Concept of Stretch/Orientation-Induced Friction Reduction Tested with a Simple Molecular Constitutive Equation

Takatoshi YAOITA†††, Yuichi MASUBUCHI††, and Hiroshi WATANABE†

†Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan
††Research Center, Asahi Glass Co., Ltd., Kanagawa 221-8755, Japan
(Received : September 10, 2013)

Under elongational flow at strain rates higher than the Rouse relaxation frequency, entangled polymer melts exhibit thinning of their elongational viscosity whereas equally entangled solutions show thickening. Yaoita et al. [Yaoita et al., Macromolecules 2012, 45, 2773] related this difference between the melts and solutions to reduction of segmental friction on enhancement of the stretch/orientation averaged for the components therein (that includes the solvent for the case of solutions). They analyzed the stress relaxation data after cessation of elongational flow to propose an empirical equation describing this friction reduction as a function of the stretch/orientation factor. Multi-chain slip-link (PCN) simulations considering this friction reduction described the thinning of melts and the thickening of solutions consistently and semi-quantitatively. This study further tests the molecular concept of the stretch/orientation-induced friction reduction with the aid of a simple molecular constitutive equation, a toy version of the Mead-Larson-Doi model [Mead et al., Macromolecules 1998, 31, 7895] (MLD toy model) being modified to incorporate this empirical equation of the friction reduction. The modified toy model mimicked the behavior of melts and solutions consistently. This consistency vanished when the friction reduction in the model was artificially switched off, even though the finite extensible nonlinear elasticity was still taken into account. These results lend further support to the molecular concept of the stretch/orientation-induced friction reduction.

Key Words: Elongational flow / Mead-Larson-Doi toy model / Stretch/orientation-induced friction reduction

1. INTRODUCTION

Recent experiments have established the thinning feature of the uniaxial steady state elongational viscosity $\eta_E$ for entangled monodisperse linear polystyrene (PS) melts and the thickening feature for equally entangled PS solutions, both occurring in the same range of strain rate $\dot{\varepsilon}$ higher than the equilibrium Rouse relaxation frequency, $\omega_R$. The classical Doi-Edwards tube theory (DE theory) assuming a constant chain length cannot describe the thickening of the solutions, whereas the extended tube theory of Marrucci and Grizzuti considering the chain stretch does not reproduce the monotonic thinning for the melts. Thus, several molecular mechanisms have been proposed for consistent description of the behavior of the melts and solutions, as explained below.

One of the important molecular mechanisms under elongational flow is the finite extensible nonlinear elasticity (FENE). Ye et al. investigated the elongational behavior of PS solutions using a modified Mead-Larson-Doi (MLD) model that incorporates reptation, contour length fluctuation, thermal constraint release (TCR), convective constraint release (CCR) and chain stretch associated with FENE. They showed quantitative agreement of the model with the solution data and reported that $\eta_E$ is sensitive to the maximum stretch ratio. Leygue et al. have developed another tube model to show that the magnitude of elongational thickening decreases with a decrease of the maximum stretch ratio. From this result, one may expect that the difference of the maximum stretch ratio between melts and solutions results in the difference of their elongational behavior. However, the reported value of the maximum stretch ratio to attain the thinning was unrealistically small. Yaoita et al. performed multi-chain slip-link (PCN) simulations with reasonable maximum stretch ratios for polystyrene melts and solutions. They showed quantitative agreement of the simulation with the solution data and confirmed the importance of the maximum stretch ratio for thinning/thickening of $\eta_E$. However, they also found that a reasonable value of this ratio for melts still leads to the thickening and thus tuning of the FENE factor alone cannot reproduce the difference between the melts and solutions. Marrucci and Ianniruberto focused on the interchain
pressure (ICP) effect to suggest that relaxation of the tube cross-section can result in the thinning observed for melts. Wagner et al.\textsuperscript{21} incorporated ICP in their molecular stress function (MSF) theory\textsuperscript{17} to report that the melt behavior is quantitatively described on adjustment of the relaxation time of the tube cross-section. However, this tube dynamics has not been specified on the basis of the chain dynamics, and the condition for the crossover from thickening (solutions) to thinning (melts) remains unclear. In fact, Dhole et al.\textsuperscript{18} suggested that ICP is conceptually incompatible with CCR, the basic relaxation mechanism under large strain/fast flow.

Considering those problems, Ianniruberto et al.\textsuperscript{19} have proposed another molecular idea, reduction of monomeric friction \(\zeta\) that could occur on stretch and orientation of entanglement segments. Following this idea, Yaoita et al.\textsuperscript{20} analyzed the stress relaxation data of PS melt\textsuperscript{15} and solution\textsuperscript{4} after cessation of elongational flow to discuss the friction reduction. They cast the results of the analysis in an empirical equation for a ratio of this reduction to the FENE factor \(f_{\text{FENE}}\): \(\zeta(F_{\text{SO}}(0))/f_{\text{FENE}}\), assuming that the magnitude of friction reduction is uniquely determined by the stretch/orientation ratio \(F_{\text{SO}} = \lambda S\), where \(\lambda (\lambda = \lambda_{\text{max}})\) is a stretch ratio of the entanglement segment normalized by the full stretch ratio \(\lambda_{\text{max}}\) and \(S\) is the orientational anisotropy averaged over all components (including solvents, if any). The empirical equation suggested that \(\zeta(F_{\text{SO}})\) remains at the equilibrium value \((\zeta(F_{\text{SO}}) = \zeta(0))\) on an increase of \(F_{\text{SO}}\) up to a threshold \((\approx 0.15)\) but decreases rather steeply with a further increase of \(F_{\text{SO}}\). Yaoita et al.\textsuperscript{20} incorporated this empirical equation in the PCN simulation to show that the simulation can consistently and semi-quantitatively describe the thinning of melts and the thickening of solutions. This result led them to suggest that the thinning of melts is mostly due to the friction reduction (achieved on high stretch/orientation of the entanglement segments) whereas the solvent in the solutions largely decreases the average orientation \(S\) thereby suppressing the friction reduction to provide the solution with the thickening feature.

The assumption underlying the above empirical equation, \(\zeta\) being uniquely determined by a single parameter \(F_{\text{SO}} = \lambda S\) and \(S\) having no contribution from the solvent, remains controversial. In fact, for PS solutions in oligomeric styrene (oS) of several molecular weights, Huang et al.\textsuperscript{22} have investigated the effect of the size of “solvent (oS)” molecules on \(\eta E\) and reported that the increase of the solvent size up to several of the Kuhn segment size suppresses the thickening of \(\eta E\) (possibly due to the nematic interaction between the polymer chains and oligomeric solvents not included in the assumption). However, the main concept, the friction reduction due to stretch/orientation (that leads to lack of thickening for melts), sounds reasonable and is, indeed, consistent with recent molecular dynamics (MD) simulations\textsuperscript{23,24} and experiments.\textsuperscript{4,21,25} Nevertheless, it is desired to further examine the concept of friction reduction without utilizing the PCN/MD simulation, partly because of the lack of thermodynamical rigorousness of the PCN simulation pointed out by Andreev et al.\textsuperscript{26} (although the thermodynamic equilibrium is not achieved under the elongational flow in any case) and also because a time-saving, analytic treatment of the friction reduction is required in computational fluid dynamics for general processing. Thus, this study examines validity of this concept with the aid of a molecular constitutive equation. Any constitutive equation that captures the thickening feature of the solution in the absence of the friction reduction can be utilized for this purpose. For simplicity, we chose the MLD toy model\textsuperscript{8,9} that has been reported to reproduce the solution data.\textsuperscript{7} We incorporated the friction reduction in this toy model\textsuperscript{7,9} to examine if the model can consistently describe the behavior of melts and solutions. It turned out that the model makes this consistent description (though not very quantitatively), which lends further support to the molecular concept of the stretch/orientation-induced friction reduction. Details of this result are presented in this paper.

2. MODEL

In the MLD toy model,\textsuperscript{8,9} the entangled polymer chain is regarded as a dumbbell that reptates in a tube. The times required for the dumbbell contraction (corresponding to the Rouse time) and the reptation in the liner regime (at equilibrium) are denoted by \(\tau R\) and \(\tau \lambda\) respectively. With the decoupling approximation proposed by Pearson et al.\textsuperscript{27} stress tensor \(\sigma\) in the model\textsuperscript{7,9} is expressed as

\[
\sigma = 5G_{\text{N}}\zeta f_{\text{FENE}} \lambda^2(t)S(t)
\]

where \(G_{\text{N}}\) is the entanglement plateau modulus, \(\lambda\) is the chain stretch ratio, and \(S\) is the orientation tensor. Following Patamaprom et al.\textsuperscript{9} and Ye et al.\textsuperscript{7}, we introduced the FENE factor, \(f_{\text{FENE}}\). In this stress expression. Earlier studies employed the Pade inverse langevin function to describe \(f_{\text{FENE}}\)\textsuperscript{20} However, this study adopts a simpler but satisfactorily accurate formulation of \(f_{\text{FENE}}\)\textsuperscript{16,26,29}

\[
f_{\text{FENE}} = \frac{1}{1 - x^2} \text{ with } x = \lambda / \lambda_{\text{max}}
\]

where \(\lambda_{\text{max}}\) is the maximum stretch ratio of the dumbbell. The time evolution of \(S\) is described by\textsuperscript{7,9}
Equation (6b) is the empirical equation for the friction reduction obtained by Yaoita et al., and the parameters therein have the values, \( \alpha = 20, \beta = 5 \times 10^6, \gamma = 0.15 \) and \( F_{\text{so}}^* = 0.14 \). The average orientation \( \bar{S} \) is calculated as \( \bar{S} = \phi_1 \phi_2 \phi_3 \), where \( \phi_i \) is the polymer volume fraction and \( S_{zz} \) and \( S_{xx} \) are the components of orientation tensor (with \( z \) and \( x \) specifying the directions parallel and perpendicular to the elongation, respectively). From Eq. (6), Equations (4) and (5) are rewritten as:

\[
\begin{align*}
\frac{1}{\tau} &= \frac{1}{\lambda^2} r(F_{\text{so}}) \tau_d^0 + \frac{1}{2} \left( \kappa : S - \frac{\dot{\lambda}}{\lambda} \kappa + \frac{1}{\lambda^2} \tau_d^0 \right) (\lambda - 1)
\end{align*}
\]

The first term on the RHS of (5) indicates the stretch due to flow, and the second term shows the release of stretch on contraction of the dumbbell affected by the FENE spring. The TCR/CCR effect on \( \dot{\lambda} \) is cast in the third term, as similar to the description in Eq. (4).

Now, we incorporate the stretch/orientation-induced friction reduction in the model. This reduction should affect both contraction and reptation times, \( \tau_R \) and \( \tau_d \). Specifically, \( \tau_R \) and \( \tau_d \) should be proportional to the friction \( \zeta \) of the dumbbell bead (chain segment). Thus, we assume that the ratio of \( \tau_R \) and \( \tau_d \) under elongation to \( \tau_R^0 \) and \( \tau_d^0 \) at equilibrium is determined by a single parameter, the stretching/orientation factor \( F_{\text{so}} = \frac{1}{\lambda} S \), as

\[
\frac{\tau_R(F_{\text{so}})}{\tau_R^0} = \frac{\tau_d(F_{\text{so}})}{\tau_d^0} = r(F_{\text{so}})
\]

with

\[
r(F_{\text{so}}) \equiv \frac{\zeta(F_{\text{so}})}{\zeta(0)} = f_{\text{FENE}} \frac{1}{1 + \beta} \left\{ \frac{1}{2} - \frac{1 - \tanh(\beta F_{\text{so}} F_{\text{FENE}} - F_{\text{so}}^*)}{\beta} \right\}
\]

The top and bottom panels of Fig. 1 show the elongational viscosity growth function \( \eta_\varepsilon(t, \varepsilon) \) and the steady state elongational viscosity \( \eta_\varepsilon(\varepsilon) \) reported for the PS solution. In the bottom panel, \( \eta_\varepsilon(\varepsilon) \) is plotted against the Weissenberg number defined with respect to the Rouse relaxation time at equilibrium, \( W_R \equiv \dot{\varepsilon} \tau_R^0 \). For this solution, the average orientation \( \bar{S} \) never exceeds 0.1 because of the solvent (90% in the system) so that the friction in the model stays at its

3. RESULTS AND DISCUSSION

The experimental data were obtained from Ref.1, Ref.2 and Ref.3.

<table>
<thead>
<tr>
<th>Table I. Model parameters for the PS melts and solution.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>PS 100(^{\circ})</td>
</tr>
<tr>
<td>PS 200(^{\circ})</td>
</tr>
<tr>
<td>PS 390(^{\circ})</td>
</tr>
</tbody>
</table>

The experimental data were obtained from Ref.1, Ref.2 and Ref.3.
equilibrium value $\zeta(0)$ even at the highest deformation rate. Consequently, the model is essentially the same with that used by Ye et al.\textsuperscript{7} The calculation results (dotted curves) are not in quantitative agreement with the data (symbols) for $\eta_e(\dot{\varepsilon})$ partly due to the uncertainty of the model parameters (see Appendix). However, the basic feature of the experimental data, upturn of $\eta_e(\dot{\varepsilon})$ for $W_{ik} \geq 1$, is reasonably captured, as reported earlier.\textsuperscript{7}

Figures 2 and 3, respectively, show $\eta_e(t, \dot{\varepsilon})$ and $\eta_e(\dot{\varepsilon})$ for the PS melts.\textsuperscript{1,2} The symbols indicate the literature data,\textsuperscript{1,2} and the solid and dotted curves, the MLD toy model calculations with and without the friction reduction. For the calculation without the friction reduction, $r(F_{SO})$ was artificially fixed at unity (i.e., Eq. (6b) was not utilized). For rather slow flow at $W_{ik} < 1$, the calculated results with and without the friction reduction are indistinguishable (because $F_{SO}$ does not exceed the threshold and $r(F_{SO})$ given by Eq. (6b) is very close to unity) and close to the data.

For faster flow ($W_{ik} > 1$), the calculated $\eta_e(\dot{\varepsilon})$ shows the upturn (as also noted in the earlier studies\textsuperscript{7,13}) if $r(F_{SO})$ is artificially fixed at unity; see the dotted curves in Fig. 3. In contrast, this upturn is essentially suppressed if $r(F_{SO})$ given by Eq. (6b) is utilized; see the solid curves. The corresponding difference is noted in Fig. 2 for $\eta_e(t, \dot{\varepsilon})$ at $W_{ik} > 1$. Clearly,

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{Elongational viscosity growth function (top panel) and steady state elongational viscosity (bottom panel) of the PS solution (M = 3.9 M, 10 wt%, 294 K). Symbols indicate the experimental data (taken from Ref. 4), and dotted curves, the MLD toy model calculations. The strain rates are $\dot{\varepsilon} = 0.1, 3.5, 7.3,$ and $11.7$ s$^{-1}$ in the top panel, where the calculation for 7.3 s$^{-1}$ is plotted in black for clarity. In the bottom panel, the steady state elongational viscosity is plotted against the $r_{SO}^0$-based Weissenberg number $W_{ik}$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2}
\caption{Elongational viscosity growth function of the PS melts with the molecular weight of (a) 100 k, (b) 200 k, and (c) 390 k at 403 K. Symbols indicate the data (taken from Refs. 1 and 2), and the solid and dotted curves, MLD toy model calculations with and without the friction reduction. The strain rates are: (a) 0.003, 0.01, 0.03, 0.1, and 0.3 s$^{-1}$, (b) 0.001, 0.003, 0.01, 0.03, and 0.1 s$^{-1}$, and (c) 0.0003, 0.001, 0.003, 0.01, 0.03, and 0.1 s$^{-1}$, respectively.}
\end{figure}
the calculation without the friction reduction significantly overestimates the $\eta_4(\dot{\varepsilon})$ and $\eta_4(t, \dot{\varepsilon})$ data at $W_{R0} > 1$ where the $\eta_4(\dot{\varepsilon})$ data exhibit monotonic decrease with $W_{R0}$. On the other hand, the calculation with this reduction reasonably describes the data within a factor $\sim 2$, although quantitative agreement cannot be obtained/expected because of the toy nature of the utilized model. This result is consistent with that found in the PCN simulation, lending further support to the concept of stretch/orientation-induced friction reduction (irrespective of the method/model of calculation).

The mechanism of suppressing the upturn of $\eta_4(\dot{\varepsilon})$ can be separately discussed for the factors appearing in the decoupled stress expression (Eq. (1)), as shown in Fig. 4 where the orientation $\bar{S}$, normalized stretch $\bar{\lambda}$, and $f_{\text{FENE}}$ calculated for PS 390k in the steady state are plotted against $W_{R0}$. For comparison, the steady state viscosity $\eta_4(\dot{\varepsilon})$ and the friction reduction ratio $r$ are also shown. Comparison of the calculations with and without the friction reduction (solid and dotted curves) clearly indicates that the reduction hardly affects $\bar{S}$ but suppresses the increase of $\bar{\lambda}$ and $f_{\text{FENE}}$, thereby suppressing the increase of the stress and the upturn of $\eta_4(\dot{\varepsilon})$. This feature is similar to that observed in the PCN simulation, but the increase of $f_{\text{FENE}}$ is more significantly suppressed in the present calculation. This difference of $f_{\text{FENE}}$ can be related to the CCR-induced decrease of the entanglement number that occurs in the PCN simulation but not in the MLD toy model, the latter regarding the chain as the dumbbell.
4. CONCLUSION

We incorporated the stretch/orientation-induced reduction of monomeric friction into the MLD toy model and examined the uniaxial elongational behavior of the PS solution and melts. For the PS solution, the calculation with and without the friction reduction gave indistinguishable results (because the solvent therein are not oriented/stretched), which captured the basic feature of the data. On the other hand, for the PS melts, the calculation with the friction reduction described the data reasonably well, whereas lack of this reduction led to significant overestimation of the data (that included divergence of the calculated viscosity at high strain rates). These results are consistent with those of the earlier PCN simulation, lending support to the molecular concept of stretch/orientation-induced friction reduction irrespective of the method/model of calculation.

ACKNOWLEDGEMENTS

YM was supported by Grant-in-Aid for Scientific Research (Grant No. 23350113).

APPENDIX

The material parameters, $\tau_0^e$, $G_N^0$, $\tau_R^0$, and $\lambda_{\text{max}}$ shown in Table I were evaluated from the linear viscoelastic data of the PS melts\(^1\)\(^2\) and solution\(^3\) as explained below.

The longest relaxation time $\tau_0^e$ was evaluated from the zero-shear viscosity $\eta_0$ and the steady state compliance $J_0^e$ as

$$\tau_0^e = \eta_0 J_0^e$$  \hspace{1cm} (A1)

$G_N^0$ and $\tau_R^0$ are coupled with each other through the entanglement molecular weight $M_e$. For a given $M_e$, they can be written, within the context of the tube model, as\(^5\hspace{1cm}31\)

$$G_N^0 = 0.8 \frac{cRT}{M_e}$$  \hspace{1cm} (A2)

$$\tau_R^0 = \frac{12 M_e^0 \eta_0}{\pi^2 cRT} \left( \frac{1.5 M_e^0}{M} \right)^{2.4}$$  \hspace{1cm} (A3)

Here, $R$, $T$, $c$ and $M$ are the gas constant, absolute temperature, and the mass concentration and molecular weight of polymer, respectively. For evaluation of $M_e$, we employed the following iteration procedure. We first adopted a presumed value of $M_e$ to calculate the Rouse contribution to the storage modulus, $G_R^e$, and subtracted $G_R^e$ from the experimental $G'$ to obtain the entanglement contribution $G_e^e = G' - G_R^e$. Then, we evaluated $G_N^0$ as the plateau value of $G_e^e$ at sufficiently high frequencies ($\omega \gg \tau_0^e$). From this $G_N^0$ value, we re-calculated $M_e$ by Eq. (A2) and compared this $M_e$ value with the initial value. We iterated this procedure until the value of $M_e$ converged. Figure 5 shows the Rouse and the entanglement contributions to the experimental data obtained after this convergence. For the solution (bottom panel), $G_e^e$ did not show the full entanglement plateau because the lack of the data at sufficiently high frequencies. Consequently, the parameters for the solution involved some uncertainties.

Finally, the maximum stretch ratio $\lambda_{\text{max}}$ was calculated from $M_e$ as

$$\lambda_{\text{max}} = \sqrt{\frac{M_e}{M_K}}$$  \hspace{1cm} (A4)

Here, $M_K$ is the molar mass of the Kuhn segment and assumed to be 720.\(^3\hspace{1cm}2\)

---

Fig. 5. Linear viscoelastic data for the examined PS melts\(^1\hspace{1cm}2\) (top panel) and solution\(^3\) (bottom panel). Unfilled and filled circles indicate experimental storage and loss moduli respectively. Thick and thin curves, respectively, show the entanglement and Rouse contributions to the storage modulus.
REFERENCES

30) Curie PK, Proc 8th Inter Rheology Conf, Naples, Italy (1980).