0)$ decrease at the high strain rates are in good agreement with the thinning behavior as seen in the experiments.

4. DISCUSSION

Desai and Larson²⁶⁾ predicted elongation thinning for entangled melts using the Doi-Edwards-Marrucci-Grizzutti (DEMG) model²⁷⁾ modified by the friction reduction which Yaoita *et al.* proposed¹⁰⁾, while modified DEMG model without the friction reduction failed to predict elongation thinning. Ianniruberto *et al.*²⁸⁾ reported elongation thinning of the melts is due to the friction reduction using more simple equation than the original one from Yaoita *et al.*¹⁰⁾. They performed nonequilibrium molecular dynamics simulation of styrene oligomers to obtain those diffusion coefficients and friction coefficients and compared with the data of the friction reduction $\zeta/\zeta(0)$ vs. the order parameter S determined from the stress-optical data on PS melts²⁹⁾. They also compared $\zeta/\zeta(0)$ vs. S to the data of Yaoita *et al.*¹⁰⁾. They explained the reason of underprediction of the friction reduction $\zeta/\zeta(0)$ vs. the order parameter S of Yaoita *et al.*¹⁰⁾ was because of higher Rouse modes included. Addition to this, their data was

calculated from steady-state stress-optical data, then it was not affected by time resolution²⁸⁾. Their results suggest that the further consideration will be needed on the stress equation derived the reduction friction. Although these results confirm that the mechanism of friction reduction is essential to explain elongational behavior under fast flows, SORF is still controversial. Thus, it is crucial that to examine the effect of SORF under not only uniaxial but equi-biaxial and other elongational flow.

When we used S_1 , friction reduction occurred below unity of $\dot{W}_R$ due to the high value of orientation anisotropy S_1 comparing with uniaxial and equi-biaxial ($S_{1/2}$), the stretch/orientation order parameter F_{SO} exceeded the threshold value of 0.14 (Eq. 1) at around 0.5 of $\dot{W}_R$ if SORF on. In cases of equi-biaxial ($S_{1/2}$) and uniaxial elongational flow, when SORF was considered, the stretch growth and FENE were suppressed, and friction decreased, consequently of this, the viscosities decreased at $\dot{W}_R \geq 1$. Friction reduction occurred at same $\dot{W}_R$ under uniaxial and equi-biaxial ($S_{1/2}$) elongational flow, due to fully orientation limit for the uniaxial flow and equi-biaxial ($S_{1/2}$) flow, respectively.

However, we have not compared these results with experimental equi-biaxial data because equi-biaxial elongational experiments for monodisperse polymer at large strain rate are not available. Furthermore, the SORF equation is empirical form derived from the experimental data of the stress relaxation after cessation of uniaxial elongational viscosities. We need more careful consideration whether we apply SORF to the different elongational flow to optimize the required parameters and investing polymer dynamics under various elongational flow manners. Indeed, as mentioned in the model description, we employed the strong assumption, in which the functional form of SORF and the parameters therein are common to those under uniaxial deformation. Experimental investigations, as well as simulation studies on this matter, are apparently required.

5. CONCLUSION

In this study, we compared the effect of the definition of orientation parameter S on the stretch/orientation-induced reduction of friction (SORF) under uniaxial and equi-biaxial elongational flow via primitive chain network simulation using newly defined $S_{1/2}$ (Eq. 9) and previously reported S_1 (Eq. 10). We calculated the steady-state viscosity of the monodisperse polymer melts under equi-biaxial elongational flow in the wide strain rate range, and then examined molecular behavior by utilizing decoupling equation. We found that the

effect of SORF under uniaxial and equi-biaxial elongational flow using equi-biaxial orientation definition $S_{1/2}$ was almost identical, and friction decreased at $Wi_R \geq 1$. Meanwhile, equi-biaxial elongational flow using the orientation definition S_1 , SORF occurred at $Wi_R < 1$. The differences in orientation anisotropy definitions affected F_{SO} and changed critical Wi_R for the onset of friction reduction under equi-biaxial elongation. To be fair, we emphasize that the results reported here be based on the strong assumption of the universality of SORF behavior for different deformation fields. For the validity of this assumption experimental and/or simulation studies are necessary.

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