Revisit the Stress-Optical Rule for Entangled Flexible Chains: 
Overshoot of Stress, Segmental Orientation, 
and Chain Stretch on Start-up of Flow

Hiroshi WATANABE*,†, Yumi MATSUMIYA*, and Tadashi INOUE**

*Institute for Chemical Research, Kyoto University
Uji, Kyoto 611-0011, Japan
**Department of Macromolecular Science, Graduate School of Science, Osaka University,
Toyonaka, Osaka 560-0043, Japan
(Received : February 22, 2015)

For flexible polymers, the deviatoric parts of the stress and optical anisotropy tensors, with the latter reflecting the orientational anisotropy of the monomeric segments, are proportional to each other. This proportionality, known as the stress-optical rule (SOR), is valid not only in the linear viscoelastic regime but also in the moderately nonlinear regime, given that the chain is not highly stretched and is free from the finite extensible nonlinear elasticity (FENE) effect. On start-up of flow in such a moderately nonlinear regime, the chain exhibits an overshoot of the shear stress and thus of the shear component of the segmental orientational anisotropy. Nevertheless, it was not clearly understood whether this overshoot is associated with an overshoot of chain stretch. This study revisited SOR to conduct a simple analysis for this problem. It turned out that the orientational anisotropy of subchains overshoots but the subchain stretch (identical to the chain stretch) does not when the shear stress overshoots in the moderately nonlinear regime.

Key Words: Stress-optical rule / Optical anisotropy / Orientational anisotropy / Subchain orientation and length / Stress overshoot on start-up of flow

1. INTRODUCTION

For flexible polymer chains, the deviatoric parts of the stress tensor and optical anisotropy tensor are proportional to each other in both linear and nonlinear regime, unless the chain is highly stretched in the latter regime and the finite extensible nonlinear elasticity (FENE) effect becomes important.1,2) This proportionality, known as the stress-optical rule (SOR) in polymer rheology, allows us to relate the stress to the orientational anisotropy/deformation of the stress-sustaining units, the subchains; see Fig.1.

In relation to this anisotropy/deformation of the subchains, Lu et al.3,4) recently conducted Brownian dynamics simulation on start-up of relatively slow shear flow at rates $\dot{\gamma}$ above the terminal relaxation frequency, $\omega_d$, but below the Rouse relaxation frequency of the chain backbone, $\omega_R$. They claimed that the overshoot of shear stress at such $\dot{\gamma}$ is mostly due to the overshoot of chain length (total length of the subchains) whereas the subchain orientation monotonically grows (no overshoot) at such $\dot{\gamma}$. For this claim, Masubuchi and Watanabe5) expressed a concern regarding the validity of SOR in Lu’s simulation, and conducted a coarse-grained primitive chain network (PCN) simulation at those $\dot{\gamma}$ ($\omega_d < \dot{\gamma} < \omega_R$). The PCN simulation showed that the subchain orientation overshoots together with the shear stress but the subchain length does not. This result is in harmony with the traditional argument of SOR.

Fig.1. Schematic illustration of chain and subchain. The short arrows in the right part indicate the segmental bond vectors. The Cartesian coordinates ($X$, $Y$, $Z$) and ($x$, $y$, $z$) are utilized in the calculation shown in Appendix A.
Nevertheless, it is desired to test, on an analytical basis, if the overshoot of the subchain length associated with lack of the overshoot of the subchain orientation is consistent with SOR. Thus, we have revisited SOR to make this test. The result indeed showed that the overshoot observed only for the subchain length, but not for the subchain orientation, is contradicting to SOR at least in the moderately nonlinear regime. Details of this result are presented in this article. In the followings, we firstly revisit SOR and confirm the molecular expression of the stress. Then, we examine the magnitudes of nonlinearities of the subchain orientation and length as functions of the shear rate \( \dot{\gamma} \) to conduct the test.

2. STRESS-OPTICAL RULE

For quantitative description of the stress, we usually divide the chain into subchains that behave as the stress-sustaining units; see Fig. 1. We model the subchain as a sequence of many freely-jointed rods (rigid monomeric segments) each having a length \( b \), and assume the Gaussian feature of the subchain at equilibrium. Then, the deviatoric part of the stress, \( \sigma \), is expressed in terms of the end-to-end vector \( \mathbf{r} \) of the subchain, given that the chain is not highly stretched and the finite extensible nonlinear elasticity (FENE) is not important:

\[
\frac{\sigma}{3vNk_BT} = \frac{1}{\beta b^2} \left\{ \langle rr \rangle - \frac{I}{3} tr(rr) \right\}
\]

(1)

Here, \( v \) is the number density of the chain, \( N \) is the number of subchains per chain, \( k_B \) and \( T \) denote Boltzmann constant and absolute temperature, respectively. \( I \) is the unit tensor. \( \langle rr \rangle \) indicates the ensemble average of the dyadic \( rr \) over the conformational distribution of all subchains (and of all monomeric segments therein). \( \beta \) (\( \gg 1 \)) is the number of monomeric segments per subchain, and the factor \( \beta b^2 \) appearing in Eq.(1) is identical to \( tr(rr) = \langle r^2 \rangle \) at equilibrium. \( \beta \) is treated as a constant independent of the shear rate even under fast flow in the nonlinear regime. In other words, we choose the subchain comprising of the fixed number (\( \beta \)) of segments as the stress-sustaining unit. This choice is valid as long as the subchain is internally equilibrated.\(^{6}\) In fact, the internal equilibration is a pre-requisite for the subchain to behave as the stress-sustaining unit to satisfy Eq.(1).\(^{6}\)

Concerning this point, we should note that the disentanglement of chains could occur under fast flow to enlarge the entanglement strand. If we choose this strand as the stress-sustaining unit, the number \( \beta \) should increase whereas the number \( N \) of the units per chain should decrease with increasing flow rate. However, even for such case, the subchain smaller than the entanglement strand and comprising of the fix number \( \beta \) of segments can be utilized as the stress sustaining unit in Eq.(1), because the stress does not change with our choice of the size of internally equilibrated stress sustaining unit.\(^{6}\) For this reason, this study focuses on the subchain with fixed \( \beta \) (that was analyzed also in the studies by Lu et al.\(^{3,4}\))

Obviously, the end-to-end vector \( \mathbf{r} \) of this subchain is expressed as a sum of the bond-vectors \( b_j \) of the monomeric segments therein (cf. Fig.1):

\[
\mathbf{r} = \sum_{j=1}^{\beta} b_j = b \sum_{j=1}^{\beta} \mathbf{u}_j = b \mathbf{b}/b
\]

(2)

Here, \( \mathbf{u}_j \) is the unit bond vector parallel to \( b_j \). From Eqs (1) and (2), we immediately find an expression of the stress tensor in terms of the unit bond vector of the segments:

\[
\frac{\sigma}{3vNk_BT} = \mathbf{O} + (\beta-1)\mathbf{C}
\]

(3)

with

\[
\mathbf{O} = \langle uu \rangle - \frac{1}{3} tr(uu) = \langle uu \rangle - \frac{I}{3}
\]

(orientation of segments)

\[
\mathbf{C} = \langle uu' \rangle - \frac{1}{3} tr(uu')
\]

(cross-correlation between segments)

(4)

\( \mathbf{O} \) represents the average orientational anisotropy of the segments, and \( \mathbf{C} \) describes the orientational cross-correlation of two different segments involved in the same subchain. (\( \mathbf{u} \) and \( \mathbf{u}' \) are unit bond vectors of arbitrarily chosen two segments in the subchain.) As noted from Eq.(3), the stress is contributed from the anisotropy of respective segments, \( \mathbf{O} \), as well as the cross-correlation of different segments, \( \mathbf{C} \). However, as explained in Appendix A, \( \mathbf{O} \) and \( \mathbf{C} \) of the segments in the internally equilibrated subchain are mutually correlated as

\[
\mathbf{C} = \hat{Q} \mathbf{O} \text{ with } \hat{Q} = 5/3 \text{ for } \beta >> 1
\]

(6)

Correspondingly, the stress \( \sigma \) is uniquely related to the segmental orientation anisotropy \( \mathbf{O} \) as

\[
\frac{\sigma}{3Q\beta vNk_BT} = \mathbf{O} = \langle uu \rangle - \frac{I}{3} \text{ (} \beta >> 1 \text{)}
\]

(7)

\( \mathbf{O} \) is proportional to the macroscopically measureable optical anisotropy tensor (e.g., birefringence) of the ensemble of
segments, and Eq. (7) is equivalent to the stress-optical rule (SOR).

Here, we should note that the orientational coupling of segments due to the nematic interaction is not incorporated in the stress expression explained above. This coupling, found in rheo-optical experiments for binary polymer blends and also detected in Brownian dynamics simulation, tends to reduce the stress for a given orientation anisotropy $O$ thereby increasing the stress-optical coefficient. However, this effect of coupling is adsorbed in the numerical constant $Q$ in Eq. (7), and the proportionality between $\sigma$ and $O$ expressed by Eq. (7) remains unchanged.

It should be also noted that Eqs. (1) and (7) holds in a long time scale where the glassy component of the stress has fully relaxed. This study focuses on the stress in such a long time scale. At shorter times, the glassy stress is not negligible as noted from experiments as well as Brownian dynamics simulation, and the modified stress optical rule (MSOR) holds instead of SOR (Eq. (7)).

Now, we focus on the orientational anisotropy $S$ and stretch ratio $\lambda$ of the subchains defined by

$$S = \left( \frac{\langle \mathbf{r} \cdot \mathbf{r} \rangle}{\langle \mathbf{r}^2 \rangle} - \frac{1}{3} \right) = \frac{\langle \mathbf{u} \cdot \mathbf{u} \rangle + (\beta - 1)\langle \mathbf{u}^2 \rangle - \frac{1}{3} \langle \mathbf{u}^2 \rangle}{1 + (\beta - 1)\langle \mathbf{u}^2 \rangle}$$

$$\lambda^2 = \frac{\langle \mathbf{r} \cdot \mathbf{r} \rangle}{\beta b^2} = 1 + (\beta - 1)\langle \mathbf{u} \cdot \mathbf{u} \rangle$$

This $\lambda$, being defined with respect to the root-mean-square end-to-end distance of the subchain at equilibrium ($r_{eq} = b^{1/2}b$), is identical to the stretch ratio of the chain length for the case of constant $\beta$ examined in this study. In Eq. (8), we have made the decoupling approximation to separate the averages $\langle \mathbf{r} \cdot \mathbf{r} \rangle$ and $\langle \mathbf{r} \rangle$. From Eqs (4)-(6) and (9), Eq. (8) is rewritten as

$$S = Q\beta \frac{O}{\lambda^2} \quad \text{with} \quad Q = 5/3 \quad \text{for} \quad \beta \gg 1$$

The overshoot of the shear stress $\sigma_\gamma$ is equivalent to the overshoot of $O_\gamma = \langle u \cdot u \rangle$, as noted from Eq. (7). Thus, if $\sigma_\gamma$ overshoots but the shear component of the orientational anisotropy of the subchain $S_\gamma$ does not (as claimed by Lu et al), and if SOR is valid, the overshoot of segmental $O_\gamma$ should be canceled by an overshoot of $\lambda^2$; see Eq. (10). Such cancellation is unlikely but not fully ruled out by SOR itself. Nevertheless, analysis of $S$ and $\lambda^2$ in the linear regime and moderately nonlinear regime suggests that such cancellation does not occur, and thus the claim by Lu et al has no sound basis. Details of this analysis are described below.

3. ORIENTATIONAL ANISOTROPY AND STRETCH OF SUBCHAIN IN THE LINEAR AND NONLINEAR REGIMES

On start-up of flow at a rate $\dot{\gamma} < \omega_d$ (i.e., in the linear regime), the shear component of the segmental orientation, $O_{\gamma}(t)$, grows with time monotonically without exhibiting the overshoot, as straightforwardly noted from the growth behavior of the shear stress $\sigma_{xy}(t)$. At higher $\dot{\gamma}$, $O_{\gamma}(t)$ exhibits nonlinearity that corresponds to the transient overshoot of $\sigma_{xy}(t)$ and thinning of the steady state shear viscosity, as noted experimentally.

$O_{\gamma}(t)$ should be an odd function of $\dot{\gamma}$ because its sign changes on reversal of flow direction. Thus, we can unequivocally expand $O_{\gamma}(t)$ with respect to $\dot{\gamma}$ as

$$O_{\gamma}(t) = \gamma K_4 g_4(t) - \gamma^3 K_5 g_5(t) + \gamma^5 K_6 g_6(t) + \ldots$$

The first term (of the order of $\dot{\gamma}$) indicates the linear behavior of $O_{\gamma}(t)$: $g_4(t)$ included in this term is a monotonically increasing function that grows from $g_4(0) = 0$ to $g_4(\infty) = 1$, and $K_4$ is a constant $> 0$: $K_4 = [O_{\gamma}(\infty)\gamma^4 K_4]/\eta_0 = \eta_0^{1/3}(3Q^0n_0N_k T)$ with $\eta_0$ being the zero-shear viscosity. The second term, of the order of $\dot{\gamma}^3$, is a leading term of the nonlinearity of $O_{\gamma}$ at $\dot{\gamma}$ above $\omega_d$ but well below $\omega_d$ (moderately nonlinear regime), and $K_5$ therein is another constant $> 0$. The function $g_5(t) (\geq 0)$ should also increase with $t$ monotonically but more slowly compared to $g_4(t)$, thereby allowing $O_{\gamma}$ to exhibit the overshoot. In addition, $g_6(t)$ should have the zero gradient ($dg_6/dt = 0$) at $t = 0$ so that the short time growth behavior of the reduced orientation $O_{\gamma}(t)/\dot{\gamma}$ is independent of $\dot{\gamma}$ and agrees with that in the linear regime, as known for the reduced shear stress $\sigma_{xy}(t)/\dot{\gamma}$ ($\cong O_{\gamma}(t)/\dot{\gamma}$; cf. Eq. (7)). Competition between $g_4(t)$ and $g_5(t)$ determines the nonlinearity at those $\dot{\gamma}$, the transient overshoot of $O_{\gamma}(t)$ and the decrease of the steady state orientation coefficient, $O_{\gamma}(\infty)\dot{\gamma}$ (that correspond to the overshoot of $\sigma_{xy}(t)$ and thinning of the steady state viscosity). Finally, $K_5$ and $g_6(t)$ are the constant and growth function (having $dg_6/dt = 0$ at $t = 0$) that describe higher order nonlinearity (of the order of $\dot{\gamma}^5$).

The squared stretch ratio $\lambda^2(t)$ remains unchanged on the reversal of flow direction so that it should be an even function of $\dot{\gamma}$. Thus, $\lambda^2(t)$ should be expanded as

$$\lambda^2(t) = 1 + \dot{\gamma}^2 P_2 h_2(t) - \dot{\gamma}^4 P_4 h_4(t) + \ldots$$

with terms of the order of $\dot{\gamma}^6$ (12)
Here, $P_{3}$ and $P_{4}$ are constants $>0$, and $h_{3}(t)$ and $h_{4}(t)$ denote functions of $t$ that grow with $t$. The $\dot{\gamma}^{2}P_{3}h_{4}(t)$ term, representing the shear effect on $\dot{\lambda}(t)^{2}$ of the order of $\dot{\gamma}^{2}$ in the limit of $\dot{\gamma} \to 0$, is the quasi-linear response as similar to the first normal stress difference in that limit, $N_{1} \propto \dot{\gamma}^{2}$. In this limit, $N_{1}(t)$ grows monotonically with time,\footnote{Ref.} and this growth is described within the framework of the quasi-linear second order fluids. As judged from this behavior of $N_{1}(t)$, $h_{3}(t)$ should be also a monotonically increasing function exhibiting no overshoot. The $\dot{\gamma}^{2}P_{3}h_{4}(t)$ term is the leading term of the nonlinearity of $\dot{\lambda}(t)^{2}$ of the order of $\dot{\gamma}^{2}$, and the function $h_{5}(t) (\geq 0)$ therein should increase with $t$ monotonically but more slowly than $h_{3}(t)$ thereby allowing $\dot{\lambda}(t)^{2}$ to exhibit the overshoot. Furthermore, $h_{3}(t)$ should have the zero-gradient ($dh_{3}/dt = 0$) at $t = 0$ so that the short time growth behavior of a reduced stretch factor $\dot{\lambda}(t)^{2-1}/\dot{\gamma}^{2}$ remains independent of $\dot{\gamma}$ (as known for $N_{1}(t)^{2}$). Competition between $h_{3}(t)$ and $h_{4}(t)$ determines the nonlinearity of $\dot{\lambda}(t)^{2}$ that could include the overshoot of $\dot{\lambda}(t)^{2}$ at sufficiently large $\dot{\gamma} \gg \alpha_{e}$.

Combining Eq.(10) with Eqs.(11) and (12), we find

$$\frac{S_{\sigma}}{Q\beta K_{1}} = \frac{O_{n}/K_{1}}{\tilde{\gamma}^{2}} - \frac{\dot{\gamma}^{2}(K_{1}/K_{s})g_{t}(t) + \dot{\gamma}^{2}(K_{s}/K_{1})g_{s}(t)}{1 + \dot{\gamma}^{2}P_{3}h_{3}(t) - \dot{\gamma}^{2}P_{4}h_{4}(t) + ...}$$

(13)

For a test of magnitudes of nonlinearity of $S_{\sigma}$ of different orders of $\dot{\gamma}$, it is convenient to expand Eq.(13) with respect to $\dot{\gamma}$.

The result is:

$$\frac{S_{\sigma}}{Q\beta K_{1}} = \frac{\dot{\gamma}^{2}(K_{1}/K_{s})g_{t}(t) + \dot{\gamma}^{2}(K_{s}/K_{1})g_{s}(t)}{1 + \dot{\gamma}^{2}P_{3}h_{3}(t) - \dot{\gamma}^{2}P_{4}h_{4}(t) + ...} + \frac{P_{3}g_{t}(t)h_{3}(t) + P_{2}g_{t}(t)h_{2}(t)}{1 + \dot{\gamma}^{2}P_{3}h_{3}(t) - \dot{\gamma}^{2}P_{4}h_{4}(t) + ...}$$

(14)

For visual test of the nonlinearities of the orientation and stretch, Fig.2 shows plots of $O_{n}/K_{1}$ (Eq.(11)), $\dot{\lambda}^{2-1}$ (Eq.(12)), and $S_{\sigma}/Q\beta K_{1}$ (Eq.(13)) calculated for adequately chosen parameters: $K_{s}/K_{1} = 0.4$, $K_{s}/K_{1} = 0$, $P_{2} = 0.4$, and $P_{2} = 0.1$. Here, the test is made for the nonlinearity up to the order of $\dot{\gamma}^{2}$, so that the fifth and higher order terms are set to be zero (hence $K_{s}/K_{1} = 0$). The growth functions appearing in Eqs.(11)-(13) are assumed to have a single-exponential type retarded growth form:

$$g_{t}(t) = 1 - \exp(-t/t)$$

(15a)

$$g_{t}(t) = (1 - \exp(-t/2t))^{2}$$

(15b)

$$h_{2}(t) = 1 - \exp(-t/1.5\tau)$$

(15c)

$$h_{4}(t) = (1 - \exp(-t/3\tau))^{2}$$

(15d)

The function $g_{t}(t)$ for the fifth order nonlinearity was not included in the calculation because $K_{s}/K_{1} = 0$. The plots were calculated in the reduced scales so that the values of $K_{s}, \beta$, and $\tau$ were not explicitly required in the calculation.

The functions shown in Eq.(15) qualitatively mimic the actual growth functions. Note also that the functions $g_{t}(t)$ and $h_{4}(t)$ satisfy the zero-gradient requirement at $t = 0$, as explained earlier. Thus, as shown in Fig.3, the initial growth behavior of the reduced quantities, $O_{n}/K_{1}$, $\{\dot{\lambda}^{2-1}\}$, and $S_{\sigma}/Q\beta K_{1}$, is independent of $\dot{\gamma}$ and the linear behavior prevails at short $t$ even in the nonlinear regime at high $\dot{\gamma}$, as known for the $\sigma_{n}(t)$ and $N_{1}(t)^{2}$ data.\footnote{Ref.}

Eq.(14) indicates that $S_{\sigma}/Q\beta K_{1}$ at sufficiently small $\dot{\gamma}$ is governed by the linear term therein, $\dot{\gamma}^{2}g_{t}(t)$, and thus exhibits no overshoot. For such small $\dot{\gamma}$, $\dot{\lambda}(t)^{2}$ grows monotonically but remains close to unity in the entire range of $t$, as also seen in Fig.2. Thus, in the linear regime, $O_{n}$ and $S_{\sigma}/Q\beta$ are identical to each other and commonly exhibit monotonic growth.

For larger $\dot{\gamma}$, $S_{\sigma}$ exhibits a clear overshoot as the nonlinearity of the order of $\dot{\gamma}^{2}$ even when $\dot{\lambda}^{2}$ does not show a prominent overshoot (nonlinearity of the order of $\dot{\gamma}^{4}$), as noted from Eq.(14) and also seen in Fig.2b: This overshoot of $S_{\sigma}$ is contributed from the overshoot of $O_{n}$, described by the $(K_{1}/K_{s})g_{t}(t)$ term $(> 0)$ in Eq.(14), and also from combination of the monotonic growth of $\dot{\lambda}^{2}$ and the linear behavior of $O_{n}$, as represented by the $P_{3}g_{t}(t)h_{3}(t)$ term $(> 0)$. Indeed, experiments show that $O_{n}(t)$ exhibits a prominent overshoot but $N_{1}(t)$ does not at $\dot{\gamma}$ a little higher than $\alpha_{e}$ but well below $\alpha_{e}$.\footnote{Ref.} This experimental observation indicates that the overshoot of $N_{1}(t)$ (and of $\dot{\lambda}(t)^{2}$) is of the higher order nonlinearity emerging at higher $\dot{\gamma}$ compared to the overshoot of $O_{n}(t)$, which lends support to the above discussion.

Furthermore, when $\dot{\lambda}(t)^{2}$ exhibits the overshoot as the nonlinearity of the order of $\dot{\gamma}^{4}$, $S_{\sigma}(t)$ given by Eq. (13) exhibits a sharper overshoot as the stronger nonlinearity (of the order of $\dot{\gamma}^{6}$); cf. Fig.2c. Thus, the claim by Lu et al\footnote{Ref.} (overshoot of $\dot{\lambda}^{2}$ associated with monotonic increase of $S_{\sigma}$) does not have a sound basis and is invalid, as long as SOR allows us to deduce the overshoot of the segmental orientation $O_{n}$ from the well-known overshoot of the shear stress $\sigma_{n}$.

Finally, we can focus on the nonlinearity of the normal component of the orientation, $O_{n}O_{n}$, that directly corresponds to the first normal stress difference $N_{1}(t)$ through SOR; cf. Eq.(7). The normal component difference of the subchain orientation, $S_{\sigma}-S_{\sigma}$, is expressed in
terms of $O_{xy} - O_{yy}$ and $\lambda^2$ as (cf. Eq. (10))

$$\frac{S_{xx} - S_{yy}}{Q\beta} = \frac{O_{xx} - O_{yy}}{\lambda^2}$$

with $Q = 5/3$ for $\beta >> 1$  \(16\)

Experiments indicate that $N_1(t)$ monotonically increases with $t$ without exhibiting a clear overshoot on start-up of flow at $\dot{\gamma}$ a little higher than $\omega_0$ but well below $\omega_R$\(^{14,16}\). This monotonic increase is the case also for $O_{xx} - O_{yy}$ (because of SOR). Then, Eq. (16) forces $S_{xx} - S_{yy}$ of the subchain to undershoot if $\lambda^2$ overshoots as Lu et al.\(^3,4\) claimed. However, this undershoot of $S_{xx} - S_{yy}$ emerging together with the monotonic increase of $S_{xy}$ as claimed by Lu et al.\(^3,4\) is quite unlikely. Thus, the behavior of $O_{xx} - O_{yy}$ (of the $N_1$ data) also rules out the claim by Lu et al.\(^3,4\) as long as SOR is valid at those $\dot{\gamma}$ in the moderately nonlinear regime.

4. CONCLUSION

We have revisited the stress-optical rule of flexible polymers to examine if the shear component of the orientational anisotropy of the subchain, $S_{xy}(t)$, can grow monotonically with $t$ when the squared stretch ratio $\lambda(t)^2$ exhibits the overshoot as claimed by Lu et al.\(^3,4\) Expanding $\lambda(t)^2$ and the segmental shear orientational anisotropy $O_{xy}(t)$ with respect to the shear rate $\dot{\gamma}$, we found that the overshoot of $S_{xy}(t)$ is a nonlinearity of the order of $\dot{\gamma}^3$ and emerges at lower $\dot{\gamma}$ compared to the overshoot of $\lambda(t)^2$ (that is a nonlinearity of the order of $\dot{\gamma}^1$), as long as SOR is valid. In other words, $\lambda(t)^2$ can monotonically grow even when $S_{xy}(t)$ exhibits the overshoot, but the overshoot of $\lambda(t)^2$ is always accompanied by the overshoot of $S_{xy}(t)$. Thus, the claim by Lu et al.\(^3,4\) does not have a sound basis and is quite unlikely at $\dot{\gamma}$ well below the Rouse relaxation frequency $\omega_R$ where SOR is experimentally known to be valid. The same conclusion was deduced also from the behavior of the normal component difference of the segmental orientation, $O_{xx} - O_{yy}$, that corresponds to the first normal stress difference $N_1$. From these results, it is highly desired to re-examine technical details of the Brownian dynamics simulation by Lu et al.\(^3,4\) that led them to make the above claim.

Fig. 2. Model calculation of the shear orientational anisotropy of segment and subchain, $O_{xy}$ (thick red curve) and $S_{xy}$ (blue dots), and squared stretch ratio of subchain, $\lambda^2$ (thin green curve).

Fig. 3. Comparison of reduced quantities, (a) $O_{xy}/K_1$, (b) $(\lambda^2 - 1)/\dot{\gamma}^2$, and (c) $S_{xy}/Q\beta K_1\dot{\gamma}$, obtained from model calculation at several shear rates as indicated.
ACKNOWLEDGMENTS

This work was partly supported by the Grant-in-Aid for Scientific Research (B) from MEXT, Japan (grant No. 15H03865), Grant-in-Aid for Scientific Research (C) from JSPS, Japan (grant No. 15K05519), and Collaborative Research Program of ICR, Kyoto University (Grant No. 2015-46).

APPENDIX A.

Relationship between O and C

A1. For large $\beta$:

We focus on the subchain comprising of $\beta$ segments; see Fig.1. The Cartesian coordinates $(x, y, z)$ is fixed to the laboratory frame, and $(X, Y, Z)$, attached to the subchain, with the $Z$ direction being chosen to be the direction of the subchain end-to-end vector $r$. The conformation of the internally equilibrated subchain is rotationally symmetric around the $Z$ axis, so that the orientational anisotropy of the segment $O_i$ averaged under a given (fixed) $r$ is expressed, in the $(X, Y, Z)$ coordinate, as

$$O_r = \langle uu \rangle_r \frac{I}{3} = \begin{bmatrix} \frac{1}{2} \langle u_x^2 \rangle_r & 0 & 0 \\ 0 & \frac{1}{2} \langle u_y^2 \rangle_r & 0 \\ 0 & 0 & \langle u_z^2 \rangle_r \end{bmatrix} \frac{I}{3}$$

(17)

with

$$\langle u_i^2 \rangle_r = \frac{1}{\beta} \sum_{i=1}^{\beta} \langle u_i^2 \rangle_r = \frac{1}{\beta} \sum_{i=1}^{\beta} (\langle u_i \cdot \vec{r} \rangle)^2$$

(18)

where $u_i$ is $i$th segmental bond vector and $u_i \cdot \vec{r}$ is its component in the $r$ direction, and $I$ is the unit tensor. $\langle \cdots \rangle_r$ indicates the average for all internal conformation of the subchain for the given $r$, and $\vec{r}$ is the unit vector in the $r$ direction; $\vec{r} = r/r$ with $r = |r|$. As can be noted from Eq.(17), $O_r$ is expressed in the compact tensorial form being valid in both $(X, Y, Z)$ and $(x, y, z)$ coordinates:

$$O_r = \begin{bmatrix} \frac{3}{2} \langle u_x^2 \rangle_r - \frac{1}{2} \frac{I - \langle \vec{r} \cdot \vec{r} \rangle}{3} \end{bmatrix}$$

(19)

Here, $\vec{r} \vec{r}$ indicates the dyadic of $\vec{r}$.

Now, we focus on the orientational cross-correlation of two segments in the same subchain. Because $\vec{r} = (b/r)\sum_{i=1}^{\beta} u_i$, we obtain

$$\langle uu \rangle_r = \frac{1}{\beta} \sum_{i=1}^{\beta} \langle u_i u_i \rangle_r$$

(21)

with

$$\langle uu \rangle_r = \frac{1}{\beta (\beta - 1)} \sum_{i=1}^{\beta} \langle u_i u_i \rangle_r$$

(22)

and

$$\vec{r} \vec{r} = \frac{r}{\beta b}$$

(23)

Note that $\vec{r}$ (Eq.(23)) is the stretch ratio of the subchain defined with respect to the fully stretched state where $r = \beta b$. From Eqs (19) and (20), we find that the orientational cross-correlation averaged under the given $r$ is expressed as

$$C_r = \langle uu \rangle_r - \{ \langle uu \rangle_r \} \frac{I}{3}$$

$$= \frac{1}{\beta - 1} \{ \vec{r} \beta \vec{r} \vec{r} - \langle uu \rangle_r \} - \frac{1}{\beta - 1} \{ \vec{r} \beta \vec{r} - \langle uu \rangle_r \} \frac{I}{3}$$

$$- \frac{1}{\beta - 1} \{ \vec{r} \beta - \frac{3}{2} \langle u_i^2 \rangle_r + \frac{1}{2} \{ \vec{r} \vec{r} - \frac{I}{3} \} \}$$

(24)

(Note that $\langle uu \rangle_r = O_r + I/3$.)

From Eqs (19) and (24), we note that the relationship between $O_r$ and $C_r$ (both being proportional to $\vec{r} \vec{r} - I/3$) is determined by a relationship between $\langle u_i^2 \rangle_r$ and $\vec{r}$ ($= r/b$). For $\beta >> 1$, the latter relationship is known to be expressed as $\langle u_i^2 \rangle_r = 1 - \frac{2}{3} \langle u_i \cdot \vec{r} \rangle^2$. For $\beta \geq 40$, we can safely utilize the relationship

$$\langle u_i^2 \rangle_r = \frac{1}{3} + \frac{2}{5} \frac{\vec{r}}{L} + \frac{24}{175} \frac{\vec{r}}{L}^2 + O(\vec{r}^3)$$

(25)

Thus, if the subchain is not very highly stretched, we obtain a simple relationship, $\langle u_i^2 \rangle_r = (1/3) + (2\vec{r}^2/5)$. This relationship holds within 1% error for $\vec{r} < 0.4$, namely, for $r < 0.4\beta b$.

Thus, for $\beta >> 1$ and $\vec{r} < 0.4$, we can safely utilize the relationship $\langle u_i^2 \rangle_r = (1/3) + (2\vec{r}^2/5)$ in Eqs (19) and (24) to find

$$C_r = -\frac{5}{3} O_r = -\vec{r} \vec{r} - \frac{I}{3}$$

(26)
Because $\beta \gg 1$, we have neglected a difference between $\beta - 1$ and $\beta - 3/5$ in derivation of Eq.(26). Namely, $C_r$ and $O_r$ are proportional to each other even when the subchain is moderately stretched. This proportionality remains after averaging over the distribution of the end-to-end vector $r$ of the subchain, i.e., $C = (5/3)O$ (cf. Eq.(6)), which results in the validity of the stress-optical rule, Eq.(7).

**A2. For small $\beta$:**

It is informative to examine the relationship between $O_r$ and $C_r$ for the cases of rather small $\beta$, although this study focuses on the cases of $\beta \gg 1$. For this purpose, we can calculate, in the $(X, Y, Z)$ coordinate introduced in Fig.1, $\langle u_{r1}^2 \rangle_r$ of the end-to-end vector $r'$ of the sequence of the remaining $\beta - 1$ segments; see Fig.4. This distribution function is given, in a non-normalized form, by

$$W(r') = \frac{k^{(\beta - 3/5)3}}{\xi! \beta} \sum_{k=0}^{\beta - 1} (-1)^k (\beta - 1)^k (\beta - 3/5) \beta^{-1}$$

with

$$\xi = \frac{r'}{b} = \left[\left(\frac{r}{b}\right)^2 + 1 - \left(\frac{r}{b}\right) \cos \theta\right]^{1/2}$$

Here, $\theta$ is the polar angle of the bond vector $b$, measured with respect to the subchain end-to-end-vector $r$, and thus $\cos \theta = b_i r/br$ with $r = |r|$. $\theta$ can vary in a range between 0 and $\theta^*$, with $\theta^*$ being determined by $r$ as

$$\theta^* = \pi \text{ for } 0 \leq r/b \leq \beta - 2$$

$$\theta^* = \cos^{-1} \left\{ \frac{(r/b)^2 + 1 - (\beta - 1)^2}{2r/b} \right\} \text{ for } \beta - 2 < r/b \leq \beta$$

(For $\beta - 2 < r/b \leq \beta$, $b_i$ cannot be oriented in a direction opposite to $r$. This leads to the upper bound $\theta^*$ given by Eq.(30)). The end-to-end length of the sequence of the $\beta - 1$ segments normalized by the segmental bond length, $\xi$, appearing in the distribution function (Eq.(27)), is determined by $\theta$ as shown in Eq.(28). Thus, the average $\langle u_{r1}^2 \rangle_r = \langle \cos^2 \theta \rangle_r$ under the given $r$ is obtained as an integral with respect to $\theta$ in the range between 0 and $\theta^*$:

$$\langle u_{r1}^2 \rangle_r = \frac{\int_0^{\pi} \cos^2 \theta W(r'(\theta)) \sin \theta \, d\theta}{\int_0^{\pi} W(r'(\theta)) \sin \theta \, d\theta}$$

Because all segments has the equivalent freedom in their configuration, $\langle u_{r1}^2 \rangle_r$ obtained from Eq.(31) can be utilized as the average $\langle u_{r1}^2 \rangle$ over all segments.

Fig.5 shows plots of $\langle u_{r1}^2 \rangle_r$ thus obtained for several values of $\beta = 6-40$. Even for these considerably small $\beta$ values, $\langle u_{r1}^2 \rangle_r$ is almost universally dependent on the subchain stretch ratio defined with respect to the fully stretched state, $\hat{\lambda}$ (Eq.(23)). Furthermore, for small $\hat{\lambda}_2 < 0.2$, the plots are surprisingly well described by the function deduced earlier for large $\beta$, $\langle u_{r1}^2 \rangle_r = (1/3) + (2\hat{\lambda}_2^2/5)$. Thus, the orientational cross-correlation $C$ and the orientational anisotropy $O$ obey the relationship $C = (5/3)O$ (cf. Eq.(6)) even for considerably short subchains.
## REFERENCES


