Effect of Orientational Coupling Due to Nematic Interaction on Relaxation of Rouse Chains

Hiroshi Watanabe,[*,†] **Tadao Kotaka,**[†] **and Matthew Tirrell**[‡]

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan, and Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

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ABSTRACT: A polymer chain in a dense and deformed matrix of other chains tends to be oriented in the direction of matrix orientation. This orientational coupling results from an interaction, which we call the *nematic* interaction in this paper, between the segments of the chain and matrix. To describe the effect of such an interaction on the dynamic behavior of a Rouse chain, we propose a model in which a force leading to the orientational coupling is taken into account. Our model indicates that linear superposability holds for the dynamic response of Rouse chains to small strains imposed, even when the orientational coupling takes place. We have found that the effects of orientational coupling on the *viscoelastic* and *orientation* relaxation functions are not necessarily the same. For the linear *viscoelastic* relaxation, our model suggests no effect of orientational coupling for the Rouse chains in both monodisperse and blend systems. For the *orientation* relaxation of the Rouse chains in monodisperse systems, we still see no significant effect. On the other hand, for the *orientation* relaxation of Rouse chains in blends with other chains, our model suggests a significant effect. For this case, the orientation relaxation function of the Rouse chains is written in terms of those of the matrix chains and of the Rouse chains subjected to *no* nematic interaction. Significant retardation is expected when the Rouse chains are placed in a matrix of much longer chains. This prediction can be tested by optical techniques.

I. Introduction

Dynamics of flexible polymer chains is an important subject in polymer physics, and many molecular models have been proposed. In the current *tube* model for entangled linear chains, the slow dynamic behavior is described in terms of several modes of molecular motion, for example, reptation, contour length fluctuation, and constraint release.[1,2] Recently, for binary blends of long and short monodisperse polymer chains, Kornfield et al.[3] have found by dynamic dichroism measurements that the orientation relaxation of short chains was substantially retarded by the presence of long chains. The relaxation of the short chains in blends *could* be conceivably retarded because of a suppression of the constraint release mechanism due to slower moving long chains. However, in the systems examined by Kornfield et al., the molecular weight of the short chains was more than 10 times larger than the molecular weight between entanglements, M_e, so that the constraint release mechanism appeared to be minor for those chains.

To explain the kind of experimental results mentioned above, two models based on an idea of *orientational coupling due to nematic interaction* have been proposed. In the model of Merrill et al.,[4] a primitive chain relaxing by reptation picks up some fraction of the average matrix orientation at its chain ends. Thus, the equation of motion of the primitive chain is identical with that for the *pure* reptation mechanism (without the orientational coupling effect), but the boundary condition representing the relaxation at chain ends is different.

In the model of Doi et al.,[5] the orientation of a chain has two contributions, one coming from the chemical bonds connecting the monomers and the other from the bonds connecting the primitive chain segments. In this model, no constraint is assumed for the ends of the primitive chain. This leads to the time evolution of the orientation of the primitive chain identical with that for the *pure* reptation mechanism.[5] The retardation of orientation relaxation is induced by the orientational coupling for the chemical bonds connecting the monomers.

The above two models, based on the reptation mechanism and predicting the retarded orientation relaxation of short chains in blends, are models for entangled chains. Here, we have to remember that the molecular origin of the orientational coupling in dense systems is found in the anisotropy of chain segments (monomers):[4] Those anisotropic segments would tend to arrange themselves in the same direction (on a microscopic level), because of an interaction similar to that for rod polymers forming nematic phases.[2] Such an interaction between the segments, which we call the *nematic interaction* in this paper, is not exclusive to entangled polymers. Therefore, it is interesting and important to examine the effect of the nematic interaction on relaxation of nonentangled chains, for which the validity of the conventional Rouse model (without considering that interaction) appears to be experimentally established.

In this paper, we propose a model for the motion of a Rouse chain expected when orientational coupling due to nematic interaction takes place. First, in section II, we consider a force leading to orientational coupling and modify the equation of motion for the Rouse chain. In sections III and IV, we calculate the orientation function after a single- and double-step shear strain. The Rouse chain considered is in two types of environments: a blend and a monodisperse system. We impose no restriction for the matrix chains in the blend; i.e., those chains can be either cross-linked, entangled, or nonentangled among themselves. However, regardless of the type of the matrix chains, the behavior of the Rouse chain in the blend is affected by the matrix chains *only* through the orientational coupling. Finally, in section V, we discuss an experimental condition with which we should be able to observe the orientational coupling effect most clearly. We also examine the effect on viscoelastic properties of the Rouse chains in section V.

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[*] To whom all correspondence should be addressed.
[†] Osaka University.
[‡] University of Minnesota.

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II. Model

Let us consider a Rouse chain (composed of $N + 1$ segments) in a *sheared* matrix. The equation of motion for this chain is

$$\zeta\, \partial \mathbf{r}(n,t)/\partial t = \kappa[\mathbf{r}(n+1,t) - 2\mathbf{r}(n,t) + \mathbf{r}(n-1,t)] + \mathbf{f}_{\mathrm{B}}(n,t) + \mathbf{f}_{\mathrm{or}}(n,t) \qquad n = 1, 2, ..., N-1 \quad (1)$$

Here $\mathbf{r}(n,t)$ is the location of the nth segment at time t, κ ($=3kT/b^2$, with b being the segment size) is the spring constant, and ζ is the segmental friction constant. The stochastic Brownian force, $\mathbf{f}_{\mathrm{B}}(n,t)$, acting on the nth segment is characterized by[2]

$$\langle \mathbf{f}_{\mathrm{B}}(n,t)\rangle = \mathbf{0}, \quad \langle \mathbf{f}_{\mathrm{B}}(n,t)\, \mathbf{f}_{\mathrm{B}}(m,t')\rangle = 2\zeta kT\delta_{nm}\delta(t-t')\,\mathbf{I} \quad (2)$$

where δ_{nm} and $\delta(t-t')$ are the Kronecker delta and Dirac delta function, respectively, $\mathbf{I}$ is a unit tensor, and $\langle ... \rangle$ indicates an ensemble average.

The second force in eq 1, $\mathbf{f}_{\mathrm{or}}(n,t)$, acting on the nth segment at time t is a force from the matrix that is interacting with that segment. The bond vectors, $\mathbf{u}(n,t) = \mathbf{r}(n,t) - \mathbf{r}(n-1,t)$ and $\mathbf{u}(n+1,t)$, tend to be oriented by this force toward the direction of matrix orientation. An interaction between the chain segment and matrix, which induces the above-mentioned orientational coupling, would be similar to that for rod polymers forming nematic phases.[2] That interaction is referred as a *nematic interaction* in this paper.

The functional form of $\mathbf{f}_{\mathrm{or}}$ for a Rouse chain can be reasonably chosen as follows. First, we need to describe the configuration of bond vectors $\mathbf{u}^*$ involved in the matrix, with which the orientation of the Rouse chain is coupled. (Hereafter, the superscript asterisk signifies quantities of the matrix.) The configuration of the *sheared* matrix considered here is characterized by an orientation tensor of the form[6a]

$$\Gamma(\gamma^*(t)) = \begin{bmatrix} 1+\gamma^*(t)^2 & \gamma^*(t) & 0 \\ \gamma^*(t) & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (3)$$

where $\gamma^*(t)$ is the average orientation (shear) in the matrix at time t. $\gamma^*(t)$ represents the anisotropy in the matrix configuration and is related to $\mathbf{u}^*$ in the sheared matrix by[2]

$$\gamma^*(t) = (3/b^2)\langle \mathbf{u}^*(t)\, \mathbf{u}^*(t)\rangle_{xy} \quad (4)$$

where $\langle \mathbf{u}^*\mathbf{u}^*\rangle_{xy}$ is the xy component of an ensemble average of the dyadic of $\mathbf{u}^*$.

Now we consider a force acting on the nth Rouse segment due to nematic interaction with the sheared matrix. The matrix is considered to be imposing an orientational (or shear) field Γ for a bond vector $\mathbf{u}(n,t)$ of the Rouse chain. $\mathbf{u}(n,t)$ tends to become $\Gamma\cdot\mathbf{u}(n,t)$ when subjected to Γ,[6b] and the resulting force $\mathbf{f}'_{\mathrm{or}}$ is proportional to a vector $\Gamma\cdot\mathbf{u}(n,t) - \mathbf{u}(n,t)$

$$\mathbf{f}'_{\mathrm{or}} \propto [\Gamma - \mathbf{I}]\cdot\mathbf{u}(n,t) \quad (5)$$

as schematically shown in Figure 1. We may consider that the effect of nematic interaction on the molecular motion of Rouse chains is equivalent to an application of the force $\mathbf{f}'_{\mathrm{or}}$ with the direction specified by eq 5 on the nth segment. Orientational coupling between the Rouse bond vector and matrix is induced by this force (as we see later in eq 18′, for example). A similar force, $\mathbf{f}''_{\mathrm{or}} \propto -[\Gamma - \mathbf{I}]\cdot\mathbf{u}(n+1,t)$, is also acting on the nth segment due to the interaction between the $(n + 1)$th bond and matrix.

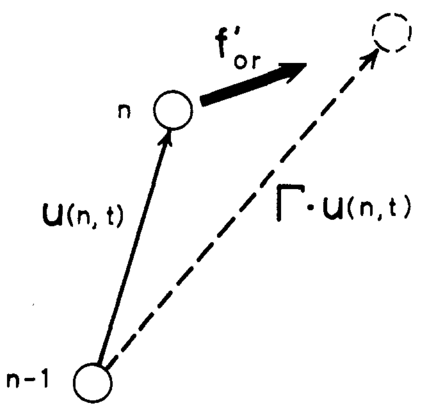

Figure 1. Schematic representation for a force $\mathbf{f}'_{\mathrm{or}}$ acting on the nth segment of the Rouse chain due to the nematic interaction with a matrix. Orientational coupling is induced by this force.

From the above argument, we may write[7a]

$$\mathbf{f}_{\mathrm{or}}(n,t) = \kappa\epsilon[\Gamma - \mathbf{I}]\cdot[\mathbf{u}(n,t) - \mathbf{u}(n+1,t)] \quad (6)$$

Here, we have introduced a parameter ϵ to represent the magnitude of the orientational force, i.e., to represent the intensity of the orientational coupling due to nematic interaction: ϵ has a value between 0 and 1, as we see later in eq 18′. It should be noted that eq 6 is based on a mean-field idea, because the average matrix orientation (shear) γ^*, not the local orientation at the location of the nth Rouse segment, is used for Γ (eq 3).

Using eq 6, we can rewrite eq 1 as

$$\zeta\, \partial \mathbf{r}(n,t)/\partial t = \kappa[\mathbf{I} - \epsilon\Gamma'(\gamma^*(t))]\cdot[\mathbf{r}(n+1,t) - 2\mathbf{r}(n,t) + \mathbf{r}(n-1,t)] + \mathbf{f}_{\mathrm{B}}(n,t) \quad (1')$$

with $\Gamma' = \Gamma - \mathbf{I}$ being given by

$$\Gamma'(\gamma^*(t)) = \begin{bmatrix} \gamma^*(t)^2 & \gamma^*(t) & 0 \\ \gamma^*(t) & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \text{ for the sheared matrix} \quad (3')$$

To obtain a boundary condition for eq 1′, we may attach two virtual segments ($n = -1, N + 1$; location $\mathbf{r}(-1,t)$ and $\mathbf{r}(N+1,t)$) to the chain ends ($n = 0$ and N). Considering those virtual segments to exert no force on the end segments, we have

$$\mathbf{r}(0,t) - \mathbf{r}(-1,t) = \mathbf{0}, \quad \mathbf{r}(N+1,t) - \mathbf{r}(N,t) = \mathbf{0} \quad (7)$$

With this condition, eq 1′ holds also for the end segment ($n = 0$ and N), as shown in the Appendix A.

In a continuous limit for N ($\cong N + 1$) $\gg 1$, eqs 1′ and 7 can be rewritten (for $\mathbf{u} = \partial\mathbf{r}/\partial n$) to give the dynamic equations for the Rouse chain with orientational coupling:[7b]

$$\zeta\, \partial \mathbf{u}(n,t)/\partial t = \kappa[\mathbf{I} - \epsilon\Gamma'(\gamma^*(t))]\cdot\partial^2\mathbf{u}(n,t)/\partial^2 n + \partial\mathbf{f}_{\mathrm{B}}(n,t)/\partial n \qquad 0 < n < N \quad (1'')$$

$$\mathbf{u}(n,t) = \mathbf{0} \qquad \text{for } n = 0 \text{ and } N \text{ (boundary condition)} \quad (7')$$

These equations are convenient to calculate the orientation relaxation function $\Phi(t)$ of a Rouse chain defined by

$$\Phi(t) = (1/N)\int_0^N (3/b^2)\langle u_x(n,t)\, u_y(n,t)\rangle\, \mathrm{d}n \quad (8)$$

with $u_\xi(n,t)$ ($\xi = x$ and y) being the ξ-component of $\mathbf{u}(n,t)$.

$\Phi(t)$ represents the average orientation (shear) of the Rouse segments at time t, and the mechanical stress is calculated from Φ (as discussed later). If the matrix orientation $\gamma^*(t)$ is known and/or if $\gamma^*(t)$ is calculated from the bond vector **u** of the Rouse chain (as in the case of monodisperse systems), we can solve eq 1″ to obtain **u** and calculate $\Phi(t)$ by eq 8.

III. Single-Step Orientation Relaxation

Here, we consider an orientation relaxation after a small-magnitude step *shear* strain γ at $t = 0$. Assuming an affine deformation at $t = 0$, we have[1,2]

$$\mathbf{u}(n,0) = \mathbf{D}(\gamma)\cdot\mathbf{u}^{\mathrm{eq}}(n,0), \qquad \mathbf{D}(\gamma) = \begin{bmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{9}$$

where $\mathbf{u}^{\mathrm{eq}}(n,0)$ is an isotropic bond vector at equilibrium just before an application of the external strain ($t = 0$). $\mathbf{u}^{\mathrm{eq}}(n,t)$ satisfies the equation of motion

$$\zeta\, \partial\mathbf{u}^{\mathrm{eq}}(n,t)/\partial t = \kappa\, \partial^2\mathbf{u}^{\mathrm{eq}}(n,t)/\partial n^2 + \partial\mathbf{f}_{\mathrm{B}}(n,t)/\partial n \tag{10}$$

and is characterized by[2]

$$\langle \mathbf{u}^{\mathrm{eq}}(n,t)\rangle = \mathbf{0} \qquad \text{for any } n \text{ and } t \tag{11a}$$

$$\langle \mathbf{u}^{\mathrm{eq}}(n,t)\, \mathbf{u}^{\mathrm{eq}}(m,t')\rangle = \mathbf{I}(2b^2/3N) \sum_{p=1}^{N} \sin\lambda_p n \sin\lambda_p m \times \exp[-D_{\mathrm{R}}\lambda_p^{\,2}(t-t')] \qquad t > t' \tag{11b}$$

$$D_{\mathrm{R}} = \kappa/\zeta, \qquad \lambda_p = p\pi/N \tag{11c}$$

where **I** represents the unit tensor. A Rouse chain composed of N beads has a large but finite number (N) of eigenmodes. To represent this fact in a continuous limit expression, we have introduced a cutoff for the mode number p (and hence for the relaxation time) in eq 11b. In fact, eq 9, with eq 11b, represents a uniform shear deformation for $\mathbf{u}(n,0)$:

$$(3/b^2)\langle u_x(n,0)\, u_y(m,0)\rangle = \gamma\delta_{nm} \qquad \text{for } n \text{ and } m = \text{nonzero integer} \tag{9'}$$

From eqs 1″, 7′, and 9, we find that the z component of $\mathbf{u}(n,t)$ is equal to that of $\mathbf{u}^{\mathrm{eq}}(n,t)$:

$$u_z(n,t) = u_z^{\,\mathrm{eq}}(n,t) \tag{12}$$

For the x and y components of $\mathbf{u}(n,t)$, we have (cf. eq 1″)

$$\zeta\frac{\partial}{\partial t}u_\xi(n,t) = \kappa\frac{\partial^2}{\partial n^2}[(1 - \epsilon\delta_{\xi x}\gamma^*(t)^2)\, u_\xi(n,t) - \epsilon\, \gamma^*(t) \times u_\eta(n,t)] + \frac{\partial}{\partial n}f_{\mathrm{B},\xi}(n,t), \quad (\xi,\eta) = (x,y) \text{ and/or } (y,x) \tag{13}$$

with the initial and boundary conditions

$$u_x(n,0) = u_x^{\,\mathrm{eq}}(n,0) + \gamma u_y^{\,\mathrm{eq}}(n,0), \quad u_y(n,0) = u_y^{\,\mathrm{eq}}(n,0), \quad \gamma^*(0) = \gamma \tag{14}$$

$$u_\xi(n,t) = 0 \qquad \text{for } n = 0 \text{ and } N, \quad \xi = x \text{ and } y \tag{15}$$

Retaining only the terms of order γ, we obtain, from eqs 11–15

$$u_\xi(n,t) = u_\xi^{\,\mathrm{eq}}(n,t) + \sum_{p=1}^{N}\upsilon_{\xi p}(t) \sin\lambda_p n, \quad \xi = x \text{ and } y \tag{16}$$

$$\upsilon_{xp}(t) = \gamma\left[(2/N)\int_0^N \mathrm{d}m \sin\lambda_p m\; u_y^{\,\mathrm{eq}}(m,0)\right] \times \exp[-D_{\mathrm{R}}\lambda_p^{\,2}t] - \epsilon D_{\mathrm{R}}\int_0^t \mathrm{d}t' \exp[-D_{\mathrm{R}}\lambda_p^{\,2}(t-t')]\, \gamma^*(t') \times \left[(2/N)\int_0^N \mathrm{d}m \sin\lambda_p m\, (\partial_m)^2 u_y^{\,\mathrm{eq}}(m,t')\right] \tag{17}$$

$$\upsilon_{yp}(t) = -\epsilon D_{\mathrm{R}}\int_0^t \mathrm{d}t' \exp[-D_{\mathrm{R}}\lambda_p^{\,2}(t-t')]\, \gamma^*(t') \times \left[(2/N)\int_0^N \mathrm{d}m \sin\lambda_p m\, (\partial_m)^2 u_x^{\,\mathrm{eq}}(m,t')\right] \tag{17'}$$

where

$$\partial_m = \partial/\partial m \tag{17''}$$

and

$$(3/b^2)\langle u_x(n,t)\, u_y(m,t)\rangle = (2/N)\sum_{p=1}^{N} w_p(t) \sin\lambda_p n \sin\lambda_p m \tag{18}$$

$$w_p(t) = \epsilon\gamma^*(t) + (1-\epsilon)\gamma \exp[-2D_{\mathrm{R}}\lambda_p^{\,2}t] - \epsilon\int_0^t \mathrm{d}t' \exp[-2D_{\mathrm{R}}\lambda_p^{\,2}(t-t')]\frac{\mathrm{d}\gamma^*(t')}{\mathrm{d}t'} \tag{19}$$

(We have introduced a cutoff for p in eqs 16 and 18, as we did in eq 11b.) Now, we calculate $\Phi(t)$ of a Rouse chain in blends and monodisperse systems.

Blends. We consider Rouse chains (composed of N segments) in a matrix of other chains. Those matrix chains can be either cross-linked, entangled, or nonentangled by themselves. In the following, for simplicity, we assume the Rouse chains to be a *dilute* component in the blend. The behavior of the matrix chains in such a *dilute* blend is identical with that at their monodisperse state.

Using a reduced orientation relaxation function, $\mu^*(t)$, of the matrix chains, we may write

$$\gamma^*(t) = \gamma\mu^*(t) \qquad \text{for } t > 0 \tag{20}$$

If μ^* is known, the orientation relaxation function of the Rouse chain in dilute blends is calculated from eqs 8 and 18–20 as

$$\Phi(t) = \gamma\mu_{\mathrm{B}}(t) \tag{21}$$

with

$$\mu_{\mathrm{B}}(t) = \epsilon\mu^*(t) + (1-\epsilon)\mu_0(t;N) - \epsilon\int_0^t \mathrm{d}t'\, \mu_0(t-t';N)\, \frac{\mathrm{d}\mu^*(t')}{\mathrm{d}t'} \tag{22}$$

and

$$\mu_0(t;N) = (1/N)\sum_{p=1}^{N} \exp[-t/\tau_p^{\,0}], \quad \tau_p^{\,0} = (N/p\pi)^2/2D_{\mathrm{R}} \tag{23}$$

Here, $\mu_0(t;N)$ is the reduced relaxation function of a Rouse chain composed of N segments obtained for $\epsilon = 0$; i.e., $\mu_0(t;N)$ is the conventional Rouse relaxation function for *no* orientational coupling. From eq 22, we see that the orientation relaxation of a Rouse chain (coupled with the matrix) is retarded by the longer matrix chains and partly accelerated by shorter ones.

The effect of the matrix on the orientation relaxation of the Rouse chain is most simply observed for a time-

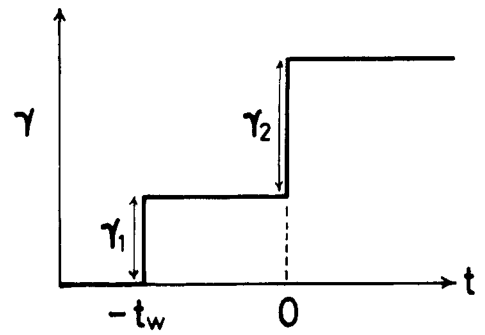

Figure 2. Schematic representation for a double-step shear strain.

independent matrix ($\mu^* = 1$). For this case, eqs 18 and 22 are simplified to

$$(3/b^2)\langle u_x(n,t)\, u_y(m,t)\rangle = \gamma\,(2/N)\sum_{p=1}^{N}\sin\lambda_p n\,\sin\lambda_p m\,\times \\ \{\epsilon + (1-\epsilon)\exp[-t/\tau_p{}^0]\}\rightarrow \epsilon\gamma\delta_{nm}\quad \text{as } t\rightarrow\infty \qquad (18')$$

$$\mu_{\mathrm{B}}(t) = \epsilon + (1-\epsilon)\mu_{\mathrm{o}}(t;N) \qquad (22')$$

From eq 18′, we see that the Rouse chain in a time-independent and oriented (sheared) matrix is uniformly sheared throughout the chain contour by a magnitude $\epsilon\gamma$ at long time. We note that ϵ should have a value between 0 and 1.

Monodisperse System. All chains are identical for monodisperse systems. Thus, the average $\langle \mathbf{u}^*\mathbf{u}^*\rangle$ in the matrix used in eq 4 is identical with an average along a chain contour, and $\gamma^*(t)$ is evaluated by[8]

$$\gamma^*(t) = (1/N)\int_0^N \mathrm{d}n\,(3/b^2)\langle u_x(n,t)\,u_y(n,t)\rangle \qquad (24)$$

The orientation function $\Phi(t)$ is identical with $\gamma^*(t)$ for this case (cf. eqs 8 and 24).

From eqs 18, 19, and 24, we find an equation for $\gamma^*(t)$:

$$\gamma^*(t) = \gamma\mu_0(t;N) - \frac{\epsilon}{1-\epsilon}\int_0^t \mathrm{d}t'\,\mu_0(t-t';N)\,\frac{\mathrm{d}\gamma^*(t')}{\mathrm{d}t'} \qquad (25)$$

Equation 25 can be solved for $N \gg 1$ (cf. Appendix B) to give

$$\Phi(t) = \gamma^*(t) = \gamma\mu_{\mathrm{m}}(t) \qquad (26)$$

$$\mu_{\mathrm{m}}(t) = (1/N)\sum_{p=1}^{N} g_p \exp[-t/\tau_p] \qquad (27)$$

$$\tau_p = (N/\theta_p)^2/2D_{\mathrm{R}} \qquad (28)$$

$$g_p = \frac{\theta_p\cos\theta_p - \sin\theta_p}{(1-\epsilon)\theta_p\cos\theta_p - (\epsilon/2N)\theta_p{}^2\sin\theta_p} \qquad (29)$$

with θ_p being the eigenvalue determined by

$$\tan\theta_p = -\frac{\epsilon\theta_p}{2N(1-\epsilon)-\epsilon} \qquad (30)$$

The reduced orientation relaxation function of the Rouse chains in a *monodisperse* system, $\mu_{\mathrm{m}}(t)$ given by eq 27, can be characterized by the moments $h_k = \int_0^\infty t^k\mu_{\mathrm{m}}(t)\,\mathrm{d}t$ (k = 0, 1, ...). As shown in Appendix B, we have, for example

$$h_0 = \frac{\pi^2\tau_1{}^0}{6N(1-\epsilon)},\quad h_1 = \frac{\{\pi^2\tau_1{}^0\}^2}{90N(1-\epsilon)}\quad \text{for } N \gg 1 \qquad (31)$$

Here, we should remember that eqs 27–31 have been obtained for $N \gg 1$. From eq 30, we note that the slower modes (smaller θ_p) are less affected by the nematic interaction and that θ_p and g_p for slow modes are very close to $p\pi$ and $1/(1-\epsilon)$ for large N even if ϵ is considerably close to unity. Correspondingly, the weight-average relaxation time, $h_1/h_0 = (\pi^2/15)\tau_1{}^0$, is independent of ϵ and identical with that obtained for no nematic interaction (ϵ = 0). Those results indicate no retardation to be expected for slow orientation relaxation. Namely, in our model, the nematic interaction changes the equation of motion (eq 1″), but the resulting μ_{m} function of the monodisperse Rouse chains is insensitive to that interaction, except for the constant multiplication factor, $1/1-\epsilon$, for g_p. Thus, we may write

$$\mu_{\mathrm{m}}(t) = [1/(1-\epsilon)]\mu_0(t;N) \quad \text{for long time} \qquad (27')$$

Here, we have to emphasize that the insensitivity of μ_{m} to the nematic interaction (cf. eq 27′) is due to the distribution of the relaxation intensity, as we can qualitatively explain. In the absence of the nematic interaction, the relaxation intensity of a Rouse chain is equally distributed to all modes, each having a contribution $1/N$ (see eq 23). Thus, the (matrix) orientation $\gamma^*(t)$ remaining at long time, by which the slow molecular motion is retarded, is of the order of γ/N for the monodisperse Rouse chains. Most of the initial orientation γ ($=\gamma^*(0)$) has been already relaxed at long time for those chains with $N \gg 1$, leading to a very small orientational coupling effect.

Now, we see a difference between the Rouse and reptation mechanisms. In contrast with the intensity distribution for the Rouse chain, the distribution for the reptating chain is highly nonuniform and concentrated in the slowest mode, indicating the initial orientation to be almost completely preserved at long time. This can lead to a strong retardation effect for the reptating chains even in a monodisperse system, as found by Merrill et al.[4]

IV. Double-Step Orientation Relaxation

In our model, the orientational force, $\mathbf{f}_{\mathrm{or}}$, involved in the equation of motion (cf. eq 1) changes according to the matrix orientation, i.e., according to the external strain history. Therefore, it is important to examine if linear superposability holds for the dynamic response of orientationally coupled Rouse chains to the external strain. To examine this point, we compare the relaxation functions after single- and double-step strains.

We consider a small-magnitude double-step shear strain, γ_1 at $t = -t_{\mathrm{w}}$ and γ_2 at $t = 0$ (see Figure 2) and calculate the orientation relaxation function for $t > 0$. For $-t_{\mathrm{w}} < t < 0$, u_x and u_y are given by eqs 16–17″ with γ and t being replaced by γ_1 and $t + t_{\mathrm{w}}$. Thus, just before the second strain γ_2, we have

$$u_\xi = u_\xi{}^0(n) = u_\xi{}^{\mathrm{eq}}(n,0) + \sum_{p=1}^{N} v_{\xi p}{}^0 \sin\lambda_p n,\quad \xi = x \text{ and } y \qquad (32)$$

$$v_{xp}{}^0 = \gamma_1\Big[(2/N)\int_0^N \mathrm{d}m\,\sin\lambda_p m\,u_y{}^{\mathrm{eq}}(m,-t_{\mathrm{w}})\Big]\times \\ \exp[-D_{\mathrm{R}}\lambda_p{}^2 t_{\mathrm{w}}] - \epsilon D_{\mathrm{R}}\int_{-t_{\mathrm{w}}}^0 \mathrm{d}t'\,\exp[+D_{\mathrm{R}}\lambda_p{}^2 t']\,\gamma_1{}^*(t')\,\times \\ \Big[(2/N)\int_0^N \mathrm{d}m\,\sin\lambda_p m\,(\partial_m)^2 u_y{}^{\mathrm{eq}}(m,t')\Big] \qquad (33)$$

$$v_{yp}{}^0 = -\epsilon D_{\mathrm{R}}\int_{-t_{\mathrm{w}}}^0 \mathrm{d}t'\,\exp[+D_{\mathrm{R}}\lambda_p{}^2 t']\,\gamma_1{}^*(t')\,\times \\ \Big[(2/N)\int_0^N \mathrm{d}m\,\sin\lambda_p m\,(\partial_m)^2 u_x{}^{\mathrm{eq}}(m,t')\Big] \qquad (34)$$

where $\gamma_1^*(t)$ is the matrix orientation (shear) for $-t_w < t < 0$ and $\mathbf{u}^{eq}(n,t)$ $(t > -t_w)$ is characterized by eq 11. Assuming an affine deformation for each of the bond vectors, we have, just after the second shear

$$u_x(n,0) = u_x^{\,0}(n) + \gamma_2 u_y^{\,0}(n), \quad u_y(n,0) = u_y^{\,0}(n) \tag{35}$$

Retaining only the terms of order γ_1 and γ_2 in eqs 1″, 7′, and 35, we obtain for $t > 0$

$$u_\xi(n,t) = u_\xi^{\,eq}(n,t) + \sum_{p=1}^{N} \upsilon'_{\xi p}(t) \sin \lambda_p n, \quad \xi = x \text{ and } y \tag{36}$$

$$\upsilon'_{xp}(t) = \upsilon'_{xp}(0) \exp[-D_R\lambda_p^{\,2}t] - \epsilon D_R \int_0^t \mathrm{d}t' \exp[-D_R\lambda_p^{\,2}(t-t')] \times \gamma_2^*(t') \left[(2/N)\int_0^N \mathrm{d}m \sin \lambda_p m \, (\partial_m)^2 u_y^{\,eq}(m,t')\right] \tag{37}$$

$$\upsilon'_{xp}(0) = \upsilon_{xp}^{\,0} + \gamma_2 \upsilon_{yp}^{\,0} + \gamma_2\left[(2/N)\int_0^N \mathrm{d}m \sin \lambda_p m \, u_y^{\,eq}(m,0)\right] \tag{38}$$

$$\upsilon'_{yp}(t) = \upsilon_{yp}^{\,0} \exp[-D_R\lambda_p^{\,2}t] - \epsilon D_R \int_0^t \mathrm{d}t' \exp[-D_R\lambda_p^{\,2}(t-t')] \times \gamma_2^*(t') \left[(2/N)\int_0^N \mathrm{d}m \sin \lambda_p m \, (\partial_m)^2 u_x^{\,eq}(m,t')\right] \tag{39}$$

From eqs 36–39, we finally obtain

$$(3/b^2)\langle u_x(n,t)\, u_y(m,t)\rangle = (2/N)\sum_{p=1}^{N} w'_p(t) \sin \lambda_p n \sin \lambda_p m \tag{40}$$

with

$$w'_p(t) = \epsilon\gamma_2^*(t) + [\gamma_2 - \epsilon\{\gamma_2^*(0) - \gamma_1^*(0)\}] \exp[-t/\tau_p^{\,0}] - \epsilon\int_0^t \mathrm{d}t' \exp[-(t-t')/\tau_p^{\,0}]\frac{\mathrm{d}\gamma_2^*(t')}{\mathrm{d}t'} + \gamma_1(1-\epsilon) \times \exp[-(t+t_w)/\tau_p^{\,0}] - \epsilon\int_{-t_w}^0 \mathrm{d}t' \exp[-(t-t')/\tau_p^{\,0}]\frac{\mathrm{d}\gamma_1^*(t')}{\mathrm{d}t'} \tag{41}$$

Here, $\gamma_2^*(t)$ is the matrix orientation (shear) for $t > 0$ and $\tau_p^{\,0}$ is given by eq 23. As in the previous section, we examine the time evolution of orientation function for the two cases.

Blends. For the double-step strain, we may in general write the matrix orientation as

$$\gamma_1^*(t) = \gamma_1\mu^*(t+t_w), \quad -t_w < t < 0 \tag{42}$$

$$\gamma_2^*(t) = \gamma_1\mu^*(t+t_w) + \gamma_2\mu^*(t), \quad 0 < t \tag{43}$$

Then, from eqs 8, 40, and 41, we have

$$\Phi(t) = \epsilon\gamma_2\mu^*(t) + (1-\epsilon)\gamma_2\mu_0(t;N) - \epsilon\gamma_2\int_0^t \mathrm{d}t' \, \mu_0(t-t';N) \frac{\mathrm{d}\mu^*(t')}{\mathrm{d}t'} + \epsilon\gamma_1\mu^*(t+t_w) + (1-\epsilon)\gamma_1\mu_0(t+t_w;N) - \epsilon\gamma_1\int_{-t_w}^t \mathrm{d}t' \, \mu_0(t-t';N) \frac{\mathrm{d}\mu^*(t'+t_w)}{\mathrm{d}t'} \tag{44}$$

Replacing the integral variable t' $(-t_w < t' < t)$ in the last term by $t'' = t' + t_w$ $(0 < t'' < t + t_w)$ and using eq 22, we see the linear superposition of the effects of the external strain:

$$\Phi(t) = \gamma_1\mu_B(t+t_w) + \gamma_2\mu_B(t) \tag{45}$$

Monodisperse System. For this case, the matrix orientation $\gamma_2^*(t)$ is identical with $\Phi(t)$ $(t > 0)$. From eqs 8, 40, and 41, $\gamma_2^*(t)$ is evaluated by

$$\gamma_2^*(t) = \gamma_1\mu_0(t+t_w;N) - \frac{\epsilon}{1-\epsilon}\int_{-t_w}^0 \mathrm{d}t' \, \mu_0(t-t';N) \frac{\mathrm{d}\gamma_1^*(t')}{\mathrm{d}t'} + \frac{1}{1-\epsilon}[\gamma_2 - \epsilon\{\gamma_2^*(0) - \gamma_1^*(0)\}] \, \mu_0(t;N) - \frac{\epsilon}{1-\epsilon}\int_0^t \mathrm{d}t' \, \mu_0(t-t';N) \frac{\mathrm{d}\gamma_2^*(t')}{\mathrm{d}t'} \tag{46}$$

Here, $\gamma_1^*(t)$ is given by $\gamma_1\mu_m(t+t_w)$ for $-t_w < t < 0$ and satisfies an equation (cf. eq 25):

$$\gamma_1^*(t) = \gamma_1\mu_0(t+t_w;N) - \frac{\epsilon}{1-\epsilon}\int_{-t_w}^t \mathrm{d}t' \, \mu_0(t-t';N) \frac{\mathrm{d}\gamma_1^*(t')}{\mathrm{d}t'} \tag{47}$$

$$\gamma_1^*(-t_w) = \gamma_1 \tag{48}$$

We define a function $\gamma_1^*(t)$ for $t > 0$ also by eq 47. Then, eq 46 becomes

$$\gamma_2^*(t) - \gamma_1^*(t) = \frac{1}{1-\epsilon}[\gamma_2 - \epsilon\{\gamma_2^*(0) - \gamma_1^*(0)\}] \, \mu_0(t;N) - \frac{\epsilon}{1-\epsilon}\int_0^t \mathrm{d}t' \, \mu_0(t-t';N) \frac{\mathrm{d}\{\gamma_2^*(t')-\gamma_1^*(t')\}}{\mathrm{d}t'} \quad (t > 0) \tag{49}$$

from which we note, for $t = 0$

$$\gamma_2^*(0) - \gamma_1^*(0) = \gamma_2 \tag{50}$$

From eqs 49 and 50, we finally reach

$$\{\gamma_2^*(t) - \gamma_1^*(t)\} = \gamma_2\mu_0(t;N) - \frac{\epsilon}{1-\epsilon}\int_0^t \mathrm{d}t' \, \mu_0(t-t';N) \frac{\mathrm{d}\{\gamma_2^*(t')-\gamma_1^*(t')\}}{\mathrm{d}t'} \tag{51}$$

This equation for $\gamma_2^*-\gamma_1^*$ is identical with that for γ^* after a single-step strain (eq 25), and the solution (for the initial condition eq 50) is $\gamma_2^*(t) - \gamma_1^*(t) = \gamma_2\mu_m(t)$. Thus, we have

$$\Phi(t) = \gamma_2^*(t) = \gamma_1\mu_m(t+t_w) + \gamma_2\mu_m(t) \quad (t > 0) \tag{52}$$

Again, we see the linear superposition of the effects of the external strain.

V. Discussion

Orientation Relaxation. We have seen in section IV that the effects of the small-magnitude external (macroscopic) strain γ on the orientation relaxation function $\Phi(t)$ of the Rouse chains are linearly superposed (eqs 45 and 52) even when orientational coupling takes place. This is not a trivial result, since the orientational force $\mathbf{f}_{or}$ (cf. eq 1) affecting the molecular motion of the Rouse chain changes according to the matrix orientation $\gamma^*(t)$, i.e., according to the external shear history. (In fact, nonlinearity prevails for a large external strain, as can be clearly seen from eq 1″.)

Because of the above-mentioned superposability, we can study the behavior of the Rouse chain by examining only the reduced orientation relaxation function, $\mu(t)$, after the single-step strain. First of all, we have found that the slow orientation relaxation of the Rouse chain in monodisperse systems is hardly affected by the nematic interaction (cf. eq 27′). Thus, those systems are not the appropriate media in which to observe the orientational coupling.

On the other hand, a significant effect of orientational coupling is expected for blends. As can be seen from eqs 22 and 22′, the orientation relaxation of the Rouse chains is strongly retarded in a matrix of much longer chains and accelerated partly in a short time region in a matrix of shorter chains. We may use chemically different (but compatible) chains as the matrix for the Rouse chain to observe this effect experimentally by optical techniques (such as birefringence, for example): The birefringence of the Rouse chain is proportional to $\Phi(t)$ after a single-step strain.

As the matrix for the dilute Rouse chains composed of N segments, we may choose cross-linked networks with cross-link spacing, N_c, extremely long and entangled chains with entanglement spacing, N_e, or short and nonentangled chains composed of N' segments.[9] For these three cases, we can write the reduced orientation function $\mu^*(t)$ of the matrix as

$$\begin{aligned}\mu^*(t) &= \phi\mu_m(t;N^*) + (1-\phi)\\ &\cong \frac{\phi}{1-\epsilon}\mu_0(t;N^*) + (1-\phi) \qquad \text{for long time}\end{aligned} \tag{53}$$

where ϕ is the fraction of the relaxable matrix orientation and $\mu_m(t;N^*)$ and $\mu_0(t;N^*)$ are given by eqs 27 and 23 with N being replaced by $N^* = N_c$, N_e, and N' for the above three cases. For the last case, $1-\phi = 0$. For the first two cases, we note $1-\phi \cong 1/N_c$ and $1/N_e$ from the comparison of the magnitudes of orientation in short-time transition zone and long-time plateau zone. Thus, ϕ is very close to 1 for these three cases.

For an orientation relaxation after a single-step strain γ at $t = 0$, eqs 22, 27′, and 53 lead to an experimentally testable relation for long time

$$\frac{\Delta n_B(t;N)}{c_B(N)} - \frac{\Delta n_B(\infty;N)}{c_B(N)} = \frac{(1-\epsilon)(1-\epsilon+\epsilon\phi)\Delta n_m(t;N)}{c_m(N)} - \frac{\phi\epsilon}{c_m(N^*)}\int_0^t \mathrm{d}t'\, \Delta n_m(t-t';N^*)\,\frac{\mathrm{d}\mu_0(t';N)}{\mathrm{d}t'} \tag{54}$$

where $c_\xi(M)$ and $\Delta n_\xi(t;M)$ are the concentration (in mass/volume) and birefringence at time t reduced to unit strain for the Rouse chain composed of M ($=N$ or N^*) segments and the subscript ξ indicates the quantities in the blend (ξ = B) and monodisperse systems (ξ = m). In particular, for the evaluation of the intensity ϵ of the orientational coupling, we have

$$\frac{\Delta n_B(\infty;N)}{c_B(N)} = \frac{6N\epsilon(1-\epsilon)(1-\phi)}{\pi^2\tau_1{}^0(N)}\int_0^\infty \frac{\Delta n_m(t;N)}{c_m(N)}\,\mathrm{d}t \tag{55}$$

$$\frac{\displaystyle\int_0^\infty\left[\frac{\Delta n_B(t;N)}{c_B(N)} - \frac{\Delta n_B(\infty;N)}{c_B(N)}\right]\mathrm{d}t - \int_0^\infty \frac{\Delta n_m(t;N)}{c_m(N)}\,\mathrm{d}t}{\displaystyle\int_0^\infty \frac{\Delta n_m(t;N)}{c_m(N)}\,\mathrm{d}t} = \frac{N^*-N}{N}\epsilon \tag{55′}$$

(The relation $\phi \cong 1$ has been used in eq 55′.) Thus, we may examine the prediction of our model (eqs 54–55′) by comparing the birefringence (or dichroism for which relations similar to eqs 54–55′ are derived) for Rouse chains in blends and in monodisperse systems.

Stress Relaxation. To calculate viscoelastic quantities predicted by our model, we need a (microscopic) expression for the stress. On the basis of the conventional theory of rubber elasticity considering *no* nematic interaction,[1,2] the shear stress, $\sigma(t)$, of polymer chains is related to the orientation function $\Phi(t)$ as

$$\sigma(t) = (cRT/m_0)\Phi(t) \tag{56}$$

where c is the concentration of those chains (in mass/volume), m_0 is the molecular weight of the segment, and R is the gas constant.

The stress expression would be changed if the nematic interaction exists to induce orientational coupling, as discussed by Merrill et al.[4] The expression they suggested can be written as

$$\sigma(t) = (cRT/m_0)[\Phi(t) - \epsilon\Phi^*(t)] \tag{57}$$

where Φ^* is the orientation of the matrix and ϵ is the intensity of orientational coupling. This expression differs from that given by eq 56 by a factor $\epsilon\Phi^*$. This extra factor represents the fact that the most stable configuration of a chain is not random and isotropic when the orientational coupling takes place. Assuming that the equilibrium is achieved instantaneously at any moment, one may consider that a chain in the matrix is most stable when the magnitude of orientation of that chain is given by $\epsilon\Phi^*(t)$ (cf. eq 18′). Then, the stress of a chain having an orientation $\Phi(t)$ is proportional to the difference of the orientation from that at the most stable state, i.e., to $\Phi(t) - \epsilon\Phi^*(t)$. On the basis of this argument, one reaches eq 57.[4]

As we have seen in section II, the equation of motion for the Rouse chain is modified by the nematic interaction. This means that the free energy expression and hence the stress expression, too, should be modified due to that interaction. Considering this point, we use eq 57 in this paper for Rouse chains to calculate viscoelastic quantities for small strain.[10]

First of all, the effects of the external strain, γ, on the stress, $\sigma(t)$, are linearly superposed (in a small γ region), as we have already seen for $\Phi(t)$. This again enables us to examine only the relaxation modulus $G(t) = \sigma(t)/\gamma$ after the single-step strain to study the orientational coupling effect.

For the monodisperse system of the Rouse chains, we find, from eqs 27′ and 57 (with $\Phi^* = \Phi$)

$$G_m(t;N) = [c_mRT/m_0]\mu_0(t;N) \qquad \text{for long time} \tag{58}$$

This $G(t)$ is identical with the Rouse relaxation modulus for *no* orientational coupling. Namely, the slow viscoelastic relaxation of monodisperse Rouse chains *does not* change even when the nematic interaction induces orientational coupling. We also note that the stress-optical law ($\sigma \propto \Delta n$) holds for this case.

For the slow viscoelastic relaxation of Rouse chains in blends, we have, from eqs 22, 53, 57, and 58

$$\frac{G_B(t;N)}{c_B(N)} = (1-\epsilon)\frac{G_m(t;N)}{c_m(N)} - \frac{\phi\epsilon}{c_m(N)}\int_0^t \mathrm{d}t'\, G_m(t-t';N)\,\frac{\mathrm{d}\mu_m(t';N^*)}{\mathrm{d}t'} \tag{59}$$

where the subscripts B and m represent the quantities for the Rouse chains composed of M ($=N$ and N^*) segments in blend and monodisperse systems. Comparing eqs 54 and 59, we note that the stress-optical law does not hold for the Rouse chain in blends. However, this law still holds for the blend as a whole, as shown in Appendix C.

From eq 59, we can see that the effect of orientational coupling on $G(t)$ is of the order of $\epsilon(1-\phi)$. For example, eq 59 gives

$$\int_0^\infty \frac{G_{\mathrm{B}}(t;N)}{c_{\mathrm{B}}(N)}\,\mathrm{d}t = [1-\epsilon(1-\phi)]\int_0^\infty \frac{G_{\mathrm{m}}(t;N)}{c_{\mathrm{m}}(N)}\,\mathrm{d}t \tag{60}$$

$$\int_0^\infty \frac{G_{\mathrm{B}}(t;N)}{c_{\mathrm{B}}(N)}t\,\mathrm{d}t = [1-\epsilon(1-\phi)]\int_0^\infty \frac{G_{\mathrm{m}}(t;N)}{c_{\mathrm{m}}(N)}t\,\mathrm{d}t \tag{61}$$

for N and $N^* \gg 1$. We remember that $1-\phi = 1/N_{\mathrm{c}}, 1/N_{\mathrm{e}}$, and 0 for the cross-linked network, highly entangled polymers, and nonentangled chains used as the matrix; i.e., $1-\phi$ is very small for all cases. Thus, the effect of orientational coupling on the mechanical relaxation is very small also for the Rouse chains in blends.

As demonstrated in eqs 58–61, our model suggests no effect of orientational coupling to be expected for the linear viscoelastic properties of the Rouse chains. This is consistent with the experimental fact[11] that the viscoelastic behavior of short and nonentangled chains is well described by the Rouse model considering no nematic interaction.

VI. Conclusion

We have examined the effect of orientational coupling due to nematic interaction on the slow dynamic behavior of the Rouse chains. For linear viscoelastic relaxation of those chains in both monodisperse and blend systems, our model indicates *no* effect to be expected. In other words, our model suggests that the Rouse model considering no nematic interaction (eq 1″ with $\epsilon = 0$), together with the stress expression usually adopted (eq 56), is valid for calculation of linear viscoelastic quantities of short and nonentangled chains. This seems to be consistent with the model for entangled chains used by Doi et al.[5]

For the orientation relaxation, we still see no significant effect in the monodisperse system of Rouse chains. On the other hand, in blends, we may observe a significant effect by using optical techniques (such as birefrigence, for example). Rouse dynamics is a very fundamental system of dynamics describing the behavior of polymer chains in condensed systems (including entangled systems). From this point, it is desired to test the prediction of our model (eqs 54–55′). This should be considered in future work.

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Appendix A

Considering the fact that the end segment ($n = N$) has only one neighbor ($n = N-1$), we obtain the equation of motion for the end segment (cf. eq 5 for $\mathbf{f}'_{\mathrm{or}}$)

$$\zeta\,\partial\mathbf{r}(N,t)/\partial t = \kappa[\mathbf{I}-\epsilon\boldsymbol{\Gamma}']\cdot[\mathbf{r}(N-1,t)-\mathbf{r}(N,t)] + \mathbf{f}_{\mathrm{B}}(N,t) \tag{A1}$$

Here, we attach a virtual segment ($n = N+1$; location $\mathbf{r}(N+1,t)$) to the Nth segment. Considering this virtual segment to exert no force on the Nth segment, we have

$$\mathbf{u}(N+1,t) = \mathbf{r}(N+1,t) - \mathbf{r}(N,t) = \mathbf{0} \tag{A2}$$

which allows us to rewrite eq A1 as

$$\zeta\,\partial\mathbf{r}(N,t)/\partial t = \kappa[\mathbf{I}-\epsilon\boldsymbol{\Gamma}']\cdot[\mathbf{r}(N+1,t) - 2\mathbf{r}(N,t) + \mathbf{r}(N-1,t)] + \mathbf{f}_{\mathrm{B}}(N,t) \tag{A1′}$$

Namely, with the boundary condition eq A2, the equation of motion eq 1′ is satisfied also for the end segment ($n = N$). Similarly, with the boundary condition $\mathbf{u}(0,t) = \mathbf{0}$, eq 1′ holds also for the other end segment ($n = 0$).

Appendix B

The time evolution equation for $\gamma^*(t)$ of monodisperse Rouse chains after a single-step shear strain is

$$\gamma^*(t) = \gamma\mu_0(t;N) - \frac{\epsilon}{1-\epsilon}\int_0^t \mathrm{d}t'\,\mu_{\mathrm{o}}(t-t';N)\,\frac{\mathrm{d}\gamma^*(t')}{\mathrm{d}t'} \tag{B1}$$

with

$$\mu_0(t;N) = (1/N)\sum_{p=1}^{N}\exp[-t/\tau_p{}^0],\quad \tau_p{}^0 = (N/p\pi)^2/2D_{\mathrm{R}} \tag{B2}$$

Equation B1 is solved by a Laplace transform method. We find

$$L(s;\gamma^*) = \int_0^\infty \gamma^*(t)\exp[-st]\,\mathrm{d}t = \frac{\gamma M_0(s)}{1-\epsilon+\epsilon s M_0(s)} \tag{B3}$$

where $M_0(s)$ is the Laplace transform of $\mu_0(t;N)$. Using a relation $\lim_{N\to\infty}\sum_{p=1}^{N} 1/[p^2+x^2] = (\pi/2x)\coth \pi x - (1/2x^2)$, we may approximate $M_0(s)$ as

$$\begin{aligned} M_{\mathrm{o}}(s) &= (1/N)\sum_{p=1}^{N}\tau_p{}^0/(1+s\tau_p{}^0) \\ &\cong (N/4D_{\mathrm{R}})m(s)^{-2}[m(s)\coth m(s) - 1] \qquad \text{for } N \gg 1 \end{aligned} \tag{B4}$$

with $m(s) = N(s/2D_{\mathrm{R}})^{1/2}$.

We note that $L(s;\gamma^*)$ has first-order poles at

$$s_p = -2D_{\mathrm{R}}(\theta_p/N)^2 \tag{B5}$$

with the eigenvalues θ_p being determined by

$$\tan\theta_p = -\frac{\epsilon\theta_p}{2N(1-\epsilon)-\epsilon} \tag{B6}$$

Thus, inversion of $L(s;\gamma^*)$ gives

$$\gamma^*(t) = \gamma\mu_{\mathrm{m}}(t) \tag{B7}$$

$$\mu_{\mathrm{m}}(t) = (1/N)\sum_{p=1}^{N} g_p\exp[-t/\tau_p],\quad \tau_p = (N/\theta_p)^2/2D_{\mathrm{R}} \tag{B8}$$

$$g_p = \frac{\theta_p\cos\theta_p - \sin\theta_p}{(1-\epsilon)\theta_p\cos\theta_p - (\epsilon/2N)\theta_p{}^2\sin\theta_p} \tag{B9}$$

In eq B8, we have introduced a cutoff for the mode number p, as we did in eqs 11b, 16, and 18.

$\mu_{\mathrm{m}}(t)$ can be characterized by the moments $h_k = \int_0^\infty t^k\mu_{\mathrm{m}}(t)\,\mathrm{d}t = (1/\gamma)(-1)^k[d^kL(s;\gamma^*)/\mathrm{d}s^k]_{s=0}$ ($k = 0, 1, ...$), which are obtained from eqs B1 and B3 as

$$h_k(t) = \frac{1}{1-\epsilon}\int_0^\infty t^k \mu_0(t;N)\,\mathrm{d}t + \frac{\epsilon}{1-\epsilon}\sum_{j=0}^{k-1} \frac{k!}{j!(k-j-1)!} \times \int_0^\infty t^j \mu_0(t;N)\,\mathrm{d}t \int_0^\infty t^{k-j-1}\mu_\mathrm{m}(t)\,\mathrm{d}t \quad \text{(B10)}$$

$$= \begin{cases} \dfrac{\pi^2 {\tau_1}^0}{6N(1-\epsilon)} & \text{for } k = 0 \\ \dfrac{\{\pi^2 {\tau_1}^0\}^2}{90N(1-\epsilon)} \dfrac{2N(1-\epsilon)+5\epsilon}{2N(1-\epsilon)} \cong \dfrac{\{\pi^2 {\tau_1}^0\}^2}{90N(1-\epsilon)} & \text{for } k = 1 \end{cases} \quad \text{(B11)}$$

for $N \gg 1$.

Appendix C

Here, we consider an expression for the stress in a linear viscoelastic regime for blends composed of long and short chains with concentrations c_L and c_S. The dilute blends for the Rouse chains examined in this paper are the extreme cases for $c_\mathrm{S} \to 0$.

From eq 57, the stress σ_L of the long chains is given by

$$\sigma_\mathrm{L} = [c_\mathrm{L}RT/m_0][\Phi_\mathrm{L} - \epsilon\Phi^*] \quad \text{(C1)}$$

and that for the short chains by

$$\sigma_\mathrm{S} = [c_\mathrm{S}RT/m_0][\Phi_\mathrm{S} - \epsilon\Phi^*] \quad \text{(C2)}$$

where Φ_L and Φ_S are the orientation relaxation functions of the long and short chains, respectively. The matrix orientation function, Φ^*, is an *average* of Φ_L and Φ_S and is given by

$$\Phi^* = \frac{c_\mathrm{L}\Phi_\mathrm{L} + c_\mathrm{S}\Phi_\mathrm{S}}{c_\mathrm{L} + c_\mathrm{S}} \quad \text{(C3)}$$

(For the dilute blends examined in this paper, we have $c_\mathrm{L} \gg c_\mathrm{S}$ so that $\Phi^* = \Phi_\mathrm{L}$.)

From eqs C1–C3, the stress of the blend as a whole is obtained as

$$\sigma^\mathrm{B} = \sigma_\mathrm{L} + \sigma_\mathrm{S} = [RT/m_0][1-\epsilon][c_\mathrm{L}\Phi_\mathrm{L} + c_\mathrm{S}\Phi_\mathrm{S}] \quad \text{(C4)}$$

The last term, $c_\mathrm{L}\Phi_\mathrm{L} + c_\mathrm{S}\Phi_\mathrm{S}$, is proportional to the orientation relaxation function of the blend, Φ^*. Thus, we see that the stress-optical law holds for the blend as a whole, irrespective of the details for Φ_L and Φ_S.

References and Notes

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(6) (a) The orientational tensor for a uniformly sheared matrix has a form identical with that of a *shear strain tensor*[6b] generally used in continuum mechanics. (b) See, for example: Lodge, A. S. *Elastic Liquids*; Academic Press: New York, 1964.
(7) (a) Equation 6 specifies the feature of the interaction being called the nematic interaction in this paper: In eq 6, we consider that both direction and length of a bond vector **u** are coupled with the matrix configuration. However, for a small strain discussed in this paper, the effect of coupling on the length of **u** is very small and neglected. (b) Because of the negligibly small coupling effect for the length of **u**,[7a] all results for a small strain deduced in this paper remain the same even if we use, instead of Γ', some other expression for matrix configuration (such as a traceless part of Γ') in eq 1″.
(8) Equation 24 holds because we have introduced the cutoff for the eigenmode number p in eqs 16 and 18.
(9) We implicitly assume N to be smaller than N_c and N_e, so that a chain composed of N segments behaves as a Rouse chain.
(10) This stress expression for a small strain can be deduced from a free energy expression: Doi, M. Private communication.
(11) See, for example: Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.