Effect of Friction Reduction Due to Weak Segment Orientation under Equibiaxial Elongational Flow

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1. Introduction:

Dynamics of polymers under the elongational flow has not been fully elucidated yet. For instance, in the high strain rates it has been known that the polystyrene (PS) melts shows the strain rate thickening of the steady-state elongational viscosity, while PS solutions indicates the strain rate thinning [1]. The steady-state viscosities at the high Weissenberg number defined by using Rouse time (Wi_R) possess a qualitative difference between polymer melts and solutions. Yaoita et al. [2] focused on the friction reduction for this issue. They analized the step-strain behavior under uniaxial elongational flow after cessation of strain for PS melts [3] and solutions [4] using PCN model [5] and found that molecular friction changed by the chain stretch and orientation (stretch/orientation-induced reduction of monomeric friction: SORF). They concluded that the difference of SORF effect between melts and solutions under the high strain rates made the noticeable difference in the uniaxial elongational viscosity. According to this concept, the molecular friction of the polymer melts reduces due to SORF under the high rates, leading to the thinning of the viscosities. In the solutions a presence of solvent suppresses the molecular orientation, and the friction reduction is less than melts. This small friction reduction in solutions results in the thickening of the viscosities as the rate increases. The SORF effect on molecular behavior under fast elongational flow is expressed as,

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

where ζ is the segmental friction, and $\zeta(0)$ is the equilibrium value. f_{FENE} is the *FENE* factor, F_{so} is the stretch/orientation order parameter, $F_{SO} = \tilde{\lambda}^2\overline{S}$ with $\tilde{\lambda}$ is the average stretch ratio normalized by the maximum stretch of entangled sub-chains, $\overline{S}$ is the average orientational anisotropy of the components, $F'_{SO}=F_{SO}f_{FENE}$, and $\alpha=20$, $\beta = 5\times10^{-9}$, $\gamma=0.15$ and $F^{*}_{so}=0.14$ [2].

In our previous paper [6], we simulated the transient equibiaxial viscosities of PS melts by Takahashi et al. [7] by using PCN simulation, our results reasonably agreed with the experimental data in the limited strain rates. In this study we investigated the steady-state viscosity of equibiaxial elongational flow in the wide strain rate region $10^{-3} < Wi_R < 10$ by the PCN simulation in which the SORF effect was taken into account to reveal the strain rate dependency of the equibiaxial elongational viscosity. We examined the stress under elongational flow using the decoupling approximation [2] as follows,

$$\sigma \approx \left(\frac{Z}{Z_0}\right)f_{FENE}\tilde{\lambda}^2 S$$
(2)

Here, Z is the average number of entanglement segments, f_{FENE} is the spring bead constant, λ is the stretch normalized by the maximum stretch, and S is the orientation anisotropy. In this study, we used two types of definition of S to examine the effect of SORF under equibiaxial elongational flow as below,

$$S_1 = \left(\left\langle u_y^2\right\rangle + \left\langle u_z^2\right\rangle\right) - 2\left\langle u_x^2\right\rangle$$
(3)

$$S_{1/2} = \left(\left\langle u_y^2\right\rangle + \left\langle u_z^2\right\rangle\right)/2 - \left\langle u_x^2\right\rangle$$
(4)

where u is the unit bond vector, and x is the squeezing direction, and y and z are the elongational directions.

2. Model:

In the PCN model, the polymer melt is expected as a set of primitive chains in 3-Dimentional spaces that are entangled with each other through slip-links. Consecutive strands (sub-chains) including two nodes which connect chains forming a group with other chains. The motion of nodes is described by a Langevin-type equation that considers the force balance, sub-chain tension, osmotic force and random Brownian force. The finite chain extensibility (FENE) is accounted as an elastic force with FENE-P approximation [8]. Chain hooking and unhooking at the chain ends leads to creation and distraction of slip-links (entanglements, Z) respectively. Therefore, the number of Z fluctuates with time. Molecular mechanisms for entangled polymers, such as reputation, contour length fluctuation, and thermal convective constraint release, are considered.

The relevant parameters used in this simulation are listed in Table 1. We neglected the molecular weight distribution for simplicity. The molecular weight of Kuhn step for PS melt (M_k=700) [9], n_0 is M_0/M_k=15. n_0 determines the maximum stretch ratio (FENE). Shift factor $G_0=\rho RT/M_0$ is 0.31 MPa (where ρ is the density). The unit time τ_0 is 0.01 sec. The Rouse relaxation time τ_R (that is 1/2 of the relaxation time for chain contraction) is as $Z_0^2\tau_0/2\pi^2 = 0.27$ sec.

Table 1 Parameters of PS used in the simulations

M_w	M_0	Z_0	G_0[MPa]	τ_0[s]	T[K]
250k	11k	23	0.31	0.01	433

Fig.1 Normalized steady state viscosity, orientation, squared reduced stretch, reduced segment number and reduced friction of PS Melt from top to bottom. Solid and dotted curves are for the results with and without friction reduction.
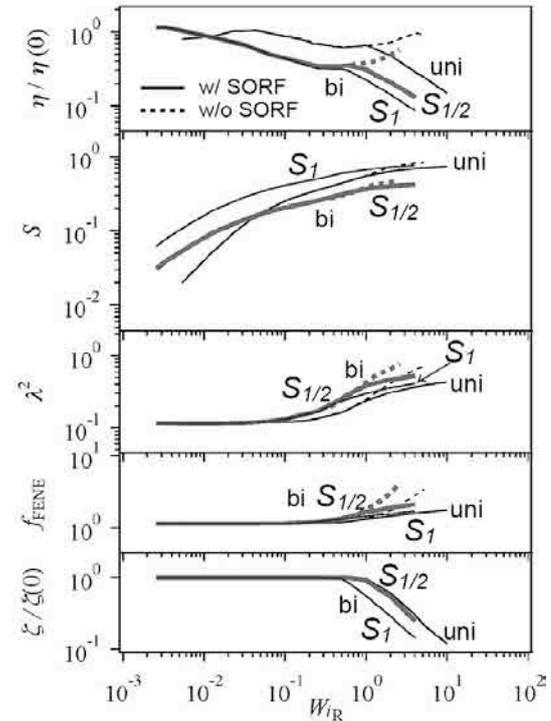
3. Results and Discussion:

Fig. 1 shows the normalized steady-state viscosity with the zero rate value, orientation, normalized square stretch with the maximum stretch, FENE factor and reduced friction with the equilibrium value from top to bottom. Taking account of SORF, $\eta/\eta(0)$ under uniaxial flow successfully showed strain rate thinning at high Wi_R [2]. We should note that under biaxial flow $\eta/\eta(0)$ showed thinning at high Wi_R, while $\eta/\eta(0)$ showed thickening without SORF. The calculated $\eta/\eta(0)$ with SORF by using S_1 showed relatively strong Wi_R dependency, comparing with that by $S_{1/2}$. Friction reduction of S_1 decreased by saturated orientation. $S_{1/2}$ orientation was also saturated, but the stretch growth is higher than of S_1 and suppressed the decrease of friction reduction and $\eta/\eta(0)$.

References:
[1] A. Bach, K. Almdal, H. K. Rasmussen, O. Hassager, *Macromolecules*, **36**, 5174 (2003).
[2] T. Yaoita, T. Isaki, Y. Masubuchi, H. Watanabe, G. Ianniruberto, G. Marrucci, *Macromolecules*, **45**, 2773 (2012).
[3] J. K. Nielsen, H. K. Rasmussen, O. Hassager, *J Rheol*, **52**, 885 (2008).
[4] P. K. Bhattacharjee, D.A. Nguyen, G. H. McKinley, T. Sridhar, *J Rheol*, **47**, 269 (2003).
[5] Y. Masubuchi Y, J-I. Takimoto, K. Koyama, G. Ianniruberto, G. Marrucci, F. Greco, *J Chem Phys*, **115**, 4387 (2001).
[6] K. Takeda, S.K. Sukumaran, M. Sugimoto, K. Koyama, Y. Masubuchi, *Nihon Reoroji Gakkaishi*, **43**, 63 (2015).
[7] M. Takahashi, T. Isaki, T. Takigawa, T. Masuda, *J Rheol*, **37**, 827 (1993).
[8] T. Yaoita, T. Isaki, Y. Masubuchi, H. Watanabe, G. Ianniruberto, G. Marrucci, *Macromolecules*, **44**, 9675 (2011).
[9] S. J. Haward , V. Sharma, J. A. Odell., *Soft Matter*, **7**, 9769 (2011).