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Conformational Changes during Creep Process of Binary Blends of Rouse Chains

Hiroshi Watanabe* and Tadashi Inoue

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

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1. Introduction

The Rouse model is a well-established model for nonentangled polymers in concentrated systems, and its conformational dynamics and rheological properties under strain-controlled conditions were fully analyzed in the literature.[1−6] However, surprisingly, the conformational dynamics under stress-controlled conditions was not examined so far. For completeness of the analysis of the model, we recently examined the orientational anisotropy of the monodisperse Rouse chains during the creep and creep recovery processes.[7] It turned out that the eigenmodes of this chain, fully characterizing the chain conformation and the stress, are correlated with each other because of the constant stress requirement during the creep/recovery processes. Consequently, the anisotropies of the higher order eigenmodes exhibit overshoot before reaching their steady state in the creep process in order to compensate a slow growth of the anisotropy of the lowest eigenmode.[7] Further analysis[8] indicated that the Rouse chain deforms affinely on imposition/removal of the stress at the onset of creep/recovery to instantaneously adjust its conformation and that the successive changes in the conformation occur through the correlated growth/decay of the anisotropies of the eigenmodes. We also examined effects of combination of Rouse and reptation mechanisms on the creep and relaxation processes (stress- and strain-controlled processes) and found that the reptation limit is less easily attained for the creep process.[9]

The above results demonstrate the importance of the interplay (correlation) of the Rouse eigenmodes of various orders under the stress-controlled conditions. For the creep process of *binary blends* of Rouse chains, we expect similar interplay of the component chains (in addition to the interplay of the eigenmodes of respective components). This paper analyzes the creep behavior of the blends from this point of view.

2. Theoretical Basis[1,3,5,6]

We consider a blend of long and short Rouse chains composed of N_2 and N_1 ($<N_2$) segments (beads). The number densities of the long and short chains are denoted by ν_2 and ν_1, respectively. The neighboring segments in each chain are connected by a Gaussian spring of the spring constant $\kappa = 3k_BT/a^2$, where a is the average size of the segment (= root-mean-square length of the spring), k_B is the Boltzmann constant, and T is the absolute temperature. In the mean-field description of the chain motion, we focus on a given chain and regard the surrounding chains as a uniform frictional medium for the focused chain. The segmental friction coefficient in this medium is denoted by ζ.

In the creep process, a small shear stress σ_0 is applied to the blend. This stress determines the flow velocity $\mathbf{V}(\mathbf{r}^{[j]}(n,t))$ of the medium at the position $\mathbf{r}^{[j]}(n,t)$ of the nth segment of the chain j (= 1 and 2 for the short and long chains). Changes of $\mathbf{r}^{[j]}(n,t)$ with t are described by the Rouse equation of motion (in the continuous limit for $N_j \to \infty$)[3,5,6] incorporating this $\mathbf{V}$

$$\zeta\left[\frac{\partial \mathbf{r}^{[j]}(n,t)}{\partial t} - \mathbf{V}(\mathbf{r}^{[j]}(n,t))\right] = \kappa\frac{\partial^2 \mathbf{r}^{[j]}(n,t)}{\partial n^2} + \mathbf{F}_{\mathrm{B}}^{[j]}(n,t) \qquad (1)$$

Here, $\mathbf{F}_{\mathrm{B}}^{[j]}(n,t)$ is the Brownian force acting on the nth segment of the chain j at time t: $\mathbf{F}_{\mathrm{B}}^{[j]}$ is modeled as a white noise characterized by the first- and second-order moments of its component $F_{\mathrm{B},\alpha}^{[j]}$ in the α direction ($\alpha = x, y, z$), $\langle F_{\mathrm{B},\alpha}^{[j]}(n,t)\rangle = 0$ and $\langle F_{\mathrm{B},\alpha}^{[j]}(n,t)F_{\mathrm{B},\beta}^{[j]}(n',t')\rangle = 2\zeta k_BT\delta(n-n')\delta(t-t')\delta_{\alpha\beta}$ with $\langle ... \rangle$ denoting the ensemble average.[3]

Under the boundary condition representing the lack of external tensile forces acting on the chain ends, $\partial\mathbf{r}^{[j]}(n,t)/\partial n = \mathbf{0}$ for $n = 0$ and N_j, $\mathbf{r}^{[j]}(n,t)$ is expanded into the Rouse eigenmodes as

$$\mathbf{r}^{[j]}(n,t) = \sum_{p=0}^{\infty}\begin{bmatrix} X_p^{[j]}(t) \\ Y_p^{[j]}(t) \\ Z_p^{[j]}(t) \end{bmatrix}\cos\left(\frac{p\pi n}{N_j}\right) \qquad (2)$$

The amplitudes of the pth eigenmode in the x-, y-, and z-directions, $X_p^{[j]}(t)$, $Y_p^{[j]}(t)$, and $Z_p^{[j]}(t)$, fully specify the conformation of the chain j. Hereafter, the x- and y-directions are chosen as the shear and shear-gradient directions.

The small stress σ_0 (in the linear viscoelastic regime) gives a uniform shear field specified by the velocity $\mathbf{V} = (\dot{\gamma}(t)r_y^{[j]}(n,t), 0, 0)^{\mathrm{T}}$, where $\dot{\gamma}(t)$ is the strain rate being uniform throughout the system and $r_y^{[j]}(n,t)$ is the y component of $\mathbf{r}^{[j]}(n,t)$. From eq 2, this $\mathbf{V}$ is written in terms of the eigenmode amplitudes:

$$\mathbf{V} = \sum_{p=0}^{\infty}\begin{bmatrix} \dot{\gamma}(t)Y_p^{[j]}(t) \\ 0 \\ 0 \end{bmatrix}\cos\left(\frac{p\pi n}{N_j}\right) \qquad (3)$$

Equations 1−3 fully specify the chain conformation that changes with t. This conformation determines the viscoelastic stress. In general, the shear stress of flexible

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* To whom correspondence should be addressed.

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polymers is given as a sum of the anisotropies of the segmental bond vectors, $\langle(\partial r_x/\partial n)(\partial r_y/\partial n)\rangle$.[3,6] Thus, the shear stress of our blend at time t is expressed in terms of the eigenmode amplitudes as (cf. eq 2)

$$\sigma(t) = \frac{3k_BT}{a^2} \times \left[\nu_1 \sum_{p=1}^{\infty} \frac{p^2\pi^2}{2N_1}\langle X_p^{[1]}(t) Y_p^{[1]}(t)\rangle + \nu_2 \sum_{p=1}^{\infty} \frac{p^2\pi^2}{2N_2}\langle X_p^{[2]}(t) Y_p^{[2]}(t)\rangle\right] \quad (4)$$

In the creep process examined in this study, this $\sigma(t)$ is externally controlled, i.e., $\sigma(t) = \sigma_0$ (constant) at $t \geq 0$. Then, the eigenmodes of different orders exhibit interplay in order to satisfy eq 4.

3. Results and Discussion

3.1. Analysis. The eigenmode anisotropies related to the shear stress (eq 4) can be obtained by solving eqs 1−3 with a standard method (utilized also in the previous study[7]). The results are summarized as

$$\langle X_p^{[j]}(t)\ Y_q^{[j]}(t)\rangle = \frac{2a^2N_j\delta_{pq}}{3\pi^2p^2}\int_0^t \mathrm{d}t'\ \dot\gamma(t') \exp\left(-\frac{p^2(t-t')}{\tau_R^{[j]}}\right) \quad (5)$$

Here, $\tau_R^{[j]}$ is the longest relaxation time of the chain component j given by

$$\tau_R^{[j]} = \frac{\zeta a^2 N_j^{\,2}}{6\pi^2 k_B T} \quad (6)$$

As noted from eq 5, the anisotropy of the chain conformation is fully specified if the shear rate $\dot\gamma(t)$ is known. For the strain-controlled process (such as the start-up of the constant rate flow), $\dot\gamma(t)$ is externally given and the eigenmode anisotropies are straightforwardly calculated from eq 5. In contrast, for the stress-controlled process (such as creep), $\dot\gamma(t)$ is self-consistently determined by the chains in a way that their stress matches the externally given stress.

For the creep process under the constant stress σ_0, eqs 4 and 5 under this matching condition give

$$\sigma_0 = \int_0^t \mathrm{d}t'\ \dot\gamma(t')\left[\nu_1 k_B T \sum_{p=1}^{\infty} \exp\left(-\frac{p^2(t-t')}{\tau_R^{[1]}}\right) + \nu_2 k_B T \sum_{p=1}^{\infty} \exp\left(-\frac{p^2(t-t')}{\tau_R^{[2]}}\right)\right] \quad (7)$$

Equation 7 can be analytically solved with a previously explained Laplace transformation method[7] to obtain an expression of the shear rate

$$\dot\gamma(t) = \sigma_0\left[\frac{1}{\eta_0} + \frac{4}{\nu_1 k_B T}\sum_{q=1}^{\infty}\frac{\theta_q^{\,2}}{h_q \pi^2 \tau_R^{[1]}}\exp\left(-\frac{\theta_q^{\,2} t}{\pi^2\tau_R^{[1]}}\right)\right] \quad (8)$$

with

$$\eta_0 = \frac{\pi^2 k_B T}{6}[\nu_1\tau_R^{[1]} + \nu_2\tau_R^{[2]}]\ (= \text{viscosity of the blend}) \quad (9)$$

and

$$h_q = \theta_q^{\,2} - (1 - \theta_q \cot\theta_q)(1 + \theta_q\cot\theta_q) + \frac{\nu_2}{\nu_1}\left[\left(\frac{N_2\theta_q}{N_1}\right)^2 - \left\{1 - \left(\frac{N_2\theta_q}{N_1}\right)\cot\left(\frac{N_2\theta_q}{N_1}\right)\right\} \times \left\{1 + \left(\frac{N_2\theta_q}{N_1}\right)\cot\left(\frac{N_2\theta_q}{N_1}\right)\right\}\right] \quad (10)$$

The numerical coefficients θ_q ($0 < \theta_1 < \theta_2 < \theta_3 < ...$) appearing in eqs 8 and 10 are determined from

$$\nu_1[\theta_q\cot\theta_q - 1] + \nu_2\left[\left(\frac{N_2\theta_q}{N_1}\right)\cot\left(\frac{N_2\theta_q}{N_1}\right) - 1\right] = 0 \quad (11)$$

Note that the normalized shear rate $\dot\gamma(t)/\sigma_0$ specified by eq 8 is identical to a time derivative of the creep compliance $J(t)$ given by

$$J(t) = \frac{t}{\eta_0} + \frac{4}{\nu_1 k_B T}\sum_{q=1}^{\infty}\frac{1}{h_q}\left[1 - \exp\left(-\frac{\theta_q^{\,2}t}{\pi^2\tau_R^{[1]}}\right)\right] \quad (12)$$

Substituting eq 8 into eq 5, we calculated the eigenmode anisotropies. The results can be summarized in a normalized form:

$$A_p^{[j]}(t) \equiv \frac{\nu_j k_B T p^2\pi^2}{2\sigma_0 a^2 N_j}\langle X_p^{[j]}(t)\ Y_p^{[j]}(t)\rangle = \frac{2\nu_j N_j^{\,2}}{p^2\pi^2(\nu_1 N_1^{\,2} + \nu_2 N_2^{\,2})} + \frac{4\nu_j}{3\pi^2\nu_1}\sum_{q=1}^{\infty}\frac{\theta_q^{\,2}}{h_q\{(N_1p/N_j)^2 - (\theta_q/\pi)^2\}}\exp\left(-\frac{\theta_q^{\,2}t}{\pi^2\tau_R^{[1]}}\right) \quad (13)$$

The stresses $\sigma^{[j]}$ sustained by the short and long chains (j = 1 and 2), representing the conformational anisotropies summed over the backbones of these chains, are expressed in terms of $A_p^{[j]}(t)$ as

$$\sigma^{[j]}(t) = 3\sigma_0\sum_{p=1}^{\infty}A_p^{[j]}(t) \quad (14)$$

For $\nu_2 = 0$ and/or $N_2 = N_1$, all of the above results are reduced to the previous results[7] for the monodisperse Rouse chain composed of N_1 segments.

3.2. Interplay of Long and Short Chains. Figure 1 shows growth of the stress $\sigma^{[j]}(t)$ sustained by the short and long chains (eq 14) in the blends having $N_2/N_1 = 3$ and 10 (dotted and dashed curves). The weight fractions of these chains are $w_j = \nu_j N_j/(\nu_1 N_1 + \nu_2 N_2) = 0.5$ (j = 1, 2 for the short and long chains). For comparison, the growth in the monodisperse system[7] ($N_2/N_1 = 1$) is also shown (solid curves). For the clearest comparison of the behavior of the blends and monodisperse system, $\sigma^{[j]}(t)$

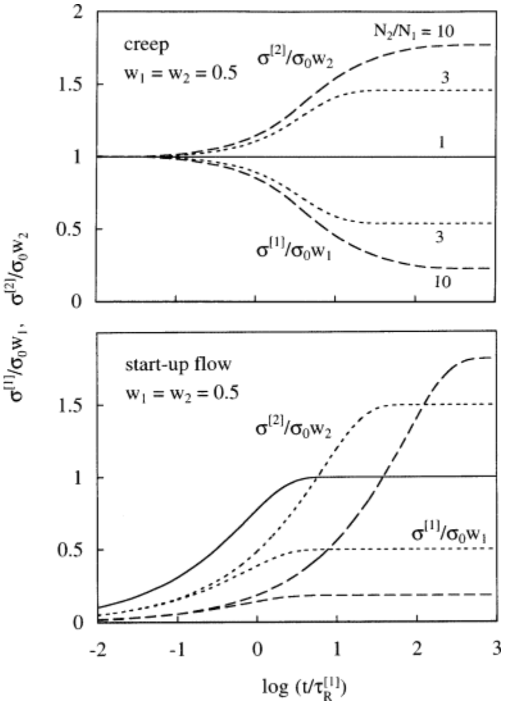

Figure 1. Stress $\sigma^{[j]}$ sustained by the short and long chains (j = 1 and 2) in the blends with the weight fractions $w_1 = w_2 = 0.5$. The top and bottom panels indicate $\sigma^{[j]}$ during the creep and start-up flow processes, respectively. In both panels, the dotted and dashed curves indicate the behavior in the blends with $N_2/N_1 = 3$ and 10, and the solid curves show that in the monodisperse system. For the clearest comparison of the creep and start-up flow processes, $\sigma^{[j]}$ is normalized by $\sigma_0 w_j$ and semilogarithmically plotted against the normalized time for the short chain, $t/\tau_R^{[1]}$. Here, σ_0 is the stress in the steadily flowing state (= externally applied stress for the creep process).

is normalized by $\sigma_0 w_j$ and semilogarithmically plotted against a normalized time defined for the short chain, $t/\tau_R^{[1]}$.

From eqs 4 and 5 with $\dot\gamma(t) = \dot\gamma$ (= constant), the $\sigma^{[j]}(t)$ after start-up of constant rate flow is easily calculated as

$$\sigma^{[j]}(t) = \nu_j k_B T \tau_R^{[j]} \left(\frac{\sigma_0}{\eta_0}\right) \sum_{p=1}^{\infty} \frac{1}{p^2}\left[1 - \exp\left(-\frac{p^2 t}{\tau_R^{[j]}}\right)\right] \quad (15)$$

Here, σ_0 and η_0 represent the steady-state stress and the viscosity of the blend as a whole, and the σ_0/η_0 ratio is identical to $\dot\gamma$. The bottom panel of Figure 1 shows normalized plots of this $\sigma^{[j]}(t)$ ($\sigma^{[j]}(t)/\sigma_0 w_j$ vs $t/\tau_R^{[1]}$). The ratio of the steady stresses of the long and short chains, $\sigma^{[2]}(\infty)/\sigma^{[1]}(\infty)$, increases with the N_2/N_1 ratio. Specifically, $\sigma^{[2]}(\infty)/\sigma^{[1]}(\infty) = N_2/N_1$ for $w_2 = w_1$ (cf. eq 15). However, this increase merely reflects a distribution of the total stress $\sigma^{[2]}(\infty) + \sigma^{[1]}(\infty)$ for the short and long chains having different relaxation times $\tau_R^{[1]}$ and $\tau_R^{[2]}$. An essential feature in the strain rate-controlled process is the *independent* changes of the conformations of the short and long chains, as clearly demonstrated in eq 15. This feature is observed in the bottom panel of Figure 1 as a coincidence of a fractional stress $\sigma^{[1]}(t)/\sigma^{[1]}(\infty)$ of the short chains in the blends and monodisperse system at *any t*. (In this panel, $\sigma^{[2]}(t)$ of the long chain is plotted against the normalized time for the short chain, $t/\tau_R^{[1]}$, and thus the growth of $\sigma^{[2]}(t)$ looks delayed with increasing N_2/N_1 ratio. However, this superficial delay vanishes when $\sigma^{[2]}(t)$ is plotted against the normalized time for the long chain $t/\tau_R^{[2]}$, as clearly noted from eq 15.)

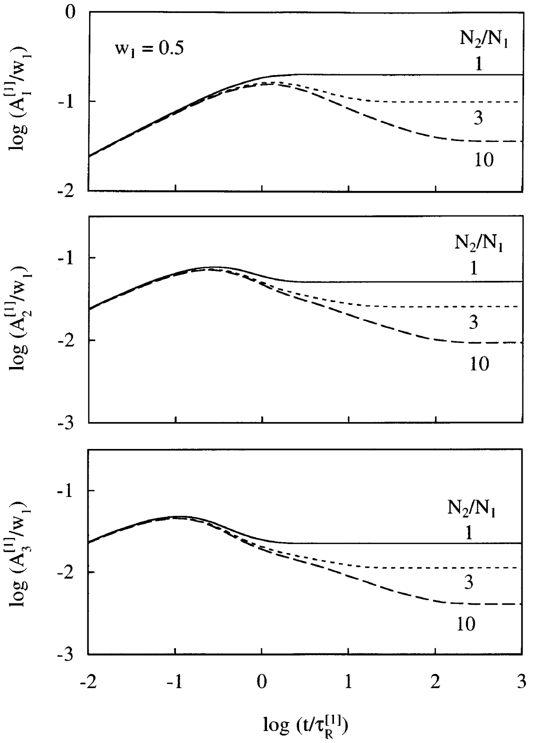

Figure 2. Anisotropies of eigenmode amplitudes $A_p^{[1]}(t)$ (p = 1−3) of the short chain in the blends with $w_1 = w_2 = 0.5$ during the creep process. The dotted and dashed curves indicate $A_p^{[1]}(t)$ in the blends with $N_2/N_1 = 3$ and 10, and the solid curves show $A_p^{[1]}(t)$ in the monodisperse system. For the clearest comparison of the behavior in the blends and monodisperse system, $A_p^{[1]}(t)$ is normalized by the weight fraction of the short chain, $w_1 = 0.5$, and double-logarithmically plotted against the normalized time for this chain, $t/\tau_R^{[1]}$.

The chain conformation and stress in the *steady state* are the same for the start-up-flow and creep processes. However, transient changes in the conformation/stress of the chains are quite different. During the creep process, the stresses $\sigma^{[1]}(t)$ and $\sigma^{[2]}(t)$ of the short and long chains synchronously decay and grow, respectively, in a way that the total stress $\sigma^{[1]}(t) + \sigma^{[2]}(t)$ is kept constant (= σ_0); see top panel of Figure 1. Consequently, a time $t_s^{[1]}$ required for achieving the steady state for the short chain increases with increasing N_2 because the conformational change of the long chain determining the growth of $\sigma^{[2]}(t)$ becomes slower for larger N_2 and the short chain having a much shorter relaxation time ($\tau_R^{[1]}$) is forced to compensate this slow growth. In relation to this point, it should be noted that $t_s^{[1]}$ for large N_2 is much longer in the creep process than in the start-up-flow process; compare the top and bottom panels of Figure 1.

These features of the creep process demonstrate the importance of the conformational interplay (correlation) of the short and long chains under the constant stress requirement. The eigenmodes of respective chains also exhibit the interplay, as demonstrated in Figures 2 and 3 where the eigenmode anisotropies $A_p^{[j]}$ (p = 1−3; cf. eq 13) of the chains in the blends are normalized by the weight fractions w_j and double-logarithmically plotted against respective normalized time $t/\tau_R^{[j]}$.

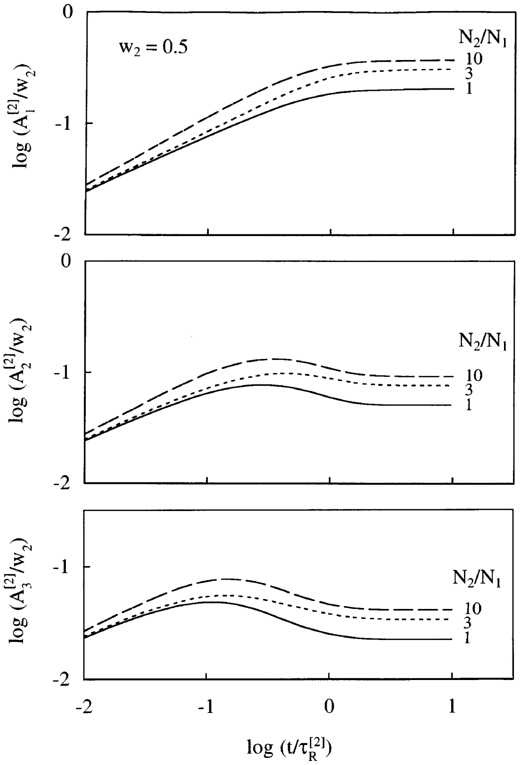

Figure 3. Anisotropies of eigenmode amplitudes $A_p^{[2]}(t)$ (p = 1−3) of the long chain in the blends with $w_1 = w_2 = 0.5$ during the creep process. The dotted and dashed curves indicate $A_p^{[2]}(t)$ in the blends with N_2/N_1 = 3 and 10, and the solid curves show $A_p^{[2]}(t)$ in the monodisperse system. For the clearest comparison of the behavior in the blends and monodisperse system, $A_p^{[2]}(t)$ is normalized by the weight fraction of the long chain, w_2 = 0.5, and double-logarithmically plotted against the normalized time for this chain, $t/\tau_R^{[2]}$.

As seen in the top panel of Figure 3, $A_1^{[2]}$ of the lowest eigenmode of the long chain increases monotonically with t. The anisotropies of the higher eigenmodes, $A_2^{[2]}$ and $A_3^{[2]}$, exhibit the overshoot before reaching the steady state, thereby compensating the slow growth of $A_1^{[2]}$; cf. middle and bottom panels. Namely, this overshoot is indicative of the interplay of the eigenmodes during the creep process, as fully discussed in the previous paper.[7] It should be also noted that the monotonic growth of $A_1^{[2]}$ and the overshoot of $A_2^{[2]}$ and $A_3^{[2]}$ are qualitatively similar in the monodisperse system (solid curves) and the blends (dotted and dashed curves). Thus, the interplay of the eigenmodes of the long chain is just moderately affected by blending.

In contrast, significant effects of blending are observed for the eigenmodes of the short chain (see Figure 2). For this chain, the overshoot of the higher eigenmodes (p = 2 and 3) is quite prominent (compared to that for the long chain), and even the lowest eigenmode exhibits the overshoot. This result indicates that even the lowest eigenmode of the short chain can adjust its amplitude quickly compared to the eigenmodes of the long chain, thereby compensating the slow growth of the latter. Namely, the eigenmodes of the short chain cooperatively compensate the slow growth of the orientational anisotropy of the long chain. Thus, the eigenmodes of the short chain is strongly affected by the orientational interplay between the long and short chains during the creep process.

4. Concluding Remarks

We have examined conformational anisotropies of long and short Rouse chains in binary blends during the creep process through the eigenmode analysis. Because of the constant-stress requirement during this process, the long and short chains exhibit mutually correlated conformations. The effect of blending on the time evolution of the conformational anisotropy during the creep process is much larger for the short chain than for the long chain: The short chain compensates a delay in the growth of the anisotropy of the long chain. Consequently, the anisotropies of the eigenmodes of the short chain exhibit remarkable overshoot before reaching their steady state, and this state is achieved only in a time scale much longer than the intrinsic relaxation time of this chain.

The creep analysis presented here can be straightforwardly extended to bead−spring chains of arbitrary polydispersity and topology (such as star branching) by utilizing the relaxation modulus of these chains in the square bracket term in the right-hand side of eq 7. It is of interest to conduct rheooptical experiments to test the conformational anisotropy thus deduced for these cases as well as for the binary blend examined in this study. This experiment is now being attempted.

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