A calculation of the diffusion coefficient based on (33) including the correlations of inter- and intramolecular distributions will be presented in a subsequent paper together with the recent data on the concentration dependence of $D(c)$ obtained by light-scattering experiments.[19]

V. Discussions

In this paper we investigated the concentration dependence of the characteristic frequency in all regions of the momentum transfer in the case of coherent scattering from a single labeled chain among other chains in a good solvent. We have demonstrated the existence of a crossover momentum transfer q^* in the q dependence of the characteristic frequency Ω in the semidilute regime and examined its asymptotic behavior above and below q^*. These results are relevant, in particular, to the interpretation of neutron scattering experiments.

We have investigated the concentration dependence of Ω in the case of scattering from identical chains only for small momentum transfers and in the dilute regime. We have shown that the diffusion coefficient increases with concentration in a good solvent whereas it decreases in a poor solvent. We have determined the slope of $D(c)$ as a function of the second virial coefficient. These results are directly applicable to the interpretation of light-scattering experiments.

Since entanglement is not included in the dynamical model, the results of this paper are expected to be valid for all q values in dilute solutions, and for $q\xi \geq 1$, and in the vicinity of the crossover line $q\xi \approx 1$ in semidilute solutions. In these regions the results are in agreement with the predictions of the dynamical scaling approach.

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(20) Adelman recently showed[10] that the screened Oseen tensor has an R^{-2} decay. It is quite long ranged, and the simple cutoff model we use here is probably cruder than it would be in the case of an exponentially decaying Oseen tensor.[9] However, our purpose here is to investigate the effect of hydrodynamic screening on the dynamic structure factor only qualitatively, and to demonstrate how the hydrodynamic screening can be included in the present calculation of the characteristic frequency.
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Dynamic Flow Birefringence and Flow Dichroism of Block-Copolymer Molecules in Solution with Application to the Free-Draining Limit

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ABSTRACT: The dynamic flow birefringence and the flow dichroism of block-copolymer molecules in solution have been calculated by modifying the bead-spring model theory of Zimm to take into account the existence of dissimilar segments in block copolymers. The expressions for the birefringence and the dichroism properties have been found to be the same as those for homopolymers except that the contributions of normal modes are weighted by generally different factors. Some calculated results in the free-draining limit are given to illustrate how the inhomogeneity in segmental optical properties is expected to affect the flow birefringence and the flow dichroism.

Recently, there has been much interest in the theoretical investigation of the dynamics of block copolymers. For example, Hall and DeWames,[1] Shen and Hansen,[2] Stockmayer and Kennedy,[3] and Wang and DiMarzio[4] have all discussed the dynamics of free-draining block copolymers. In our previous papers,[5,6] we have extended the bead-spring model theory of Zimm[7] to treat the viscoelasticity and the translational diffusion of non-free-draining block copolymers in dilute solutions. In this paper the bead-spring model is again used to discuss the flow birefringence and the flow dichroism of block copolymers in solution. In treating the viscoelasticity and the translational diffusion of block copolymers,[4-6] we have taken into account the differences in flexibility and cross-sectional size of the dissimilar blocks. In discussing the flow birefringence and the flow dichroism of block copolymers, we must consider not only these differences, but also differences in optical properties. We shall show here that these additional differences may in some instances make the flow birefringence and the flow dichroism of block copolymers markedly different from those of homopolymers.

The Model and the Diffusion Equation

The representation of the A-B-C type linear block-copolymer molecule by a bead-spring model has been discussed in detail in a previous paper,[5] hereafter referred to as paper 1. Here, we describe briefly the bead-spring model in order to introduce the notations. The block-copolymer molecule is represented as a chain of N Hookean springs joining $(N + 1)$ beads with complete flexibility at each bead. The solvent is treated as a hydrodynamic continuum with a viscosity η. The A block is represented by a chain of $(N_a - 1)$ springs joining N_a beads, each of which is characterized by the translational friction constant ρ_a. The force constant of each of the springs is $3kT/b_a^2$, where b_a^2 is its mean-square length, and k and T are the Boltzman constant and the absolute temperature. The symbols N_b, N_c, ρ_b, ρ_c, b_b, and b_c are similarly defined for the B and C blocks. The beads of the model for the A block are numbered serially from 0 to $(N_a - 1)$, correspondingly from N_a to $(N_a + N_b - 1)$ for the B block and from $(N_a + N_b)$ to N for the C block. The last bead of the A block $(j = N_a - 1)$ and the first bead of the B block $(j = N_a)$ are connected by free joints to the ends of a spring whose root-mean-square length b_{ab} is given by $b_{ab}^2 = (b_a^2 + b_b^2)/2$. Finally, the bead-spring model for the block-copolymer molecule as a whole is formed by connecting with free joints the last bead of the B block $(j = N_a + N_b - 1)$ and the first bead of the C block $(j = N_a + N_b)$ to the ends of a spring of root-mean-square length b_{bc} which is defined in the same manner as b_{ab}.

In paper 1, the equations of motion of a block-copolymer molecule have been written in matrix form by introducing the matrices **A** and **H** of order $(N + 1)$. The elements of **H** are given by

$$H_{jj} = \rho/\rho_j \tag{1a}$$

$$H_{jk} = \rho T_{jk} \qquad j \neq k \tag{1b}$$

where ρ is an arbitrary friction constant, ρ_j is the translational friction constant of the jth bead, and the interaction coefficients T_{jk} are given by

$$T_{jk} = [(6\pi^3)^{1/2}\eta\langle R_{jk}^2\rangle^{1/2}]^{-1} \tag{2}$$

with $\langle R_{jk}^2\rangle$ the mean-square distance between the jth and the kth beads. The nonzero elements of the tridiagonal matrix **A** are defined for $j = 0, 1, 2, \ldots, N$ as follows:

$$A_{0k} = k_1\delta_{0k} - k_1\delta_{1k} \tag{3a}$$

$$A_{jk} = -k_j\delta_{j-1,k} + (k_j + k_{j+1})\delta_{jk} - k_{j+1}\delta_{j+1,k} \tag{3b}$$

for $1 \leq j \leq (N - 1)$

$$A_{Nk} = -k_N\delta_{N-1,k} + k_N\delta_{N,k} \tag{3c}$$

where k_j is given by

$$k_j = b^2/b_j^2 \tag{3d}$$

Here, b_j^2 is the mean-square length of the spring between the $(j - 1)$th and the jth beads, and b^2 is the mean-square length of an arbitrary spring. For the case of a homopolymer with $\rho_a = \rho_b = \rho_c = \rho$ and $b_a = b_b = b_c = b$, the matrices **A** and **H** reintroduced here become identical to **A** and **H** given by Zimm.[7] It has been shown in paper 1 that the equations of motion of a block-copolymer molecule are identical in form with the equations of motion obtained by Zimm[7] for a homopolymer, with **H**, **A**, b, and ρ defined here replacing the very same symbols (**H**, **A**, b, and ρ) defined differently by Zimm. In a later work,[6] we have pointed out that, for a block copolymer, the diffusion equation for the distribution function of the coordinates of the beads is again identical in form with the diffusion equation for a homopolymer.[7] Thus, if we use t to denote time and let $\sigma = 3kT/b^2\rho$ and $D = kT/\rho$, the distribution function $\psi(x_0,y_0,\ldots,z_N)$, which gives the probability of finding the jth bead with coordinates between x_j and $x_j + dx_j$, y_j and $y_j + dy_j$, and z_j and $z_j + dz_j$ may be written as follows:

$$\partial\psi/\partial t = \sum_{u=x,y,z} \{-(\partial\psi/\partial\mathbf{u})^{\mathrm{T}}\cdot\mathbf{v}_u - \psi(\partial/\partial\mathbf{u})^{\mathrm{T}}\cdot\mathbf{v}_u + D(\partial/\partial\mathbf{u})^{\mathrm{T}}\cdot\mathbf{H}\cdot(\partial\psi/\partial\mathbf{u}) + \sigma(\partial\psi/\partial\mathbf{u})^{\mathrm{T}}\cdot\mathbf{H}\cdot\mathbf{A}\cdot\mathbf{u} + \sigma\psi(\partial/\partial\mathbf{u})^{\mathrm{T}}\cdot\mathbf{H}\cdot\mathbf{A}\cdot\mathbf{u}\} \tag{4}$$

Here, the $(N + 1)$-dimensional column vectors $\mathbf{x}$, $\partial/\partial\mathbf{x}$, and $\mathbf{v}_x$ are defined as

$$\mathbf{x} = (x_0,x_1,\ldots,x_N)^{\mathrm{T}} \tag{5}$$

$$\partial/\partial\mathbf{x} = (\partial/\partial x_0,\partial/\partial x_1,\ldots,\partial/\partial x_N)^{\mathrm{T}} \tag{6}$$

$$\mathbf{v}_x = (v_{x1},v_{x2},\ldots,v_{xN})^{\mathrm{T}} \tag{7}$$

where v_{xj} is the x component of the velocity that the fluid would have at the position of the jth bead in the absence of the chain and the superscript T is used to denote the transpose of a matrix or a vector. Corresponding column vectors are defined in the same form for the y and z components.

Since the matrices **H** and **A** are symmetric and the eigenvalues of **H·A** turn out to be distinct, we can facilitate the solution of eq 4 by choosing a set of normal coordinates in the manner described by Zimm.[7] Let the $(N + 1)$ eigenvectors and eigenvalues of **H·A** be α_k and λ_k, respectively,

$$\mathbf{H}\cdot\mathbf{A}\cdot\alpha_k = \lambda_k\alpha_k \qquad 0 \leq k \leq N \tag{8}$$

We also introduce a square matrix **Q** whose $(N + 1)$ columns are the eigenvectors α_k and whose inverse is denoted by $\mathbf{Q}^{-1}$. Then it follows that

$$\mathbf{Q}^{-1}\cdot\mathbf{H}\cdot\mathbf{A}\cdot\mathbf{Q} = \Lambda \tag{9}$$

where Λ is the diagonal matrix with the elements λ_k. The matrix **Q** is used to transform coordinates from **x**, **y**, **z** to ξ, η, ζ, according to the relations:

$$\mathbf{x} = \mathbf{Q}\cdot\xi \tag{10a}$$

$$\mathbf{y} = \mathbf{Q}\cdot\eta \tag{10b}$$

$$\mathbf{z} = \mathbf{Q}\cdot\zeta \tag{10c}$$

The following properties of this transformation are obtained by analogy from the properties of the coordinate transformation for the case of a homopolymer,[7]

$$\mathbf{Q}^{\mathrm{T}}\cdot\mathbf{A}\cdot\mathbf{Q} = \mathbf{M} \tag{11}$$

$$\mathbf{Q}^{-1}\cdot\mathbf{H}\cdot(\mathbf{Q}^{-1})^{\mathrm{T}} = \mathbf{N} \tag{12}$$

$$\nu_k = \lambda_k/\mu_k \tag{13}$$

where **M** and **N** are the diagonal matrices with the elements μ_k and ν_k, respectively.

We assume that the following unperturbed flow field exists in the fluid in the absence of the chain:

$$v_{xj} = \kappa z_j \tag{14a}$$

$$v_{yj} = 0 = v_{zj} \tag{14b}$$

with the shear rate κ a harmonic function of time t:

$$\kappa = \kappa_0 \cos \omega t \tag{15}$$

where ω is the angular frequency and κ_0 is assumed to be small. Substituting these expressions for the components of the unperturbed fluid velocity into eq 4 yields the following special case of the diffusion equation in the normal coordinates:

$$\frac{\partial\psi}{\partial t} = \sum_{k=1}^{N} \left\{ -\kappa\zeta_k \frac{\partial\psi}{\partial\xi_k} + D\nu_{\rm k} \left[\frac{\partial^2\psi}{\partial{\xi_k}^2} + \frac{\partial^2\psi}{\partial{\eta_k}^2} + \frac{\partial^2\psi}{\partial{\zeta_k}^2} \right] + \sigma\lambda_k \left[\xi_k \frac{\partial\psi}{\partial\xi_k} + \eta_k \frac{\partial\psi}{\partial\eta_k} + \zeta_k \frac{\partial\psi}{\partial\zeta_k} \right] + 3\sigma\lambda_k\psi \right\} \tag{16}$$

Oscillatory Flow Birefringence and Flow Dichroism

We now derive the theoretical expressions for the magnitude of birefringence Δn and the extinction angle χ of the block-copolymer solution. As in Zimm's treatment[7] of the homopolymer solution, we shall apply the formula of Kuhn and Grün[8] to each segment which connects two consecutive beads and is represented by a spring. Let $\gamma_{1\rm a}$ be the polarizability component along the vector between the ends of a segment of the A block and $\gamma_{2\rm a}$ be the value of the two equal components normal to this vector, then the Kuhn and Grün formula gives

$$\gamma_{1\rm a} = p_{\rm a} + 2q_{\rm a}{l_{\rm a}}^2 \tag{17a}$$

$$\gamma_{2\rm a} = p_{\rm a} - q_{\rm a}{l_{\rm a}}^2 \tag{17b}$$

where $l_{\rm a}$ is the length of the segment and the optical constants $p_{\rm a}$ and $q_{\rm a}$ are given by

$$p_{\rm a} = (n_{\rm a}/3)(\alpha_{1\rm a} + 2\alpha_{2\rm a}) \tag{18a}$$

$$q_{\rm a} = (\alpha_{1\alpha} - \alpha_{2\rm a})/(5{b_{\rm a}}^2) \tag{18b}$$

Here, $\alpha_{1\rm a}$ is the polarizability component along the vector between the ends of a Kuhn statistical chain element of the A block, $\alpha_{2\rm a}$ is the value of the two equal components normal to this vector, and $n_{\rm a}$ is the number of Kuhn statistical chain elements in the segment. The lengths, the polarizability components, and the optical constants, distinguished by the subscripts b, c, ab, and bc, are similarly defined for the B and C blocks, for the segment joining the A and B blocks, and for the segment joining the B and C blocks. Thus, the optical constants of the jth spring, which joins the $(j-1)$th and the jth beads, are given by

$$p_j = p_{\rm a}, \quad q_j = q_{\rm a} \quad \text{for } 1 \le j \le (N_{\rm a} - 1) \tag{19a}$$

$$p_j = p_{\rm ab}, \quad q_j = q_{\rm ab} \quad \text{for } j = N_{\rm a} \tag{19b}$$

$$p_j = p_{\rm b}, \quad q_j = q_{\rm b} \quad \text{for } (N_{\rm a} + 1) \le j \le (N_{\rm a} + N_{\rm b} - 1) \tag{19c}$$

$$p_j = p_{\rm bc}, \quad q_j = q_{\rm bc} \quad \text{for } j = (N_{\rm a} + N_{\rm b}) \tag{19d}$$

$$p_j = p_{\rm c}, \quad q_j = q_{\rm c} \quad \text{for } (N_{\rm a} + N_{\rm b} + 1) \le j \le N \tag{19e}$$

We also introduce a matrix $\mathbf{P}$ of order $(N + 1)$ with elements P_{jk} given by

$$P_{0k} = q_1\delta_{0k} - q_1\delta_{1k} \tag{20a}$$

$$P_{jk} = -q_j\delta_{j-1,k} + (q_j + q_{j+1})\delta_{jk} - q_{j+1}\delta_{j+1,k} \tag{20b}$$

for $1 \le j \le (N - 1)$

$$P_{Nk} = -q_N\delta_{N-1,k} + q_N\delta_{N,k} \tag{20c}$$

The polarizability of the whole molecule is the sum of the polarizabilities of the separate segments, and the average of this is designated by $\boldsymbol{\Gamma}$. When all the individual polarizability tensors are referred to the x, y, z coordinate system and added, we find that the elements of $\boldsymbol{\Gamma}$ are given by

$$\Gamma_{11} = \sum_{j=1}^{N} p_j + 2\langle \mathbf{x}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{x} \rangle - \langle \mathbf{y}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{y} \rangle - \langle \mathbf{z}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{z} \rangle \tag{21a}$$

$$\Gamma_{22} = \sum_{j=1}^{N} p_j + 2\langle \mathbf{y}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{y} \rangle - \langle \mathbf{z}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{z} \rangle - \langle \mathbf{x}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{x} \rangle \tag{21b}$$

$$\Gamma_{33} = \sum_{j=1}^{N} p_j + 2\langle \mathbf{z}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{z} \rangle - \langle \mathbf{x}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{x} \rangle - \langle \mathbf{y}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{y} \rangle \tag{21c}$$

$$\Gamma_{12} = \Gamma_{21} = 3\langle \mathbf{x}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{y} \rangle \tag{21d}$$

$$\Gamma_{23} = \Gamma_{32} = 3\langle \mathbf{y}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{z} \rangle \tag{21e}$$

$$\Gamma_{31} = \Gamma_{13} = 3\langle \mathbf{z}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{x} \rangle \tag{21f}$$

where the angular parentheses indicate the averaging to be done over all configurations of the chain with the distribution ψ. We shall assume that the light beam used to measure the birefringence of the block-copolymer solution progresses along the y axis. Then, the electric vectors in the x–z plane are the only ones of interest and we may omit the second row and column of $\boldsymbol{\Gamma}$. Let the extinction angle χ be the smaller of the angles formed between the x axis and the principal optic axes of $\boldsymbol{\Gamma}$ in the x–z plane. Then, in exact analogy with Zimm's treatment for a homopolymer, we find by means of a formula used earlier by Boeder[9]

$$\tan 2\chi = 2\langle \mathbf{x}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{z} \rangle / (\langle \mathbf{x}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{x} \rangle - \langle \mathbf{z}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{z} \rangle) \tag{22}$$

Similarly, the difference in polarizabilities projected along the principal axes is given by

$$\Delta\Gamma(\omega) = 3[(\langle \mathbf{x}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{x} \rangle - \langle \mathbf{z}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{z} \rangle)^2 + 4\langle \mathbf{x}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{z} \rangle^2]^{1/2} \tag{23}$$

The magnitude of the birefringence of the solution, $\Delta n(\omega)$, is given by [10,11]

$$\Delta n(\omega) = [2\pi(n^2 + 2)^2 cN_0/9nM]\Delta\Gamma(\omega) \tag{24}$$

where n is the refractive index of the solvent, c is the concentration of the polymer in mass per unit volume, N_0 is the Avogadro number, and M is the molecular weight of the polymer. It is evident from eq 22–24 that the extinction angle and the magnitude of the birefringence depend on $q_{\rm v}$ (v = a, b, c, ab, bc) and not on $p_{\rm v}$.

We now proceed to evaluate the averages in eq 22 and 23. After transformation to normal coordinates we find, for example,

$$\langle \mathbf{z}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{z} \rangle = J\langle \boldsymbol{\zeta}^{\rm T}\cdot(\mathbf{Q}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{Q})\cdot\boldsymbol{\zeta} \rangle \tag{25}$$

where J is the Jacobian of the coordinate set $\boldsymbol{\xi}$, $\boldsymbol{\eta}$, $\boldsymbol{\zeta}$. Since, for a block-copolymer, $(\mathbf{Q}^{\rm T}\cdot\mathbf{P}\cdot\mathbf{Q})$ is not necessarily diagonal, we shall consider whether $\langle \xi_i\xi_j \rangle$, $\langle \zeta_i\zeta_j \rangle$, and $\langle \xi_i\zeta_j \rangle$ contribute to the averages in eq 22 and 23 when i and j are different. By multiplying both sides of eq 16 by $\xi_i\xi_j$, $\zeta_i\zeta_j$, and $\xi_i\xi_j$ in order, and integrating over the space coordinates with the use of the conditions that ψ and its derivatives vanish at infinity, we obtain the following set of differential equations:

$$(\mathrm{d}/\mathrm{d}t)\langle \zeta_i\zeta_j\rangle = -\sigma(\lambda_i + \lambda_j)\langle \zeta_i\zeta_j\rangle + 2\delta_{ij}Dv_i/J \qquad (26)$$

$$(\mathrm{d}/\mathrm{d}t)\langle \xi_i\zeta_j\rangle = \kappa\langle \zeta_i\zeta_j\rangle - \sigma(\lambda_i + \lambda_j)\langle \xi_i\zeta_j\rangle \qquad (27)$$

$$(\mathrm{d}/\mathrm{d}t)\langle \xi_i\xi_j\rangle = \kappa(\langle \xi_j\zeta_i\rangle + \langle \xi_i\zeta_j\rangle) - \sigma(\lambda_i + \lambda_j)\langle \xi_i\xi_j\rangle + 2\delta_{ij}Dv_i/J \qquad (28)$$

The solutions of these equations, when i and j are different, consist exclusively of transient terms containing the factor

$$\exp\,[-\sigma(\lambda_i + \lambda_j)t]$$

Thus, in the evaluation of the averages in eq 22 and 23, the terms containing $\langle \xi_i\xi_j\rangle$, $\langle \zeta_i\zeta_j\rangle$, or $\langle \xi_i\zeta_j\rangle$, where $i \neq j$, may be omitted, and we obtain from eq 25 and its analogues

$$\langle \mathbf{x}^{\mathrm{T}}\cdot\mathbf{P}\cdot\mathbf{x}\rangle = J\sum_{j=1}^{N}\pi_j\langle \xi_j^2\rangle \qquad (29)$$

$$\langle \mathbf{z}^{\mathrm{T}}\cdot\mathbf{P}\cdot\mathbf{z}\rangle = J\sum_{j=1}^{N}\pi_j\langle \zeta_j^2\rangle \qquad (30)$$

$$\langle \mathbf{x}^{\mathrm{T}}\cdot\mathbf{P}\cdot\mathbf{z}\rangle = J\sum_{j=1}^{N}\pi_j\langle \xi_j\zeta_j\rangle \qquad (31)$$

where π_j is the diagonal elements of $(\mathbf{Q}^{\mathrm{T}}\cdot\mathbf{P}\cdot\mathbf{Q})$, and the terms with $j = 0$ have been omitted since $\pi_0 = 0$. The averages $\langle \xi_j^2\rangle$, $\langle \zeta_j^2\rangle$, and $\langle \xi_j\zeta_j\rangle$ in eq 29–31 are evaluated by solving eq 26–28. They are given by

$$\langle \xi_k^2\rangle = \left(\frac{D}{\sigma\mu_k J}\right)\left\{1 + \frac{\kappa_0^2\tau_k^2}{1 + \omega^2\tau_k^2} + \frac{\kappa_0^2\tau_k^2[(1 - 2\omega^2\tau_k^2)\cos 2\omega t + 3\omega\tau_k \sin 2\omega t]}{(1 + \omega^2\tau_k^2)(1 + 4\omega^2\tau_k^2)}\right\} \qquad (32)$$

$$\langle \zeta_{\mathrm{k}}^2\rangle = (D/\sigma\mu_k J) \qquad (33)$$

$$\langle \xi_k\zeta_k\rangle = \left(\frac{\kappa_0 D\tau_k}{\sigma\mu_k J}\right)\left(\frac{\cos \omega t}{1 + \omega^2\tau_k^2} + \frac{\omega\tau_k \sin \omega t}{1 + \omega^2\tau_k^2}\right) \qquad (34)$$

with the relaxation times

$$\tau_k = (2\sigma\lambda_k)^{-1} \qquad (35)$$

In these equations, transient terms containing the factor $\exp(-2\sigma\lambda_k t)$ have been omitted. Using these equations, we obtain

$$\Delta\Gamma(\omega) = 3(\mathcal{D}^2 + 4\langle \mathbf{x}^{\mathrm{T}}\cdot\mathbf{P}\cdot\mathbf{z}\rangle^2)^{1/2} \qquad (36)$$

$$\tan 2\chi = 2\langle \mathbf{x}^{\mathrm{T}}\cdot\mathbf{P}\cdot\mathbf{z}\rangle/\mathcal{D} \qquad (37)$$

where

$$\mathcal{D} = \left(\frac{D}{\sigma}\right)\sum_{k=1}^{N}\left(\frac{\pi_k}{\mu_k}\right)\left\{\frac{\kappa_0^2\tau_k^2}{1 + \omega^2\tau_k^2} + \frac{\kappa_0^2\tau_k^2[(1 - 2\omega^2\tau_k^2)\cos 2\omega t + 3\omega\tau_k \sin 2\omega t]}{(1 + \omega^2\tau_k^2)(1 + 4\omega^2\tau_k^2)}\right\} \qquad (38)$$

and

$$\langle \mathbf{x}^{\mathrm{T}}\cdot\mathbf{P}\cdot\mathbf{z}\rangle = \left(\frac{\kappa_0 D}{\sigma}\right)\sum_{k=1}^{N}\left(\frac{\pi_k}{\mu_k}\right)\tau_k\left\{\frac{\cos \omega t}{1 + \omega^2\tau_k^2} + \frac{\omega\tau_k \sin \omega t}{1 + \omega^2\tau_k^2}\right\} \qquad (39)$$

In the limit of low shear rate ($\kappa \ll \tau_1^{-1}$), the term $\mathcal{D}^2$ in eq 36 may be neglected. The ratio $|\Delta n(\omega)|/\Delta n(0)$ and the phase agle δ between birefringence and shear rate are then given by

$$\frac{|\Delta n(\omega)|}{\Delta n(0)} = \left\{\left[\sum_{j=1}^{N}\frac{(\pi_j/\mu_j)(\lambda_1/\lambda_j)}{1 + (\omega\tau_1)^2(\lambda_1/\lambda_j)^2}\right]^2 + \left[\sum_{j=1}^{N}\frac{(\pi_j/\mu_j)(\omega\tau_1)(\lambda_1/\lambda_j)^2}{1 + (\omega\tau_1)^2(\lambda_1/\lambda_j)^2}\right]^2\right\}^{1/2}\bigg/\left[\sum_{j=1}^{N}(\pi_j/\mu_j)(\lambda_1/\lambda_j)\right] \qquad (40)$$

$$\tan \delta = \left[\sum_{j=1}^{N}\frac{(\pi_j/\mu_j)(\omega\tau_1)(\lambda_1/\lambda_j)^2}{1 + (\omega\tau_1)^2(\lambda_1/\lambda_j)^2}\right]\bigg/\left[\sum_{j=1}^{N}\frac{(\pi_j/\mu_j)(\lambda_1/\lambda_j)}{1 + (\omega\tau_1)^2(\lambda_1/\lambda_j)^2}\right] \qquad (41)$$

for $\kappa \ll \tau_1^{-1}$. At zero frequency, the extinction angle and the difference in principal polarizabilities are given by

$$\cot 2\chi = (\tau_1\kappa_0)\left[\sum_{j=1}^{N}(\pi_j/\mu_j)(\lambda_1/\lambda_j)^2\right]\bigg/\left[\sum_{j=1}^{N}(\pi_j/\mu_j)(\lambda_1/\lambda_j)\right] \qquad (42)$$

$$\Delta\Gamma = 6\kappa_0(D/\sigma)\left\{\left[\sum_{j=1}^{N}(\pi_j/\mu_j)\tau_j\right]^2 + \kappa_0^2\left[\sum_{j=1}^{N}(\pi_j/\mu_j)\tau_j^2\right]^2\right\}^{1/2} \qquad (43)$$

For the special case of a homopolymer with $\rho_{\mathrm{a}} = \rho_{\mathrm{b}} = \rho_{\mathrm{c}}$, $b_{\mathrm{a}} = b_{\mathrm{b}} = b_{\mathrm{c}}$, and $q_{\mathrm{a}} = q_{\mathrm{b}} = q_{\mathrm{c}} = q_{\mathrm{ab}} = q_{\mathrm{bc}}$, we have $\mathbf{P} = q_{\mathrm{a}}\mathbf{A}$, and the ratios (π_j/μ_j) in eq 40–43 all become q_{a}.

Callis and Davidson[12] have used the bead-spring model and the method of Kuhn and Grün[8] to develop a theory of the flow dichroism of chain-molecule solutions. We present here an extension of their theory to block-copolymer solutions. We define an absorptive constant q_{a}' by the expression

$$q_{\mathrm{a}}' = (\epsilon_{1\mathrm{a}} - \epsilon_{2\mathrm{a}})/(5b_{\mathrm{a}}^2) \qquad (44)$$

where $\epsilon_{1\mathrm{a}}$ is the extinction coefficient for the electric vector polarized along the vector between the ends of a Kuhn statistical chain element of the A block and $\epsilon_{2\mathrm{a}}$ is the value of the two equal extinction coefficients for the electric vectors normal to this end-to-end vector. Other absorptive constants q_{v}' (v = b, c, ab, bc) are similarly defined. We also introduce a matrix $\mathbf{P}'$ of order $(N + 1)$ with elements P_{jk}' which are identical to P_{jk} in form with q_j' and q_{v}' replacing q_j and q_{v} in eq 18 and 19. As in the discussion of flow birefringence, we shall assume that the light beam used to measure the dichroism of the block-copolymer solution progresses along the y axis and that the unperturbed flow field is as given by eq 14 and 15.

Let the extinction angle χ' be the smaller of the angles formed between the x axis and the principal axes of the absorption in the x–y plane. Then in exact analogy with our treatment of flow birefringence, we obtain

$$\tan 2\chi' = 2\langle \mathbf{x}^{\mathrm{T}}\cdot\mathbf{P}'\cdot\mathbf{z}\rangle/(\langle \mathbf{x}^{\mathrm{T}}\cdot\mathbf{P}'\cdot\mathbf{x}\rangle - \langle \mathbf{z}^{\mathrm{T}}\cdot\mathbf{P}'\cdot\mathbf{z}\rangle) \qquad (45)$$

The difference in absorption ΔA for the whole block-copolymer molecule for light vibrating along the two principal axes in the x–z plane is given by

$$\Delta A(\omega) = 3[(\langle \mathbf{x}^{\mathrm{T}}\cdot\mathbf{P}'\cdot\mathbf{x}\rangle - \langle \mathbf{z}^{\mathrm{T}}\cdot\mathbf{P}'\cdot\mathbf{z}\rangle)^2 + 4\langle \mathbf{x}^{\mathrm{T}}\cdot\mathbf{P}'\cdot\mathbf{z}\rangle^2]^{1/2} \qquad (46)$$

The averages in eq 45 and 46 are given by equations identical in form to eq 29–31, with $\mathbf{P}'$ and π_j' replacing $\mathbf{P}$ and π_j where π_j' are the diagonal elements of $(\mathbf{Q}^{\mathrm{T}}\cdot\mathbf{P}'\cdot\mathbf{Q})$.

In the limit of low shear rate, the ratio $|\Delta A(\omega)|/\Delta A(0)$ and the phase angle δ' between dichroism and shear rate are given by the right sides of eq 40 and 41, respectively, with π_j' replacing π_j. Similarly, the zero-frequency expressions for cot $(2\chi')$ and ΔA are identical in form with eq 42 and 43, respectively, with π_j' replacing π_j.

Relaxation of Flow Birefringence and Flow Dichroism

We shall now examine the decays of birefringence and dichroism when the unperturbed flow field is abruptly removed after the establishment of a steady state. We shall assume that the unperturbed flow field is given by eq 14 and 15 with $\omega = 0$ during the establishment of a steady state before $t = 0$. Then, we obtain from eq 32–34 the following steady-state values of the normal coordinates,

$$\langle \xi_k^2 \rangle_s = [D/(\sigma\mu_k J)](1 + 2\kappa_0^2\tau_k^2) \tag{47}$$

$$\langle \zeta_k^2 \rangle_s = D/(\sigma\mu_k J) \tag{48}$$

$$\langle \xi_k\zeta_k \rangle_s = \kappa_0 D\tau_k/(\sigma\mu_k J) \tag{49}$$

When eq 26–28 are solved with the conditions that κ is zero after $t = 0$ and that the steady state as described by eq 47–49 has been reached prior to $t = 0$, we obtain the following equations for the decays of the normal coordinates,

$$\langle \xi_k^2 \rangle_R = [D/(\sigma\mu_k J)][1 + 2\kappa_0^2\tau_k^2 \exp(-t/\tau_k)] \tag{50}$$

$$\langle \zeta_k^2 \rangle_R = D/(\sigma\mu_k J) \tag{51}$$

$$\langle \xi_k\zeta_k \rangle_R = \kappa_0 D\tau_k(\sigma\mu_k J)^{-1} \exp(-t/\tau_k) \tag{52}$$

Equations 50–52 are identical in form with the equations obtained by Thompson and Gill[13] for homopolymer solutions.

The averages in eq 46 are evaluated with the use of eq 50–52 and the equations analogous to eq 29–31 with $\mathbf{P}'$ and π_j' replacing $\mathbf{P}$ and π_j. The decay of flow dichroism is then given by

$$\Delta A(t) = 6k_0(D/\sigma)\{[\sum_{j=1}^{N}(\pi_j'/\mu_j)\tau_j \exp(-t/\tau_j)]^2 + \kappa_0^2[\sum_{j=1}^{N}(\pi_j'/\mu_j)\tau_j^2 \exp(-t/\tau_j)]^2\}^{1/2} \tag{53}$$

Similarly, the c and s mode transitions defined by Thompson and Gill[13] in their discussion of the flow birefringence experiments are given by

$$\Delta I_c(t) = C_1 J\sum_{j=1}^{N}\pi_j(\langle \xi_j^2 \rangle - \langle \zeta_j^2 \rangle) \tag{54}$$

$$\Delta I_s(t) = -2C_1 J\sum_{j=1}^{N}\pi_j\langle \xi_j\zeta_j \rangle \tag{55}$$

where C_1 is the product of the factors preceding the summation sign in their eq 60. Substitution of eq 50–52 into eq 54 and 55 yields

$$\Delta I_c(t) = 2C_1(D/\sigma)\kappa_0^2\sum_{j=1}^{N}(\pi_j/\mu_j)\tau_j^2 \exp(-t/\tau_j) \tag{56}$$

$$\Delta I_s(t) = -2C_1(D/\sigma)\kappa_0\sum_{j=1}^{N}(\pi_j/\mu_j)\tau_j \exp(-t/\tau_j) \tag{57}$$

Results and Discussion

In order to calculate the flow birefringence and the flow dichroism properties of a block-copolymer solution from the equations presented in the last two sections, it is necessary to evaluate first the eigenvalues λ_k as well as μ_k, π_k, and π_k'. The evaluation of λ_k by a numerical method has been discussed by Wang[5] and by Wang and DiMarzio.[4] The evaluation of μ_k, π_k, and π_k' in turn requires the computation of the eigenvectors α_k for a block-copolymer solution.

We shall not attempt to compute here the eigenvectors for a block-copolymer solution. Instead, we shall approximate them by the Rouse eigenvectors[14] for a free-draining homopolymer. Furthermore, we shall use the Rouse eigenvalues λ_k instead of those for a block-copolymer solution. Thus, strictly speaking, our results apply only to free-draining block copolymers the dissimilar blocks of which are not significantly different in flexibility and cross-sectional size. However, since these differences do not lead to inordinately large effects on the frequency dependence of the viscoelastic properties as shown by Stockmayer and Kennedy[3] and by Wang and DiMarzio,[4] these approximations should be adequate for our purpose. Thus, α_k, μ_k, and λ_k are given by[7,15,16] eq 58a for $k = 0$, by eq 58b for $k > 0$ ($l = 0, 1, 2, ..., N$), and by eq 59,

$$\alpha_k(l) = \left(\frac{2}{N+1}\right)^{1/2}\left(\frac{1}{2}\right)^{1/2} \tag{58a}$$

$$\alpha_k(l) = \left(\frac{2}{N+1}\right)^{1/2} \cos\left[\left(\frac{k\pi}{N+1}\right)\left(l + \frac{1}{2}\right)\right] \tag{58b}$$

$$\mu_k = \lambda_k = 4 \sin^2 [k\pi/(2N + 2)] \tag{59}$$

We discuss in this and the next paragraphs the flow birefringence and the flow dichroism properties of some special block copolymers for which simple relations for the weighting factors (π_k/μ_k) or (π_k'/μ_k) can be obtained. For the case of a diblock copolymer with $q_b = q_c = q_{bc}$, if we make the approximation $q_{ab} = q_a$ we obtain with the use of eq 58

$$\pi_k = \left(\frac{4}{N+1}\right)\sin^2\left(\frac{\beta}{2}\right)\left\{(q_a + q_b) \times \left[N - N_a - \frac{\cos[(N - N_a + 1)\beta] \sin[(N - N_a)\beta]}{\sin\beta}\right] + q_a\left[2N_a - N - \frac{\sin[(2N_a - N)\beta] \cos k\pi}{\sin\beta}\right]\right\} \tag{60}$$

where

$$\beta = k\pi/(N + 1) \tag{61}$$

When $N = 2N_a$, we obtain from eq 59 and 60

$$\pi_k/\mu_k = (q_a + q_b)/2 \tag{62}$$

and, by analogy

$$\pi_k'/\mu_k = (q_a' + q_b')/2 \tag{63}$$

Thus, for this particular case, the weighting factors are independent of the index k. Consequently, while the values of $\Delta\Gamma$ and ΔA are different from those for a homopolymer by a constant factor, the values of $|\Delta n(\omega)|/\Delta n(0)$, tan δ, cot 2χ, and the analogous flow dichroism properties are the same as those for a homopolymer. The decay of flow dichroism, and the c and s mode transmissions are also different from those for a homopolymer by a constant factor. It is evident from eq 62 and 63 that when $N = 2N_a$ and $q_a = -q_b$ (or $q_a' = -q_b'$), all the weighting factors are zero. Thus, when the anisotropy in polarizability of one block's Kuhn statistical element differs from that of the other block only in sign, the birefringence Δn vanishes at some block composition. An analogous statement can be made about the difference in absorption,

Table I
Calculated Values of the Flow Birefringence Properties of Some Diblock Copolymers[a]

				$(\pi_k/\mu_k)/(\pi_1/\mu_1)$			
q_b	S_1*	S_2*	S_1*/S_2*	$k = 2$	$k = 3$	$k = 4$	$k = 5$
-8.0	-0.71	0.05	-14.02	-7.98	-10.80	-7.72	-6.08
-6.5	-0.31	0.22	-1.41	-3.02	-4.28	-2.90	-2.16
-5.0	0.08	0.39	0.20	-1.19	-1.88	-1.13	-0.78
-4.5	0.21	0.45	0.46	-0.82	-1.39	-0.77	-0.43
-3.5	0.47	0.57	0.83	-0.25	-0.64	-0.22	0.01
-3.0	0.60	0.62	0.96	-0.03	-0.35	0.00	0.19
-2.3	0.78	0.70	1.11	0.23	-0.01	0.25	0.39
-1.0	1.12	0.85	1.32	0.60	0.48	0.61	0.69
0.0	1.38	0.97	1.43	0.82	0.76	0.83	0.86
1.0	1.64	1.08	1.52	1.00	1.00	1.00	1.00
2.3	1.98	1.23	1.61	1.19	1.25	1.18	1.15
5.0	2.69	1.54	1.76	1.47	1.62	1.46	1.37

[a] Symbols employed are defined in the text. $N_a = 81$, $N_b + N_c = 28$; $q_a = q_{ab} = 1.0$, $q_b = q_c = q_{bc}$. q_v are given in arbitrary units.

ΔA. Another interesting case arises when $N = 2N_a - 1$. Then, eq 59 and 60 lead to

$$\pi_k/\mu_k = (1/2)\{(q_a + q_b) + (q_a - q_b)[1 - (-1)^k]/(N + 1)\} \quad (64)$$

the last term of which is absent in eq 62. However, since this term is inversely proportional to $(N + 1)$, for a long block copolymer represented by a chain with large N, this term is negligible and the case for $N = 2N_a - 1$ is indistinguishable from the case for $N = 2N_a$.

For the case of a symmetric triblock copolymer with $q_a = q_c$, if we make the approximation $q_{ab} = q_a = q_{bc}$ we obtain with the use of eq 58

$$(N + 1)\pi_k = 4q_a\{2N_a + 1 - \sin [(2N_a + 1)\beta]/\sin \beta\} \sin^2 (\beta/2) + 4q_b\{N_b - 1 - (-1)^k \times \sin [(N_b - 1)\beta]/\sin \beta\} \sin^2 (\beta/2) \quad (65)$$

When $2N_a = N_b - 2$, we obtain from eq 59 and 65

$$\pi_k/\mu_k = (q_a + q_b)/2 + [1 - (-1)^k](-1)^{(k-1)/2}(q_b - q_a)/[2(N + 1) \sin \beta] \quad (66)$$

the last term of which vanishes when k is even and alternates in sign with increasing odd value of k. Since this term is inversely proportional to $[(N + 1) \sin \beta]$, which is of order unity when k is small, it contributes significantly to the weighting factors of the lower modes. In particular, when $q_a = -q_b$, the first term of eq 66 vanishes and only odd modes contribute to the flow birefringence properties.

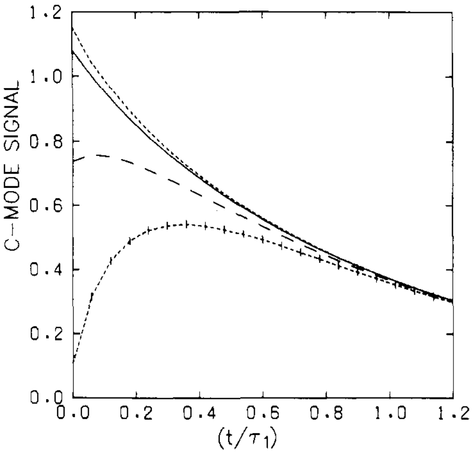

Figure 1. c-mode transmissions calculated for some triblock copolymers with $N_a = 26$, $N_b = 56$, $N_c = 26$, $q_b = 1.0$, and $q_a = q_{ab} = q_{bc} = q_c$. Symbols employed are defined in the text. c-mode signals and q_v are given in arbitrary units. Uppermost curve, $q_a = 5.0$; solid curve, homopolymer with $q_a = 1.0$; long dashes, $q_a = -3.0$; lowermost curve, $q_a = -4.0$.

Statements analogous to those made in this paragraph for flow birefringence properties may be made for flow dichroism properties.

Tables I and II give respectively the calculated flow birefringence properties of some diblock copolymers and triblock copolymers. In these tables, q_v (v = a, ab, b, bc, c) are given in arbitrary units and S_1* and S_2* are defined by

$$S_1^* = \sum_{k=1}^{N} (\pi_k/\mu_k)(\lambda_1/\lambda_k) \quad (67)$$

$$S_2^* = \sum_{k=1}^{N} (\pi_k/\mu_k)(\lambda_1/\lambda_k)^2 \quad (68)$$

As is evident from eq 36, 39, and 42, at low shear rate, S_1* is proportional to the birefringence at zero frequency and (S_1*/S_2*) is related to the extinction angle. In agreement with eq 60 and 65 which are linear in q_a and q_b, S_1* and S_2* in Table I vary linearly with q_b while S_1* and S_2* in Table II vary linearly with q_a. S_1* vanishes near $q_b = -5.0$ for these diblock copolymers and vanishes near $q_a = -2.3$ for these triblock copolymers. In addition, we see that for both diblock and triblock copolymers the weighting factors of normal modes are generally different, sometimes in sign as well as in magnitude when the blocks have different signs for the anisotropy in polarizability.

Table II
Calculated Values of the Flow Birefringence Properties of Some Triblock Copolymers[a]

				$(\pi_k/\mu_k)/(\pi_1/\mu_1)$			
q_a	S_1*	S_2*	S_1*/S_2*	$k = 2$	$k = 3$	$k = 4$	$k = 5$
-8.0	-2.83	-0.84	3.36	6.03	7.90	6.33	5.15
-5.0	-1.34	-0.20	6.70	53.7	73.4	56.9	44.5
-4.5	-1.09	-0.09	11.8	-32.2	-44.6	-34.2	-26.4
-4.0	-0.84	0.01	-59.0	-10.2	-14.4	-10.9	-8.28
-3.5	-0.59	0.12	-4.88	-5.22	-7.54	-5.59	-4.13
-3.0	-0.34	0.23	-1.50	-2.99	-4.47	-3.23	-2.29
-2.5	-0.09	0.34	-0.28	-1.73	-2.75	-1.89	-1.25
-2.3	0.01	0.38	0.01	-1.37	-2.25	-1.51	-0.95
-1.5	0.40	0.55	0.73	-0.36	-0.86	-0.44	-0.12
-1.0	0.65	0.66	0.99	-0.06	-0.29	0.00	0.22
0.0	1.15	0.87	1.32	0.63	0.49	0.60	0.69
1.0	1.64	1.08	1.52	1.00	1.00	1.00	1.00
2.5	2.39	1.40	1.70	1.36	1.50	1.39	1.30
5.0	3.63	1.94	1.88	1.73	2.00	1.78	1.60

[a] Symbols employed are defined in the text. $N_a = 26$, $N_b = 56$, $N_c = 26$; $q_b = 1.0$; $q_a = q_{ab} = q_{bc} = q_c$. q_v are given in arbitrary units.

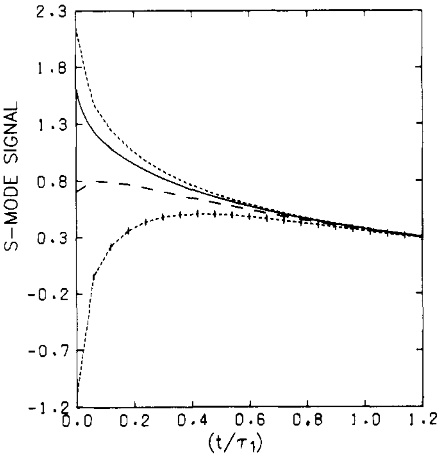

Figure 2. s-mode transmissions calculated for some triblock copolymers with $N_a = 26$, $N_b = 56$, $N_c = 26$, $q_b = 1.0$, and $q_a = q_{ab} = q_{bc} = b_c$. Symbols employed are defined in the text. s-mode signals and q_v are given in arbitrary units. Uppermost curve, $q_a = 5.0$; solid curve, homopolymer with $q_a = 1.0$; long dashes, $q_a = -1.5$; lowermost curve, $q_a = -3.0$.

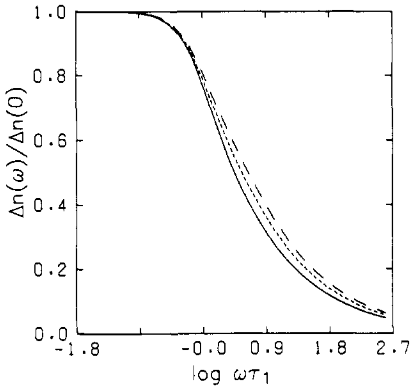

Figure 3. Magnitudes of birefringence calculated for some triblock copolymers with $N_a = 26$, $N_b = 56$, $N_c = 26$, $q_b = 1.0$, and $q_a = q_{ab} = q_{bc} = q_c$. Symbols employed are defined in the text. q_v are given in arbitrary units. Long dashes, $q_a = 5.0$ and $S_1^* = 3.6$; short dashes, $q_a = 2.5$ and $S_1^* = 2.4$; solid curve, homopolymer with $q_a = 1.0$ and $S_1^* = 1.6$.

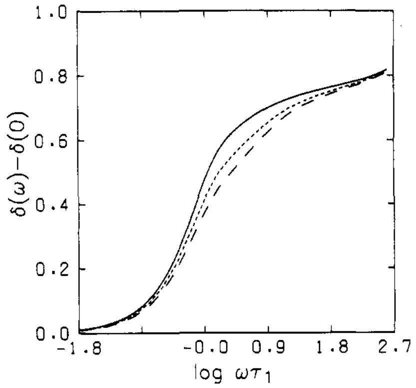

Figure 4. Phase angles between birefringence and shear rate calculated for some triblock copolymers with $N_a = 26$, $N_b = 56$, $N_c = 26$, $q_b = 1.0$, and $q_a = q_{ab} = q_{bc} = q_c$. Symbols employed are defined in the text. q_v are given in arbitrary units. Curve labels are the same as for Figure 3.

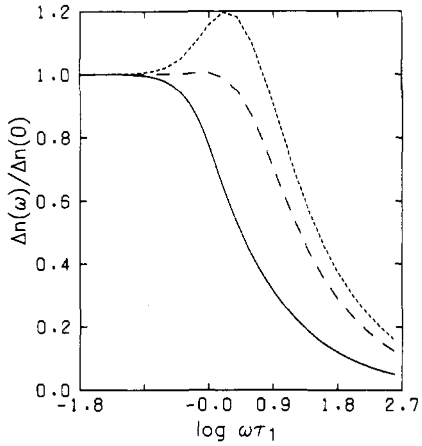

Figure 5. Magnitudes of birefringence calculated for some triblock copolymers with $N_a = 26$, $N_b = 56$, $N_c = 26$, $q_b = 1.0$, and $q_a = q_{ab} = q_{bc} = q_c$. Symbols employed are defined in the text. q_v are given in arbitrary units. Long dashes: $q_a = -4.5$ and $S_1^* = -1.09$; short dashes, $q_a = -3.5$ and $S_1^* = -0.59$; solid curve, homopolymer with $q_a = 1.0$ and $S_1^* = 1.6$.

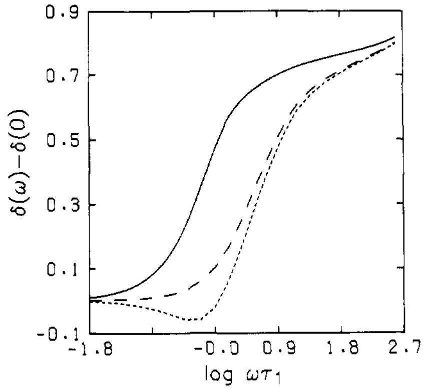

Figure 6. Phase angles between birefringence and shear rate calculated for some triblock copolymers with $N_a = 26$, $N_b = 56$, $N_c = 26$, $q_b = 1.0$, and $q_a = q_{ab} = q_{bc} = q_c$. Symbols employed are defined in the text. q_v are given in arbitrary units. Curve labels are the same as for Figure 5.

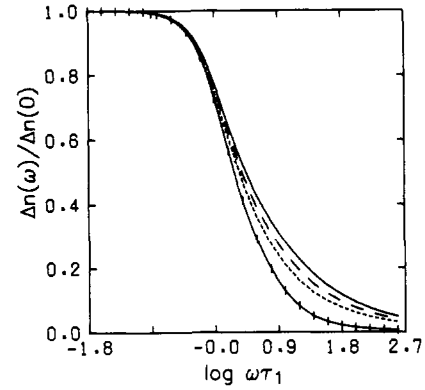

Figure 7. Magnitudes of birefringence calculated for some diblock copolymers with $N_a = 90$, $N_b + N_c = 18$, $q_a = q_{ab} = 1.0$, and $q_b = q_{bc} = q_c$. Symbols employed are defined in the text. q_v are given in arbitrary units. Uppermost curve, homopolymer with $q_b = 1.0$ and $S_1^* = 1.6$; long dashes, $q_b = -1.0$ and $S_1^* = 1.4$; short dashes, $q_b = -2.3$ and $S_1^* = 1.3$; lowermost curve, $q_b = -5.0$ and $S_1^* = 1.1$.

An effect of the different signs among the weighting factors is seen vividly in the decay of birefringence. Figures 1 and 2 give respectively the decays of c and s mode transmissions for some triblock copolymers. In both figures, the two lower curves are for triblock copolymers with weighting factors different in sign as well as magnitude while the topmost curve is for a triblock copolymer with weighting factors different only in magnitude. We see in these figures that while these triblock copolymers all differ from a homopolymer in the decay of birefringence, the difference is more striking with the former than the latter.

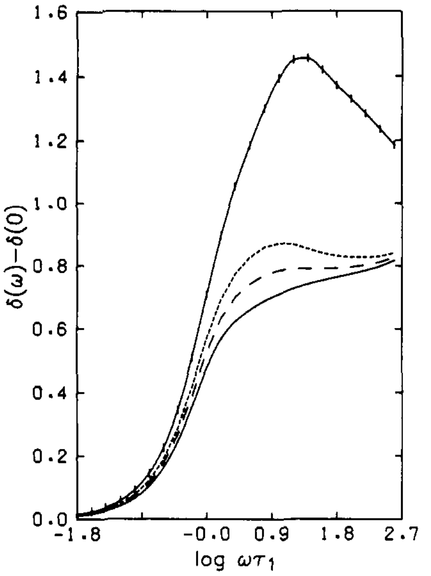

Figure 8. Phase angles between birefringence and shear rate calculated for some diblock copolymers with $N_a = 90$, $N_b + N_c = 18$, $q_a = q_{ab} = 1.0$, and $q_b = q_{bc} = q_c$. Symbols employed are defined in the text. q_v are given in arbitrary units. Curve labels are the same as for Figure 7.

In Figures 3 to 8, the calculated results for the oscillatory flow birefringence of some triblock and diblock copolymers are compared with those for a homopolymer. The values of the parameters used in the calculations as well as the calculated values of S_1^*, which is proportional to the magnitude of birefringence at zero frequency, are given in the captions. Figures 3 and 4 are for two triblock copolymers in which the blocks are different in magnitude but not the sign of polarizability anisotropy. We see in these figures that, for these block copolymers, the shapes of the curves for $\Delta n(\omega)/\Delta n(0)$ (the magnitude of birefringence) and $\delta(\omega)$ (the phase angle between birefringence and shear rate) are not markedly different from those for a homopolymer. However, the curves for the block copolymer clearly deviate from those for a homopolymer toward higher frequency.

Figures 5 and 6 are for two triblock copolymers in which the blocks are different in magnitude and the sign of the polarizability anisotropy. For these block copolymers, in addition to the aforementioned shift toward higher frequency from the curves for a homopolymer, we see for the case with $(q_a/q_b) = -3.5$ the appearance of a maximum in $\Delta n(\omega)/\Delta n(0)$ and a minimum in $\Delta(\omega) - \delta(0)$ when $(\omega\tau_1)$ is near zero. Since the value of S_1^* for this case is not much less than that for a homopolymer, the maximum and the minimum should be observable for some properly designed block copolymers.

Figures 7 and 8 are for some diblock copolymers the blocks of which are different in magnitude and the sign of the polarizability anisotropy. We see for these diblock copolymers that the curves for $\Delta n(\omega)/\Delta n(0)$ and $\delta(\omega) - \delta(0)$ are shifted from those for a homopolymer toward lower frequency. Furthermore, for the cases with (q_b/q_a) of -2.3 and -5.0, there appears a maximum in $\delta(\omega) - \delta(0)$. Here again, the calculated values of S_1^* are not much smaller than that for a homopolymer and the maximum should be observable for diblock copolymers.

Concluding Remarks

We have used the bead-spring model to obtain the equations for the flow birefringence and the flow dichroism of block copolymers in solution. The application of these equations to some free-draining block copolymers has shown that the differences in optical properties of the dissimilar blocks may in some cases make the flow birefringence and the flow dichroism of block copolymers strikingly different from those of homopolymers. It may be interesting to take advantage of the calculated results that the contributions of normal modes to flow birefringence and flow dichroism properties are weighted by generally different factors. For example, the determination of longer relaxation times may be facilitated if, by manipulating block copolymer structure, the even normal modes are made to contribute very little to the flow birefringence or flow dichroism properties.

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