Matrix Representation of the Dynamical Structure Factor of a Solution of Rodlike Polymers in the Isotropic Phase. 2. VH-Depolarized Scattering

Tadakazu Maeda

Mitsubishi Kasei Institute of Life Sciences, 11 Minami-ooya, Machida-shi, Tokyo 194, Japan. *Received May 31, 1989; Revised Manuscript Received August 11, 1989*

ABSTRACT: The theory of the dynamical structure factor, $g(\mathbf{k},t)$, of rodlike polymers for the isotropic scattering was extended to the case of VH-depolarized scattering, where the polarization of the incident light wave is vertical to the scattering plane and that of the scattered one horizontal. The effects of the intramolecular interference and translation–rotation coupling of rod diffusion were explicitly taken into account, the excluded-volume interaction among rods was included using the mean-field approximation, and other types of rod–rod interactions, such as the entanglement effect and hydrodynamic interaction, were taken into consideration using the concentration-dependent self-diffusivities. The evaluation of the VH-depolarized dynamical structure factor, $g_{\mathrm{VH}}(\mathbf{k},t)$, and its initial decay rate, Γ_{VH}, is quite easy and straightforward in the entire region of $\mathbf{k}$, t, and ν, where $\mathbf{k}$ is the scattering vector, t the delay time, and ν the number concentration of the rods. Results of numerical computation showed that, contrary to the case of the isotropic scattering, the excluded-volume interaction causes a *decrease* in Γ_{VH}. The magnitude of the decrease, being largest in the forward depolarized scattering, depends in general on kL, ϑ, and ν/ν^*, where L is the rod length, ϑ the scattering angle, and ν^* the characteristic concentration above which the isotropic phase becomes unstable. The theory of the dynamical structure factors $g(\mathbf{k},t)$ and $g_{\mathrm{VH}}(\mathbf{k},t)$ will be useful for studying the excluded-volume interaction among rodlike polymers and the concentration dependence of the self-diffusivities in the strongly entangled state.

1. Introduction

The dynamic light scattering (DLS) technique is a powerful tool for studying the Brownian motion of rodlike polymers in solutions, where various factors, such as the anisotropy in the translational diffusion coefficients, the excluded-volume interaction, rod entanglement, and hydrodynamic interaction, must be taken into account. Including all of these features, we presented in our previous paper[1] (hereafter to be reffered to as 1) a theory of the dynamical structure factor, $g(\mathbf{k},t)$, of rodlike polymers in the isotropic phase, where $\mathbf{k}$ is the scattering vector and t the delay time. Though the theory does not include the polarizability anisotropy of the rod, the dynamical structure factor obtained is in most cases valid for evaluating the polarized DLS spectrum of rigid-rod suspensions, because the polarizability anisotropy of the molecule ($\Delta\alpha \equiv \alpha_{\parallel} - \alpha_{\perp}$) is usually negligible[2] compared to the average molecular polarizability ($\alpha \equiv (\alpha_{\parallel} + 2\alpha_{\perp})/3$), where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the polarizabilities parallel and perpendicular to the rod axis, respectively.

The theory showed that the excluded-volume interaction among rods affects the polarized (or, to be more exact, isotropic) DLS spectrum of rod suspensions in the less dilute regime: The apparent diffusion coefficient, $\Gamma_{\mathbf{k}}/k^2$, is expressed as a weighted sum of diffusion coefficients

$$\Gamma_{\mathbf{k}}/k^2 = {}^*D_{\parallel}W_{\parallel}(kL) + {}^*D_{\perp}W_{\perp}(kL) + (L^2/12){}^*D_{\mathrm{r}}W_{\mathrm{r}}(kL) \tag{1}$$

where $\Gamma_{\mathbf{k}}$ is the initial decay rate of the dynamical structure factor, $g(\mathbf{k},t)$, ${}^*D_{\parallel}$ and ${}^*D_{\perp}$ are the apparent diffusion coefficients for the lengthways and sideways translation of a rod, respectively, ${}^*D_{\mathrm{r}}$ is the rotational one, and L is the rod length. The weighting factors, $W_i(kL)$, for i = "$\parallel$", "$\perp$", and "r" are known functions[3] of kL. Limiting values of W_i for $kL \to 0$ and $kL \to \infty$ are $W_{\parallel}(0) = 1/3$, $W_{\parallel}(\infty) = 0$, $W_{\perp}(0) = 2/3$, $W_{\perp}(\infty) = 1$, $W_{\mathrm{r}}(0) = 0$, and $W_{\mathrm{r}}(\infty) = 1$. ${}^*D_i$ is related to the self-diffusion coefficient, D_i, as

$${}^*D_i = D_iA(kL,\nu) \qquad \text{for } i = \text{“}\parallel\text{”, “}\perp\text{”, and “r”} \tag{2}$$

where $A(kL,\nu)$ expresses the excluded-volume effect, ν being the number concentration. The asterisk of ${}^*D_i$ denotes that this quantity includes the repulsive thermodynamic interaction term $A(kL,\nu)$.

Equations 1 and 2 tell us the importance of discriminating D_i from ${}^*D_i$, the latter of which we can measure with the DLS technique, but the former many polymer physicists are interested in. We know from eq 2 that two opposing factors, D_i and $A(kL,\nu)$, determine whether ${}^*D_i$ increases with increase of the polymer concentration, ν. The self-diffusivities, D_i, of a rod in a good solvent, in general, decrease below the infinite dilution value, $D_{i,0}$, with increasing ν because of the rod entanglement and hydrodynamic interaction, but the excluded-volume effect term $A(kL,\nu)$ is an increasing function of ν, the increase of which is largest in the forward scattering. The relation ${}^*D_i = D_i$, of course, holds at infinite dilution, because $A(kL,0) = 1$. When $kL \lesssim 1$, the increase of $A(kL,\nu)$ exceeds the decrease of D_i and the measured mutual diffusion coefficient, ${}^*D_{\mathrm{G}}$ ($\equiv(2{}^*D_{\perp} + {}^*D_{\parallel})/3$) *increases* above $D_{\mathrm{G},0}$. For larger kL, however, the increase of $A(kL,\nu)$ becomes weaker, and the measured apparent diffusion coefficient, $\Gamma_{\mathbf{k}}/k^2$ can *decrease* with the concentration. Since $A(kL,\nu)$ and $W_i(kL)$ are known functions, we are able to estimate from $\Gamma_{\mathbf{k}}/k^2$ the self-diffusivities, D_i, individually.

Though the depolarized DLS technique is less popular than the polarized one because of the weak intensity of the depolarized scattered light ($\Delta\alpha \ll \alpha$), the merit of this technique is that the forward depolarized DLS can measure the rotational diffusion coefficient of rodlike polymers without any interference from the translational modes of rod diffusion. Combination of the polarized and depolarized DLS techniques would surely be much more desirable in studying the concentration dependence of each self-diffusivity, D_i, of the rod. In order to realize this

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combination, however, we have to know how the excluded-volume interaction affects the depolarized DLS spectrum, which, as far as we know, has not been theoretically discussed so far.

The aim of this paper is to develop a theory of the VH-depolarized dynamical structure factor, $g_{\mathrm{VH}}(\mathbf{k},t)$, that complements $g(\mathbf{k},t)$ previously derived for the isotropic scattering.[1] Following Doi et al.'s treatment,[4] first, we derive $g_{\mathrm{VH}}(\mathbf{k},t)$ in the operator formalism. Second, we rewrite $g_{\mathrm{VH}}(\mathbf{k},t)$ in the matrix representation and give a practical procedure for computing the depolarized DLS spectrum of rigid-rod suspensions for arbitrary $\mathbf{k}$, t, and ν. Third, the kL dependence of various scattering factors and profiles of the correlation function are shown. It will be also shown that, similar to $\Gamma_{\mathbf{k}}/k^2$, the apparent rotational diffusion coefficient, $\Gamma_{\mathrm{VH}}/f_1(kL,\vartheta)$, is expressed as a weighted sum of diffusion coefficients, $^*D_i$, where $f_1(kL,\vartheta)$ is the weighting factor for the rotational mode. Finally, reanalyzing Zero and Pecora's data[5] of depolarized DLS of poly(γ-benzyl L-glutamate) (PBLG) in the semidilute regime, we shall show their data exactly support the prediction of the Doi–Edwards theory[6] that the rotational self-diffusion coefficient, D_r, of a rod is inversely proportional to the ninth-power of the rod length in the strongly entangled state.

2. Scattering Geometry

We use a scattering geometry shown in Figure 1, to which two-coordinate systems are attached: The one is a laboratory-fixed Cartesian coordinate system (x, y, z) having the origin O in the scattering volume, and the other, a laboratory-fixed polar coordinate system, the origin and polar axis of which, respectively, coincide with the origin and $-z$ axis of the Cartesian coordinate system. The azimuthal angle, ϕ, is measured from the x axis. We assume the incident beam with wave vector $\mathbf{k}_i$ and polarization unit vector $\mathbf{e}_{\mathrm{v}}$ propagates from the negative x side in the x–z plane, and the scattered radiation with wave vector $\mathbf{k}_s$ and polarization $\mathbf{e}_{\mathrm{H}}$ propagates to the positive x side in the x–z plane. The x axis being assumed to divide the scattering angle, ϑ, into exact halves, the scattering vector, $\mathbf{k} = \mathbf{k}_i - \mathbf{k}_s$, is parallel to the polar axis, i.e., antiparallel to the z axis. The initial polarization $\mathbf{e}_{\mathrm{V}}$ is vertical to the scattering plane (the x–z plane), and the final one $\mathbf{e}_{\mathrm{H}}$, horizontal:

$$\mathbf{e}_{\mathrm{v}} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \qquad \mathbf{e}_{\mathrm{H}} = \begin{pmatrix} -\sin(\vartheta/2) \\ 0 \\ \cos(\vartheta/2) \end{pmatrix} \tag{3}$$

The polymer we shall consider is a rigid rod of length L and diameter b. We specify the configuration of a rod by two vectors, $\mathbf{r}$ and $\mathbf{u}$, where $\mathbf{r}$ is the position vector of the center of mass and $\mathbf{u}$ the unit vector parallel to the rod axis. The (x, y, z) components of the vector $\mathbf{u}$ are[7]

$$\mathbf{u} = \begin{pmatrix} \sin(\pi-\theta)\cos(-\phi) \\ \sin(\pi-\theta)\sin(-\phi) \\ \cos(\pi-\theta) \end{pmatrix} \tag{4}$$

The polymer is assumed to have a molecule-fixed polarizability component $\alpha_{\parallel}$ parallel to the rod axis and $\alpha_{\perp}$ in any direction perpendicular to this axis. The molecular polarizability tensor, $\alpha(\mathbf{u})$ is given by

$$\alpha(\mathbf{u}) = \alpha_{\parallel}\mathbf{u}\mathbf{u} + \alpha_{\perp}(\mathbf{I} - \mathbf{u}\mathbf{u}) \tag{5}$$

3. Depolarized Dynamical Structure Factor

Let $d_{\mathbf{k}}(\mathbf{u})$ be the $\mathbf{k}$-component of the normalized electric field of the VH-depolarized light scattered from a rod with orientation $\mathbf{u}$

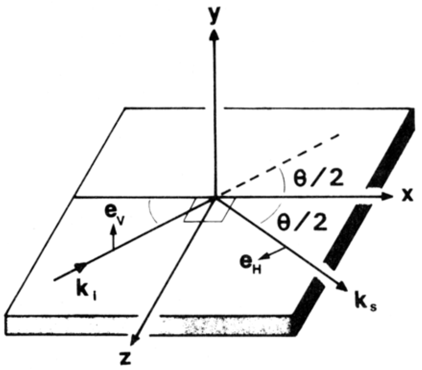

Figure 1. Scattering geometry. In this geometry the x–z plane is the scattering plane. The angle ($\mathbf{k}_i$,$\mathbf{k}_s$) is the scattering angle, and the scattering vector $\mathbf{k} = \mathbf{k}_i - \mathbf{k}_s$ is antiparallel to the z axis. A polar coordinate system is attached to the Cartesian coordinate system (x,y,z), the polar axis of which is $\mathbf{k}$, and the azimuthal angle, ϕ, is measured from the x axis.

$$d_{\mathbf{k}}(\mathbf{u}) = \hat{\alpha}_{\mathrm{VH}}(\mathbf{u})\, s_{\mathbf{k}}(\mathbf{u}) \tag{6}$$

where $\hat{\alpha}_{\mathrm{VH}}(\mathbf{u})$ ($\equiv \mathbf{e}_{\mathrm{V}}\cdot\alpha(\mathbf{u})\cdot\mathbf{e}_{\mathrm{H}}/\Delta\alpha$) is the normalized projection of the polarizability tensor, $\alpha(\mathbf{u})$, onto the polarization directions of the incident and scattered light waves and $s_{\mathbf{k}}(\mathbf{u})$ ($\equiv\int_{-L/2}^{L/2}\exp(i\mathbf{k}\cdot\mathbf{u}s)\,\mathrm{d}s/L$) expresses the intramolecular interference.

We express $\hat{\alpha}_{\mathrm{VH}}(\mathbf{u})$ and $s_{\mathbf{k}}(\mathbf{u})$ using spherical harmonics $Y_{lm}(\mathbf{u})$:

$$\hat{\alpha}_{\mathrm{VH}}(\mathbf{u}) = i(2\pi/15)^{1/2}\left[\sin\frac{\vartheta}{2}(Y_{2,-2} - Y_{22}) + \cos\frac{\vartheta}{2}(Y_{2,-1} + Y_{21})\right] \tag{7}$$

$$s_{\mathbf{k}}(\mathbf{u}) = (4\pi)^{1/2}\sum_{lm} s_{lm}\, Y_{lm}(\mathbf{u}) \tag{8}$$

where

$$\begin{aligned} s_{lm} &= (-1)^{l/2}(2l+1)^{1/2} b_l(K)\delta_{m,0} \quad \text{for even } l \\ &= 0 \quad \text{otherwise} \end{aligned} \tag{9}$$

$$b_l(K) = \frac{1}{K}\int_0^K j_l(x)\,\mathrm{d}x \tag{10}$$

$$K = kL/2 \tag{11}$$

and $j_l(x)$ is the lth-order spherical Bessel function.

Let $f(\mathbf{r},\mathbf{u},t)$ be the average number density of rods in the configuration ($\mathbf{r}$,$\mathbf{u}$). In the scattering geometry shown in Figure 1, the depolarized scattered field at the detector, placed far from the scattering volume, is proportional to[2]

$$c_{\mathbf{k}}(t) = L\int \mathrm{d}\mathbf{r}\int \mathrm{d}\mathbf{u}\, \exp(i\mathbf{k}\cdot\mathbf{r})\, d_{\mathbf{k}}(\mathbf{u})\, f(\mathbf{r},\mathbf{u},t) \tag{12}$$

We define the depolarized dynamical structure factor[8] as

$$g_{\mathrm{VH}}(\mathbf{k},t) = \frac{1}{\nu L V}\langle c_{\mathbf{k}}(t)\, c_{\mathbf{k}}^*(0)\rangle \tag{13}$$

where V is the system volume and the asterisk of $c_{\mathbf{k}}^*$ stands for the complex conjugate.

Following Doi et al.'s procedure,[4] we have from eq 13 an explicit form of $g_{\mathrm{VH}}(\mathbf{k},t)$ as

$$g_{\mathrm{VH}}(\mathbf{k},t) = \frac{L}{4\pi}\int_t^{\infty}\mathrm{d}t'\int \mathrm{d}\mathbf{u}\, d_{\mathbf{k}}(\mathbf{u})\exp[-t'\Omega_{\mathbf{k}}]\Theta_{\mathbf{k}}\, d_{\mathbf{k}}^*(\mathbf{u}) \tag{14}$$

where $\Theta_{\mathbf{k}}$ is the translational–rotational diffusion operator for a rod, and $\Omega_{\mathbf{k}} \equiv \Theta_{\mathbf{k}}\Phi_{\mathbf{k}}$. Operator $\Phi_{\mathbf{k}}$ expresses the rod–rod interaction in the mean-field approximation. Operators $\Theta_{\mathbf{k}}$ and $\Phi_{\mathbf{k}}$ are defined by the equations

$$\Theta_{\mathbf{k}} d_{\mathbf{k}}^*(\mathbf{u}) = [D_{\parallel}(\mathbf{k}\cdot\mathbf{u})^2 + D_{\perp}\{\mathbf{k}^2 - (\mathbf{k}\cdot\mathbf{u})^2\} - D_{\mathrm{r}}\mathcal{R}^2]\, d_{\mathbf{k}}^*(\mathbf{u}) \tag{15}$$

$$\Phi_{\mathbf{k}} d_{\mathbf{k}}^*(\mathbf{u}) = \int \mathrm{d}\mathbf{u}' \left[\delta(\mathbf{u} - \mathbf{u}') + \frac{\nu}{4\pi} W_{\mathbf{k}}(\mathbf{u},\mathbf{u}') \right] d_{\mathbf{k}}^*(\mathbf{u}') \tag{16}$$

where $W_{\mathbf{k}}(\mathbf{u},\mathbf{u}')$ is the spatial Fourier transform of the interaction potential $W(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}')$ between two rods in the configurations $(\mathbf{r},\mathbf{u})$ and $(\mathbf{r}',\mathbf{u}')$. Assuming the rigid-body interaction potential for $W(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}')$, we have[4]

$$W_{\mathbf{k}}(\mathbf{u},\mathbf{u}') = 2bL^2|\mathbf{u}\times\mathbf{u}'|\, s_{\mathbf{k}}(\mathbf{u})\, s_{\mathbf{k}}(\mathbf{u}') \tag{17}$$

Though $d_{\mathbf{k}}(\mathbf{u})$ is real, we intentionally leave the asterisk of $d_{\mathbf{k}}^*(\mathbf{u})$ in eq 14 for later use. It should be noted that a simple replacement of $d_{\mathbf{k}}(\mathbf{u})$ with $s_{\mathbf{k}}(\mathbf{u})$ in eq 14 gives the dynamical structure factor, $g(\mathbf{k},t)$, for the isotropic scattering.

4. Matrix Representation of $g_{\mathrm{VH}}(\mathbf{k},t)$

In this section, we rewrite $g_{\mathrm{VH}}(\mathbf{k},t)$ using spherical harmonics $Y_{lm}(\mathbf{u})$. The mathematics used here is very similar to, but slightly different from, that employed in 1; the difference solely comes from the fact that expansion of $s_{\mathbf{k}}(\mathbf{u})$ with spherical harmonics uses only Y_{l0}, but that of $d_{\mathbf{k}}(\mathbf{u})$ requires Y_{lm} having $m = \pm 1$ and ± 2

$$d_{\mathbf{k}}(\mathbf{u}) = i(4\pi)^{1/2} \sum_{\substack{l=2\\ \text{even}}} [\{\partial_{l2} Y_{l2}^*(\mathbf{u}) - \partial_{l,-2} Y_{l,-2}^*(\mathbf{u})\} \sin(\vartheta/2) + \{\partial_{l1} Y_{l1}^*(\mathbf{u}) + \partial_{l,-1} Y_{l,-1}^*(\mathbf{u})\} \cos(\vartheta/2)] \tag{18}$$

where

$$\partial_{lm} = [(2l+1)/6]^{1/2} \times \sum_{\substack{l'=|l-2|\\ \text{even}}}^{l+2} (-1)^{l'/2} b_{l'}(K) C(l2l';m,-m,0) C(l2l';000) \tag{19}$$

and $C(l_1l_2l_3;m_1m_2m_3)$ is the Clebsch–Gordan or C coefficient. We define a column vector $\mathbf{d}$, the lmth element of which is

$$\begin{aligned} d_{lm} &= \partial_{lm} \cos(\vartheta/2) && \text{if } l \text{ is even and } m = \pm 1 \\ &= \pm\partial_{lm} \sin(\vartheta/2) && \text{if } l \text{ is even and } m = \pm 2 \\ &= 0 && \text{otherwise} \end{aligned} \tag{20}$$

We have from operator $\Theta_{\mathbf{k}}$ matrix Θ, the $(lm,l'm')$th element of which we compute by $\langle lm|\Theta|l'm'\rangle = \int \mathrm{d}\mathbf{u}\, Y_{lm}^* \Theta_{\mathbf{k}} Y_{l'm'}$. We express matrix Θ as[9]

$$\Theta = D_{\perp}k^2\mathbf{E} + D_{\mathrm{r}}(\mathbf{R} + \mu^2\mathbf{T}) \tag{21}$$

where $\mathbf{E}$ is an identity matrix, $\mathbf{R}$ a rotational eigenvalue matrix, $\mathbf{T}$ a symmetric tridiagonal matrix that expresses the anisotropic translation, and μ^2 the coupling constant between $\mathbf{R}$ and $\mathbf{T}$.

$$\langle lm|\mathbf{E}|l'm'\rangle = \delta_{ll'}\delta_{mm'} \tag{22}$$

$$\langle lm|\mathbf{R}|l'm'\rangle = l(l+1)\delta_{ll'}\delta_{mm'} \tag{23}$$

$$\langle lm|\mathbf{T}|l'm'\rangle = \frac{1}{3}\delta_{ll'}\delta_{mm'} + \frac{2}{3}\left[\frac{2l'+1}{2l+1}\right]^{1/2} C(l'2l;m'0m) C(l'2l;000) \tag{24}$$

$$\mu^2 = (D_{\parallel} - D_{\perp})k^2/D_{\mathrm{r}} \tag{25}$$

Let W be an operator

$$W d_{\mathbf{k}}^*(\mathbf{u}) = (1/4\pi^2 bL^2) \int \mathrm{d}\mathbf{u}'\, W_{\mathbf{k}}(\mathbf{u},\mathbf{u}')\, d_{\mathbf{k}}^*(\mathbf{u}')$$

Matrix form of operator W is[9]

$$\mathbf{W} = \frac{1}{2}\mathbf{s}\mathbf{s}^{\mathrm{T}} - \mathbf{PQP} \tag{26}$$

where $\mathbf{s}$ is a column vector, the lmth element of which is given by eq 9, superscript T of $\mathbf{s}^{\mathrm{T}}$ stands for the transposition, and $\mathbf{P}$ and $\mathbf{Q}$ are matrices defined as follows.

$$\langle lm|\mathbf{P}|l'm'\rangle = \left[\frac{2l'+1}{2l+1}\right]^{1/2} \times \sum_{\substack{n=|l-l'|\\ \text{even}}}^{l+l'} (-1)^{n/2}(2n+1) b_n(K) C(l'nl;m'0m)\, C(l'nl;000) \tag{27}$$

$$\begin{aligned} \langle lm|\mathbf{Q}|l'm'\rangle &= \frac{l-1}{l+2}\left[\frac{(l-3)!!}{l!!}\right]^2 \delta_{ll'}\delta_{mm'} && \text{for } l = 2, 4, \ldots \\ &= 0 && \text{otherwise} \end{aligned} \tag{28}$$

From these, we have matrices Φ and Ω as

$$\Phi = \mathbf{E} + \pi\nu bL^2\mathbf{W} \tag{29}$$

$$\Omega = \Theta\Phi \tag{30}$$

Solving the matrix eigenvalue problem for Ω, we have the eigenvector matrix $\mathbf{U}$ and eigenvalue matrix Λ of matrix Ω: $\Omega\mathbf{U} = \mathbf{U}\Lambda$. Using $\mathbf{U}$ and Λ, we rewrite eq 14 in the matrix form as

$$g_{\mathrm{VH}}(\mathbf{k},t) = L\mathbf{d}^{\mathrm{T}}\mathbf{U} \exp[-\Lambda t]\mathbf{U}^{-1}\Phi^{-1}\mathbf{d} \tag{31}$$

We express $g_{\mathrm{VH}}(\mathbf{k},t)$ using subvector $\boldsymbol{\partial}^{(m)}$ and submatrix $\Omega^{(m)}$, the lth and ll'th elements of which are ∂_{lm} and $\langle lm|\Omega|l'm\rangle$, respectively.

$$g_{\mathrm{VH}}(\mathbf{k},t) = F(L\boldsymbol{\partial}^{\mathrm{T}}\mathbf{U} \exp[-\Lambda t]\mathbf{U}^{-1}\Phi^{-1}\boldsymbol{\partial}, \vartheta) \tag{32}$$

$$F(x,\vartheta) = 2[\{x\}^{(1)} \cos^2(\vartheta/2) + \{x\}^{(2)} \sin^2(\vartheta/2)] \tag{33}$$

$\{\ldots\}^{(m)}$ stands for the operation that extracts the mth subvector or submatrix from vectors and matrices placed between the two braces, and we made use of the diagonality and symmetry[10] of matrix Ω, $\langle lm|\Omega|l'm'\rangle = 0$ unless $m = m'$, and $\langle lm|\Omega|l'm'\rangle = \langle l,-m|\Omega|l',-m'\rangle$. [Matrix Ω is diagonal in m and symmetrical with respect to $\pm m$.] The numerical factor 2 in the right-hand side of eq 33 comes from the symmetry of the subvectors and submatrices with respect to $\pm m$.

The main results of this paper are eqs 32 and 33, which give the depolarized dynamical structure factor in the matrix representation. Though eq 31 is quite similar to the one previously derived[1] for $g(\mathbf{k},t)$, we prefer eqs 32 and 33 to eq 31 because of the complexity of the depolarized dynamical structure factor, $g_{\mathrm{VH}}(\mathbf{k},t)$. The isotropic dynamical structure factor, $g(\mathbf{k},t)$, is a function of kL (through vector $\mathbf{s}$) and ν (through matrix Φ). Since vector $\mathbf{d}$ is a function of two variables, kL and ϑ (cf. eqs 19 and 20), the depolarized dynamical structure factor, $g_{\mathrm{VH}}(\mathbf{k},t)$, is a function of three variables, kL, ϑ, and ν. Function $F(x,\vartheta)$, which describes the ϑ dependence of $g_{\mathrm{VH}}(\mathbf{k},t)$, makes it possible for us to concentrate our interest on the kL and ν dependence of $g_{\mathrm{VH}}(\mathbf{k},t)$.

5. Initial Decay Rate, Γ_{VH}

We can easily derive from eqs 32 and 33 an expression for the initial decay rate, $\Gamma_{\mathrm{VH}} \equiv -[\lim_{t\to 0}(\mathrm{d}/\mathrm{d}t)g_{\mathrm{VH}}$-

Table I
kL and ν/ν^* Dependence of $1 - R_\varphi^{(m)}$ for $m = 1$ and 2

	$\nu/\nu^* = 0.01$		$\nu/\nu^* = 0.05$		$\nu/\nu^* = 0.10$		$\nu/\nu^* = 0.50$		$\nu/\nu^* = 1.00$	
kL	$m = 1$, ×0.01	$m = 2$, ×0.01	$m = 1$, ×0.10	$m = 2$, ×0.10	$m = 1$, ×0.10	$m = 2$, ×0.10	$m = 1$	$m = 2$	$m = 1$	$m = 2$
2	0.8679	0.9548	0.4340	0.4774	0.8680	0.9548	0.4340	0.4774	0.8680	0.9548
4	0.5786	0.8435	0.2893	0.4217	0.5786	0.8435	0.2894	0.4218	0.5791	0.8438
6	0.3239	0.7149	0.1620	0.3574	0.3240	0.7149	0.1621	0.3576	0.3245	0.7154
8	0.1822	0.6026	0.0911	0.3013	0.1822	0.6027	0.0912	0.3014	0.1825	0.6030
10	0.1163	0.5155	0.0582	0.2577	0.1163	0.5155	0.0582	0.2578	0.1165	0.5158

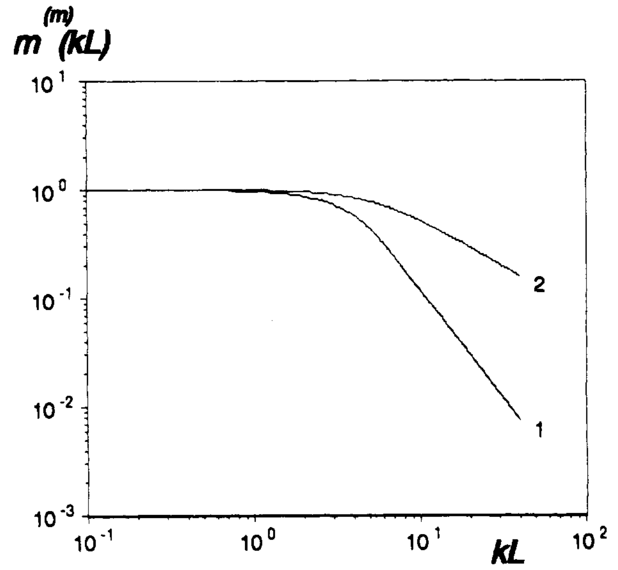

Figure 2. Double-logarithmic plot of the $\mathbf{m}^{(m)}(kL)$ vs kL relationships, where $\mathbf{m}^{(m)}(kL)$ is the strength of the concentration dependence of $R_\varphi^{(m)} \equiv \{\hat{\mathbf{d}}^T\hat{\mathbf{d}}/\hat{\mathbf{d}}^T\boldsymbol{\Phi}^{-1}\hat{\mathbf{d}}\}^{(m)}$ [$=1 - \mathbf{m}^{(m)}(kL)\ (\nu/\nu^*)$]. The numbers in the figure stand for m values.

$(\mathbf{k},t)]/g_{VH}(\mathbf{k},0)$. The denominator $g_{VH}(\mathbf{k},0)$ is given by

$$g_{VH}(\mathbf{k},0) = F(L\hat{\mathbf{d}}^T\boldsymbol{\Phi}^{-1}\hat{\mathbf{d}},\vartheta) \qquad (34)$$

As regards the numerator, it is evident that

$$\lim_{t\to 0}\,(d/dt)\{\mathbf{U}\exp(-\Lambda t)\mathbf{U}^{-1}\}^{(m)} = -\{\mathbf{U}\Lambda\mathbf{U}^{-1}\}^{(m)} = -\Omega^{(m)}$$

Therefore we have an expression for Γ_{VH} without any detailed information on Λ and $\mathbf{U}$

$$\Gamma_{VH} = [D_\perp k^2 + D_r f_1(kL,\vartheta) + (D_\parallel - D_\perp)k^2 f_2(kL,\vartheta)] \times A(kL,\vartheta,\nu) \qquad (35)$$

where

$$A(kL,\vartheta,\nu) = F(\hat{\mathbf{d}}^T\hat{\mathbf{d}},\vartheta)/F(\hat{\mathbf{d}}^T\boldsymbol{\Phi}^{-1}\hat{\mathbf{d}},\vartheta) \qquad (36)$$

$$f_1(kL,\vartheta) = F(\hat{\mathbf{d}}^T\mathbf{R}\hat{\mathbf{d}},\vartheta)/F(\hat{\mathbf{d}}^T\hat{\mathbf{d}},\vartheta) \qquad (37)$$

$$f_2(kL,\vartheta) = F(\hat{\mathbf{d}}^T\mathbf{T}\hat{\mathbf{d}},\vartheta)/F(\hat{\mathbf{d}}^T\hat{\mathbf{d}},\vartheta) \qquad (38)$$

Since only $A(kL,\vartheta,\nu)$ in eq 35 includes the mean-field hard-rod interaction potential, W, the $A(kL,\vartheta,\nu)$ term expresses the effect of the excluded-volume interaction on the initial decay rate, Γ_{VH}. Because $\boldsymbol{\Phi} = \mathbf{E}$ at $\nu = 0$, it is evident that $A(kL,\vartheta,\nu) = 1$ in the infinitely dilute regime.

6. Numerical Methods

We computed $g_{VH}(\mathbf{k},t)$ and Γ_{VH} using a 16-bit microcomputer equipped with an 80286 processor, 80287 math coprocessor, and 640K bytes of memory. The algorithm of our program[11] is almost the same as that used in 1, except we use a recurrence formula[12] for the C coefficient to compute $C(l_1l_2l_3;m0m)$ for $m = 1$, 2 from $C(l_1l_2l_3;000)$. The time typically required for computing 19 values of $g_{VH}(\mathbf{k},t)$ at $kL = 4$ was less than 2 min on our microcomputer running at 8 MHz of clock speed.[13] Using about 470K bytes of memory, we could solve the eigenvalue problem of the maximum size of 120 × 120 in double precision.

7. Results and Discussion

The depolarized dynamical structure factor, $g_{VH}(\mathbf{k},t)$, and the initial decay rate, Γ_{VH}, are functions of three variables, kL, ϑ, and ν/ν^* having three adjustable parameters, $D_\parallel$, $D_\perp$, and D_r, where ν^* ($\equiv 16/\pi bL^2$) is the characteristic concentration above which the isotropic phase becomes unstable.[14] Since we already know that function $F(x,\vartheta)$ describes the ϑ dependence of $g_{VH}(\mathbf{k},t)$ and Γ_{VH}, we shall concentrate for the moment our interest on the kL and ν/ν^* dependence of various quantities shown below:

$$R_\varphi^{(m)} \equiv \{\hat{\mathbf{d}}^T\hat{\mathbf{d}}/\hat{\mathbf{d}}^T\boldsymbol{\Phi}^{-1}\hat{\mathbf{d}}\}^{(m)}$$

eigenvalues λ_{lm} of Ω

$$S_t^{(m)} \equiv \{\hat{\mathbf{d}}^T\hat{\mathbf{d}}\}^{(m)} \text{ and } S_l^{(m)} \equiv \hat{d}_{lm}^{\,2}$$

$$R_t^{(m)} \equiv \{\hat{\mathbf{d}}^T\mathbf{T}\hat{\mathbf{d}}/\hat{\mathbf{d}}^T\hat{\mathbf{d}}\}^{(m)}$$

$$R_r^{(m)} \equiv \{\hat{\mathbf{d}}^T\mathbf{R}\hat{\mathbf{d}}/\hat{\mathbf{d}}^T\hat{\mathbf{d}}\}^{(m)}$$

7.1. kL and ν/ν^* Dependence of $R_\varphi^{(m)}$.

$R_\varphi^{(m)}$ is a quantity used for computing the excluded-volume effect term $A(kL,\vartheta,\nu)$. Table I roughly shows the kL and ν/ν^* dependence of $R_\varphi^{(m)}$ for $m = 1$ and 2, the characteristics of which are summarized as follows.

When the kL value is fixed, the ν dependence of $R_\varphi^{(m)}$ is almost linear:

$$R_\varphi^{(m)} = 1 - \mathbf{m}^{(m)}(kL)\ \nu/\nu^* \qquad (39)$$

The sign of the concentration dependence is negative, and its strength is smaller for larger kL values: $\mathbf{m}^{(m)}(0) = 1$ for both $m = 1$ and 2, $\mathbf{m}^{(m)}(4) = 0.5786$ and 0.8435 and $\mathbf{m}^{(m)}(8) = 0.1822$ and 0.6027 for $m = 1$ and 2, respectively. Figure 2 shows the kL dependence of $\mathbf{m}^{(m)}(kL)$, which we computed from the decrease of $R_\varphi^{(m)}$ from $\nu/\nu^* = 0.0$ to 0.1.

Except for the negative sign, these characteristics are quite similar to those of the excluded-volume effect term $A(kL,\nu)$ ($\equiv \mathbf{s}^T\mathbf{s}/\mathbf{s}^T\boldsymbol{\Phi}^{-1}\mathbf{s}$) for the isotropic scattering.[1] The negative sign of the ν dependence of $R_\varphi^{(m)}$ means that the excluded-volume effect causes a *decrease* of Γ_{VH} in the depolarized scattering. This is physically reasonable, because the depolarized DLS sensitively detects the orientational fluctuation of the rods, the relaxation time of which would be longer when the nematic interaction tends to align rods with increasing the rod concentration. It should be noted that both $R_\varphi^{(1)}$ and $R_\varphi^{(2)}$ become negative for $kL = 0$ and $\nu/\nu^* > 1$. The negative $R_\varphi^{(m)}$ is,

Table II
Normalized Eigenvalues $\lambda_{lm}/\lambda_{lm,0}$ of Matrix Ω for $m = 1$ and 2

	$l = 2$		$l = 4$		$l = 6$		$l = 8$		$l = 10$	
kL	$m = 1$	$m = 2$	$m = 1$	$m = 2$	$m = 1$	$m = 2$	$m = 1$	$m = 2$	$m = 1$	$m = 2$
0.2	0.9001	0.9000	0.9875	0.9875	0.9961	0.9961	0.9983	0.9983	0.9991	0.9991
2.0	0.9133	0.9046	0.9892	0.9890	0.9967	0.9966	0.9985	0.9985	0.9992	0.9992
20.0	0.9999	0.9859	0.9998	0.9930	0.9994	0.9942	0.9983	0.9974	0.9993	0.9994

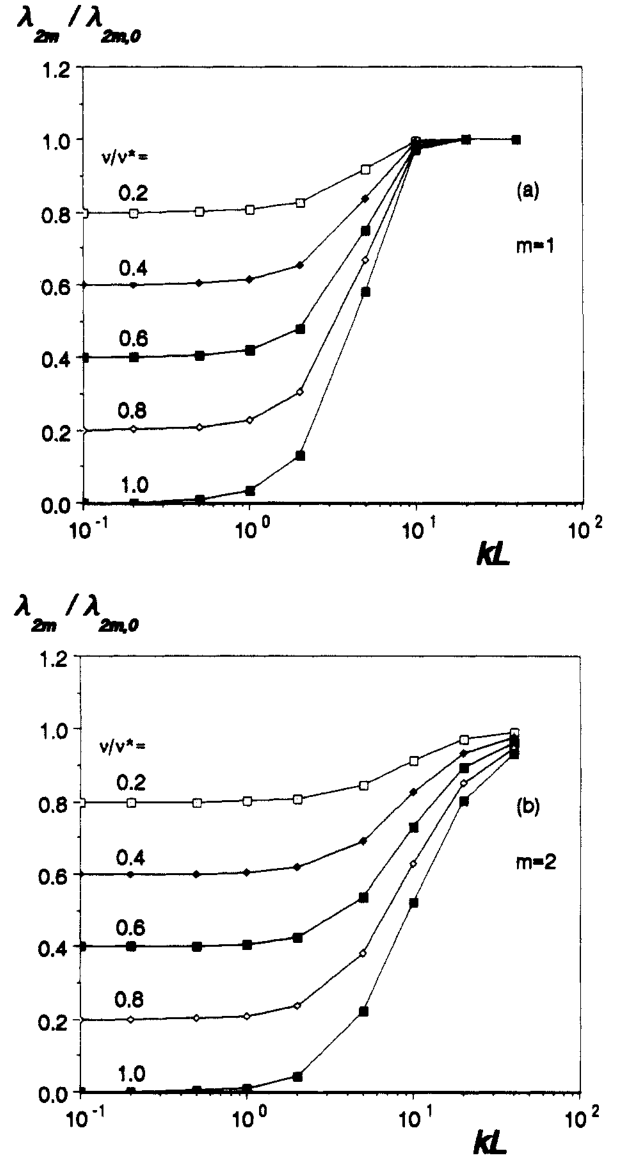

Figure 3. Semilogarithmic plot of the $\lambda_{2m}/\lambda_{2m,0}$ vs kL relationships, where λ_{2m} is the eigenvalue of matrix Ω computed for various ν/ν^* and $\lambda_{2m,0}$ is for $\nu/\nu^* = 0.0$. (a) For $m = 1$. (b) For $m = 2$. The numbers in the figures stand for ν/ν^* values.

of course, unphysical and corresponds to the fact that the isotropic phase is unstable at this concentration.

7.2. kL and l Dependence of the Eigenvalues of Matrix Ω. Table II shows normalized eigenvalues $\lambda_{lm}/\lambda_{lm,0}$ for $kL = 0.2$, 2, and 20, where λ_{lm} and $\lambda_{lm,0}$ are the lth eigenvalues of $\Omega^{(m)}$ for $\nu/\nu^* = 0.1$ and 0.0, respectively. We can see from Table II that the mean-field hard-rod interaction potential, W, affects only the lowest few eigenvalues. Figure 3 shows how the potential W affects the lowest eigenvalue λ_{2m} with increasing ν/ν^* and kL. Even when the rod concentration is high, the potential affects λ_{2m} little for $kL \geq 20$. It is evident from Figure 3 and Table II that W affects only the spatially long and temporarily slow modes of fluctuation in the solution.

7.3. kL Dependence of $S_t^{(m)}$ and $S_l^{(m)}$. The particle structure factor S_t ($\equiv \mathbf{d}^{\mathrm{T}}\mathbf{d}$) being given by $S_t = F(\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}},\vartheta)$, the quantities $S_t^{(m)}$ ($\equiv\{\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}}\}^{(m)}$) and $S_l^{(m)}$ ($\equiv \hat{d}_{lm}^{\,2}$) are, if we call them, the "cosine" ($m = 1$) or "sine" ($m = 2$) components of the particle structure factor and lth scattering factor, respectively.

Figure 4a shows semilogarithmic plots of the $S_t^{(m)}$ and $S_l^{(m)}$ vs kL relationships for $m = 1$, and Figure 4b is for $m = 2$. We can see in these figures the following two features.

1. At $kL = 0$, $S_t^{(m)} = S_2^{(m)} = 1/30$, and $S_l^{(m)} = 0$ for $l = 4, 6, ...$

2. At fixed kL, $S_l^{(m)}$ rapidly decreases with increasing subscript l. At $kL = 10$, for example, the modes that appreciably contribute to $S_t^{(m)}$ are the ones for $l = 2$, 4, and 6, and at $kL = 20$, for $l = 2, 4, ..., 14$.

Figure 4c is a double-logarithmic plot of the $S_t^{(m)}$ vs kL relationship, from which we easily estimate the exponent of the kL dependence for $kL \gg 1$ as -2 for $m = 1$ and -1 for $m = 2$. The proof for this guess is given in Appendix B.

7.4. kL Dependence of $R_t^{(m)}$ and $R_r^{(m)}$. Figures 5 and 6 are double-logarithmic plots of the $R_t^{(m)}$ ($\equiv\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{T}\hat{\mathbf{d}}/\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}}\}^{(m)}$) and $R_r^{(m)}$ ($\equiv\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{R}\hat{\mathbf{d}}/\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}}\}^{(m)}$) vs kL relationships for $m = 1$ and 2.

Table III is a summary of the asymptotic behavior of various scattering factors for $kL \to 0$ and $kL \to \infty$, the analytical forms of which are derived in Appendices A and B.

7.5. Apparent Rotational Diffusion Coefficient. Using Table III, we reinterpret eq 35 in the following way. Let us define an apparent rotational diffusion coefficient as $\Gamma_{\mathrm{VH}}/f_1(kL,\vartheta)$, which we express as a weighted sum of diffusion coefficients

$$\Gamma_{\mathrm{VH}}/f_1(kL,\vartheta) = (12/L^2)^*D_{\parallel}W_{\parallel} + (12/L^2)^*D_{\perp}W_{\perp} + {}^*D_{\mathrm{r}}W_{\mathrm{r}} \quad (40)$$

where ${}^*D_i$ for $i = \parallel, \perp$, and r are $D_{\parallel}A(kL,\vartheta,\nu)$, $D_{\perp}A(kL,\vartheta,\nu)$, and $D_{\mathrm{r}}A(kL,\vartheta,\nu)$, respectively. The weights W_i for $i = \parallel, \perp$, and r are $[(kL)^2/12](f_2/f_1)$, $[(kL)^2/12][(1-f_2)/f_1]$, and 1, respectively. Note that, if we consider $(12/L^2)^*D_i$ for $i = \parallel$ and $\perp$ as the translational diffusion coefficients expressed in units of 1/s, all the diffusion coefficients in eq 40 are similar in magnitude for $\nu/\nu^* \to 0$, because $(1/2)(12/L^2)D_{\parallel,0} = (12/L^2)D_{\perp,0} = D_{\mathrm{r},0}$ for the long rod limit.

Figure 7 shows the relationships of W_i vs $(k/k_{\max})^2$ for $k_{\max}L = 5$–20, where $k_{\max}$ ($=4\pi n/\lambda$) is the maximum length of the scattering vector. We can see from Table III and Figure 7 that

(1) $W_{\parallel}$ is at least 1 order of magnitude smaller than W_{r};

(2) $W_{\parallel} \simeq W_{\perp} \simeq O\{(kL)^2\}$ for $kL \to 0$; and

(3) $W_{\parallel} \simeq O\{(kL)^{-1}\}$ and $W_{\perp} = 1$ when $kL \to \infty$ and $\vartheta \to \pi$. Though the first and third features mean $(12/L^2)^*D_{\parallel}$ contributes much less than the others to the apparent rotational diffusion coefficient, Γ_{VH}/f_1, it does not necessarily mean that we may always neglect the lengthways translation of a rod in the depolarized DLS. If Doi and Edwards' conjecture[6] holds for the self-diffusivities

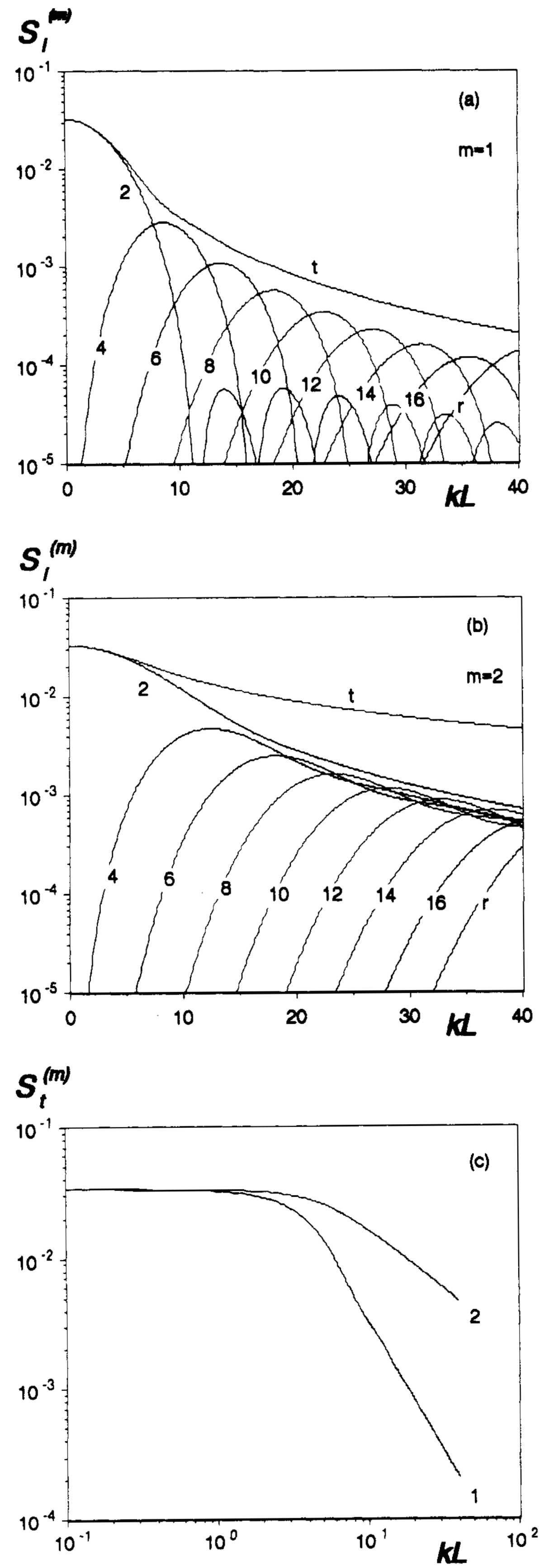

Figure 4. Relationships of various scattering factors $S_l^{(m)}$ vs kL, where $S_t^{(m)} = \{\hat{\mathbf{d}}^T\hat{\mathbf{d}}\}^{(m)}$, $S_l^{(m)} = d_{lm}^2$ for $l = 2, 4, ..., 16$, and $S_r^{(m)} = S_t^{(m)} - \sum_l S_l^{(m)}$ is the residual. (a) Semilogarithmic plot for $m = 1$. (b) Semilogarithmic plot for $m = 2$. (c) Double-logarithmic plot of $S_t^{(m)}$ for $m = 1$ and 2. Numbers and characters in (a) and (b) stand for subscript l of $S_l^{(m)}$, and numbers in (c), for m values.

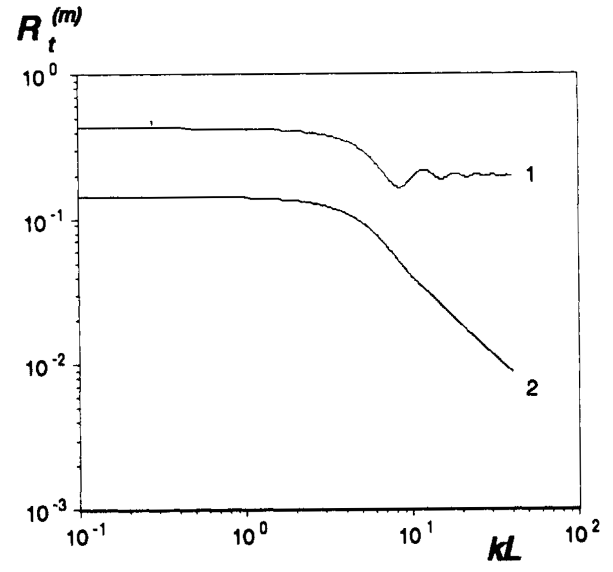

Figure 5. Double-logarithmic plot of the $R_t^{(m)}$ vs kL relationships, where $R_t^{(m)} = \{\hat{\mathbf{d}}^T\mathbf{T}\hat{\mathbf{d}}/\hat{\mathbf{d}}^T\hat{\mathbf{d}}\}^{(m)}$. The numbers in the figure stand for m values.

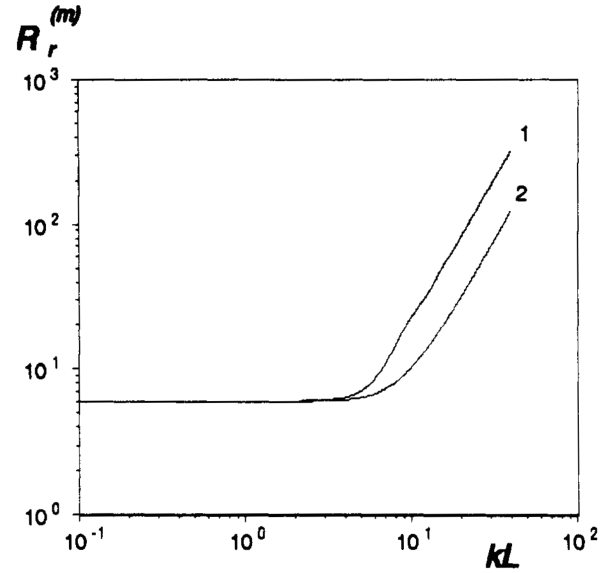

Figure 6. Double-logarithmic plot of the $R_r^{(m)}$ vs kL relationships, where $R_r^{(m)} = \{\hat{\mathbf{d}}^T\mathbf{R}\hat{\mathbf{d}}/\hat{\mathbf{d}}^T\hat{\mathbf{d}}\}^{(m)}$. The numbers in the figure stand for m values.

of a rod in the highly entangled state that $D_\parallel \simeq D_{\parallel,0}$, $D_\perp \simeq 0$, and $D_r \simeq \beta D_{r,0}(\nu L^3)^{-2}$ where β is an empirical parameter of the order of 10^3, the lengthways term $(12/L^2)^*D_\parallel W_\parallel$ would, on the contrary, dominate Γ_{VH}/f_1. From the second and third features, we have the asymptotic behavior of Γ_{VH}/f_1 in the forward and backward scattering as follows.

$$\begin{aligned}\Gamma_{VH}/f_1 &= {}^*D_r \qquad \text{for } kL \rightarrow 0 \\ &= (12/L^2)^*D_\perp + {}^*D_r \qquad \text{for } kL \rightarrow \infty \text{ and } \vartheta \rightarrow \pi\end{aligned} \tag{41}$$

In the limit of large kL and $\vartheta \simeq \pi$, the sideways translation and rotation of a rod equally contribute to the apparent rotational diffusion coefficient, and the lengthways translation does not contribute at all. This conclusion exactly corresponds to the one drawn for the isotropic scattering,[3] where $\Gamma_\mathbf{k}/k^2 = {}^*D_\perp + (L^2/12)^*D_r$ for $kL \rightarrow \infty$. When $kL \gg 1$, only those rods, the axes of which are perpendicular to the scattering vector, $\mathbf{k}$, contribute to the scattering intensity, but their lengthways transla-

Table III
Asymptotic Forms of $S_t^{(m)}$, $R_t^{(m)}$, $R_r^{(m)}$, and $\mathbf{m}^{(m)}(kL)$ for $kL = 0$ and ∞

		$S_t^{(m)}$		$R_t^{(m)}$		$R_r^{(m)}$		$\mathbf{m}^{(m)}(kL)$	
kL		$m = 1$	$m = 2$	$m = 1$	$m = 2$	$m = 1$	$m = 2$	$m = 1$	$m = 2$
0	a[a]	1/30	1/30	3/7	1/7	6	6	1	1
	b[a]	0	0	0	0	0	0	0	0
∞	a[a]	1/3	$\pi/16$	1/5	$4/3\pi$	1/5	1/12	11.72 ± 0.01[b]	4.433 ± 0.007[b]
	b[a]	−2	−1	0	−1	2	2	-1.994 ± 0.0003[b]	-0.903 ± 001[b]

[a] a and b stand for the parameters in an expression $a(kL)^b$. [b] These values were estimated from results of numerical computation for $kL = 20$–40.

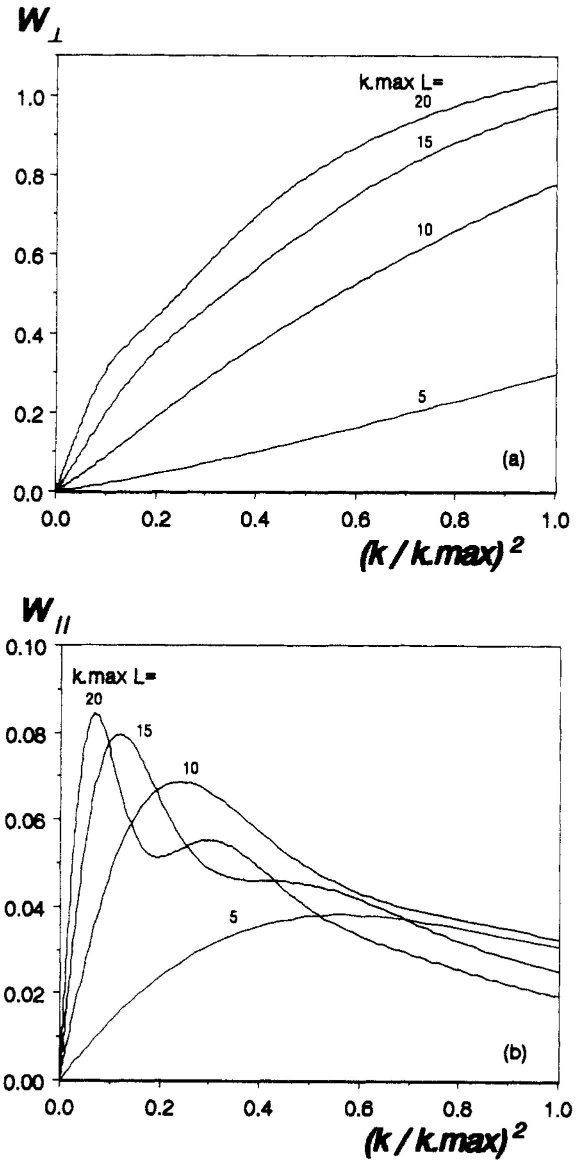

Figure 7. Relationships of $W_\perp$ and $W_\parallel$ vs $(k/k_{\max})^2$, where $W_\perp = [(kL)^2/12](f_2/f_1)$, $W_\parallel = [(kL)^2/12][(1 - f_2)/f_1]$, and $k_{\max}$ is the maximum length of the scattering vector ($=4\pi n/\lambda$, n being the refractive index of the solvent and λ the wavelength of light): (a) $W_\perp$. (b) $W_\parallel$.

tion, being perpendicular to **k**, cannot contribute to the intensity fluctuation of the scattered light.

7.6. Excluded-Volume Effect Term $A(kL,\vartheta,\nu)$. Having computed $S_t^{(m)}$ and $\mathbf{m}^{(m)}(kL)$ for $m = 1$ and 2 as functions of kL, we can easily compute $A(kL,\vartheta,\nu)$ for various L values. Figure 8 is an example of the relationships of $A(kL,\vartheta,\nu)$ vs $(k/k_{\max})^2$ for $k_{\max}L = 10$. It is evident that $A(kL,\vartheta,\nu)$ decreases with increasing ν/ν^*, and the excluded-volume effect is most conspicuous in the forward depolarized scattering.

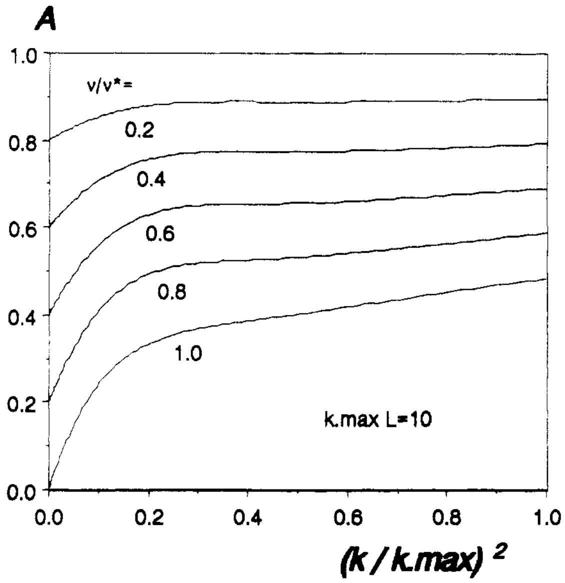

Figure 8. Relationships of $A(kL,\vartheta,\nu)$ vs $(k/k_{\max})^2$ for $k_{\max}L = 10$ and various ν/ν^*, where $k_{\max} = 4\pi n/\lambda$. The numbers in the figure stand for ν/ν^* values.

7.7. Correlation Function Profiles. Our theory, presented in 1 and the present paper, assumes that $D_\parallel$, $D_\perp$, and D_r are concentration-dependent adjustable parameters. Since there is no satisfactory theory for the concentration dependence of D_i's, we utilized in 1 an experimental datum of the strength, k_ζ, of the concentration dependence of the friction coefficient, ζ, to simulate correlation function profiles, $g(\mathbf{k},t)/g(\mathbf{k},0)$, of PBLG of molecular weight 300K. At $kL = 4$, profiles of $g(\mathbf{k},t)/g(\mathbf{k},0)$ decayed a little more *quickly* with the increase of the polymer concentration and showed no anomaly in the tail part even at $\nu L^3 = 350$, where a slow tail was observed experimentally.[15]

For comparison, using the same parameter values adopted in 1, we computed profiles of the depolarized correlation functions, $g_{\mathrm{VH}}(\mathbf{k},t)/g_{\mathrm{VH}}(\mathbf{k},0)$. If we compare the depolarized correlation functions shown in Figure 9 with the polarized ones given in Figure 2 of 1, we can easily notice that the profiles of the VH-depolarized DLS spectrum decay more *slowly* with increasing ν and are markedly concentration dependent. The reason for this difference is as follows. The self-diffusivities of a rod, in general, decrease with the increase of the polymer concentration, but $A(kL,\nu)$ for the isotropic scattering, being an increasing function of ν/ν^*, largely cancels (and sometimes overcancels) the decrease of the self-diffusivities. In the case of the VH-depolarized scattering, however, the effect of $A(kL,\vartheta,\nu)$, being a decreasing function of ν/ν^*, augments that of the decreasing self-diffusivities and makes the concentration dependence of the spectrum more marked.

7.8. On the Inverse Ninth-Power Dependence of D_r on the Rod Length. In the strongly entangled state,

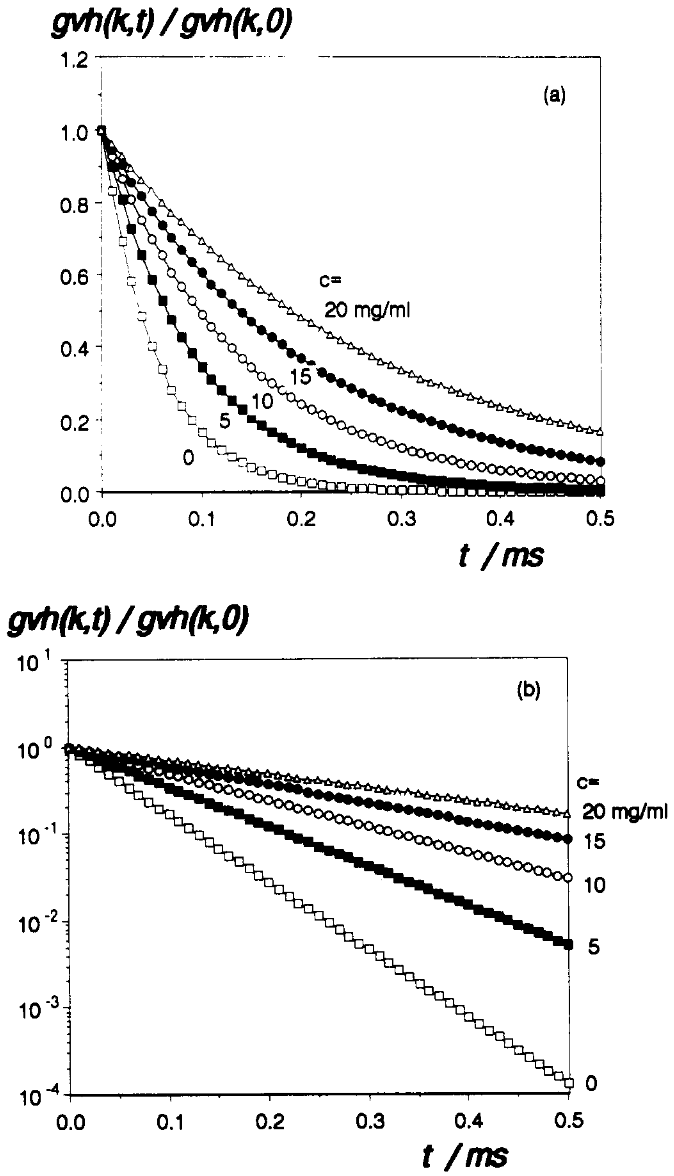

Figure 9. (a) Profiles of simulated correlation functions $g_{\mathrm{VH}}(\mathbf{k},t)/g_{\mathrm{VH}}(\mathbf{k},0)$ for suspensions of hypothetical rods of the size of the PBLG used by Russo et al.[15] (b) In semilogarithmic form. Parameter values used are the same as those used in 1: L = 205.5 nm, kL = 4, $\vartheta = \pi/2$, $D_{\mathbf{k},0} = 1.33 \times 10^{-7}$ cm²/s, $\mathbf{m}^{(m)}(kL)$ = 0.5786 for m = 1 and 0.8435 for m = 2, $\bar{v}_2$ = 0.791 cm³/g, and k_ζ = 111 cm³/g. Weight concentration c is 0, 5, 10, 15, and 20 mg/mL from bottom to top. ($\nu L^3 = 17.4c$ and $\nu/\nu^* = 2.397 \times 10^{-2}c$ with c in milligrams per milliliters.) See details in the text and 1.

the Doi–Edwards theory predicts the length dependence of D_r as[5]

$$D_r = \beta \frac{3k_BT \ln (L/b)}{\pi\eta_0}\left(\frac{M}{N_A}\right)^2 L^{-x} c^{-2} \qquad (42)$$

where η_0 is the solvent viscosity, c the weight concentration, and M the molecular weight. Here the exponent x is theoretically 9.

Using polarized and depolarized DLS techniques, Zero and Pecora[5] measured $^*D_G$ and $^*D_r$ of PBLG in 1,2-dichloroethane (DCE) in the semidilute regime. Because the theory they used for analyzing their data is equivalent to a particular case of the present theory for $kL \to 0$ and $\nu \to 0$ (cf. Appendix C), their analysis was, in the light of the present theory, done on the implicit assumption that $A(kL,\vartheta,\nu) = 1$ or $^*D_r = D_r$. Zero and Pecora, comparing the slopes of the $^*D_r$ vs c^{-2} relationships of PBLG samples having different molecular weights, estimated that $x = 7.6 \pm 0.6$. They concluded the observed x value was reasonably close to 9, but we shall show in this section that their data in fact give $x = 9.1 \pm 0.4$.

The molecular weights of the PBLG they used were 150, 170, and 210 kDa. We estimated from Figure 5 in ref 5 the values of $^*D_r$ for c = 10 and 20 mg/mL (or c^{-2} = 0.01 and 0.0025 mL²/mg², respectively) as follows: $^*D_{r,150K}$ = 13.8, $^*D_{r,170K}$ = 7.7, $^*D_{r,210K}$ = 4.8 krad/s at c^{-2} = 0.01 mL²/mg², and $^*D_{r,150K}$ = 5.41, $^*D_{r,170K}$ = 3.73, and $^*D_{r,210K}$ = 3.38 krad/s at c^{-2} = 0.0025 mL²/mg², where subscripts 150K, 170K, and 210K of $^*D_r$ stand for the molecular weight.

We estimate D_r from the $^*D_r$ values as follows.

(1) Since L_{150K} = 102.7, L_{170K} = 116.4, and L_{210K} = 143.8 nm, the kL values for these three samples at ϑ = 90° (the scattering angle used in Zero and Pecora's experiments) are kL = 2.71, 3.07, and 3.80, respectively.

(2) Our theory requires ν/ν^*, which is related to c as

$$\nu/\nu^* = Lc/4b\rho \qquad (43)$$

where ρ (=1.32 g/mL) is the density of PBLG in DCE. Adopting[1] b = 1.44 nm, we know from eq 43 the 10 mg/mL solutions of M = 150K, 170K, and 210K PBLG molecules correspond to ν/ν^* = 0.1351, 0.1531, and 0.1891, respectively, and the 20 mg/mL solutions to ν/ν^* = 0.2702, 0.3062, and 0.3783, respectively.

(3) From the values of kL, ϑ, and ν/ν^*, we have $A(kL,\vartheta,\nu)$ = 0.8846, 0.8742, and 0.8568 for the 10 mg/mL solutions and $A(kL,\vartheta,\nu)$ = 0.7690, 0.7466, and 0.7120 for the 20 mg/mL solutions of M = 150K, 170K, and 210K PBLG molecules, respectively.

(4) Dividing the previous $^*D_r$ values with these A values, we have D_r as D_r = 15.6, 8.81, and 5.60 krad/s for the 10 mg/mL solutions and D_r = 7.04, 5.00, and 4.75 krad/s for the 20 mg/mL solutions of the PBLG.

We compute from these D_r values the corrected exponent x as x = 8.69, 9.33, and 9.09, the average of which is 9.1 ± 0.4. Though the $^*D_r$ values we estimated from Figure 5 in ref 5 may not be so precise, it may be well to say that Zero and Pecora's data of $^*D_r$ give D_r, which is inversely proportional to the ninth-power of the rod length.

8. Conclusion

We formulated the VH-depolarized dynamical structure factor, $g_{\mathrm{VH}}(\mathbf{k},t)$, in the matrix representation, which complements $g(\mathbf{k},t)$ previously derived for the isotropic scattering. The evaluation of both structure factors being quite easy and straightforward, we are now able to compute such quantities as the static structure factor, initial decay rate, and profile of the dynamic light scattering spectrum in the entire range of $\mathbf{k}$, t, and ν for both polarized and depolarized scatterings.

The quantity $A(kL,\vartheta,\nu)$ expresses the excluded-volume effect in the depolarized scattering as $A(kL,\nu)$ does in the isotropic scattering. The effect of the concentration increase on $A(kL,\nu)$ and $A(kL,\vartheta,\nu)$ is most conspicuous in the forward scattering, but the sign is opposite; the former increases but the latter decreases with ν. The mean-field hard-rod interaction among rods in both cases affects only the spatially long and temporarily slow modes of fluctuation in the solution. While the excluded-volume effect causes an *increase* in the initial decay rate, $\Gamma_{\mathbf{k}}$, of the isotropic scattering, it causes a *decrease* in Γ_{VH} of the depolarized scattering. The self-diffusivities of a rod, in general, decrease with the concentration because of the rod entanglement and hydrodynamic interaction, but $A(kL,\nu)$ for the isotropic scattering largely cancels the decrease and thus makes the polarized DLS spec-

Table IV
Various Scattering Factors as Functions of kL^a

kL	$S_t^{(m)}$		$R_t^{(m)}$		$R_r^{(m)}$		$\mathbf{m}^{(m)}(kL)$	
	$m = 1$	$m = 2$	$m = 1$	$m = 2$	$m = 1$	$m = 2$	$m = 1$	$m = 2$
0.0	$3.3333^{(-2)}$	$3.3333^{(-2)}$	$4.2857^{(-1)}$	$1.4286^{(-1)}$	6.0000	6.0000	1.0000	1.0000
1.0	3.2165	3.2941	4.2401	1.4060	6.0013	6.0007	$9.6499^{(-1)}$	$9.8825^{(-1)}$
2.0	2.8909	3.1814	4.1005	1.3402	6.0223	6.0105	8.6795	9.5478
3.0	2.4234	3.0094	3.8590	1.2363	6.1202	6.0526	7.3010	9.0438
4.0	1.9019	2.7979	3.5067	1.1035	6.4132	6.1630	5.7863	8.4350
5.0	1.4094	2.5684	3.0436	$9.5432^{(-2)}$	7.1125	6.3864	4.3812	7.7861
6.0	1.0036	2.3400	2.5044	8.0371	8.5394	6.7676	3.2395	7.1490
7.0	$7.0776^{(-3)}$	2.1266	1.9947	6.6607	$1.1032^{(+1)}$	7.3421	2.4012	6.5571
8.0	5.1426	1.9362	1.6869	5.5199	1.4626	8.1270	1.8220	6.0266
9.0	3.9694	1.7711	1.6902	4.6559	1.8763	9.1199	1.4299	5.5607
10.0	3.2549	1.6299	1.9029	4.0425	2.2722	$1.0305^{(+1)}$	1.1632	5.1549
11.0	2.7613	1.5090	2.1065	3.6112	2.6408	1.1667	$9.7321^{(-2)}$	4.8015
12.0	2.3577	1.4045	2.1668	3.2873	3.0354	1.3195	8.2630	4.4920
13.0	2.0030	1.3132	2.0889	3.0167	3.5142	1.4887	7.0604	4.2189
14.0	1.7024	1.2326	1.9642	2.7747	4.0945	1.6748	6.0712	3.9762
15.0	1.4656	1.1609	1.8958	2.5577	4.7388	1.8780	5.2714	3.7591
16.0	1.2877	1.0970	1.9247	2.3699	5.3858	2.0985	4.6323	3.5639
17.0	1.1508	1.0396	2.0063	2.2122	6.0108	2.3359	4.1173	3.3878
18.0	1.0355	$9.8791^{(-3)}$	2.0646	2.0794	6.6486	2.5900	3.6875	3.2280
19.0	$9.3089^{(-4)}$	9.4108	2.0594	1.9636	7.3569	2.8606	3.3154	3.0826
20.0	8.3560	8.9844	2.0072	1.8584	8.1638	3.1480	2.9893	2.9495
21.0	7.5284	8.5943	1.9581	1.7611	9.0446	3.4521	2.7063	2.8273
22.0	6.8444	8.2363	1.9518	1.6720	9.9423	3.7731	2.2641	2.7148
23.0	6.2835	7.9067	1.9864	1.5921	$1.0822^{(+2)}$	4.1109	2.2572	2.6108
24.0	5.8010	7.6024	2.0265	1.5210	1.1703	4.4653	2.0774	2.5145
25.0	5.3588	7.3206	2.0382	1.4571	1.2641	4.8364	1.9170	2.4250
26.0	4.9445	7.0589	2.0162	1.3981	1.3673	5.2241	1.7719	2.3416
27.0	4.5663	6.8150	1.9836	1.3428	1.4789	5.6286	1.6412	2.2637
28.0	4.2359	6.5873	1.9692	1.2910	1.5937	6.0498	1.5249	2.1909
29.0	3.9533	6.3743	1.9829	1.2430	1.7071	6.4878	1.4221	2.1225
30.0	3.7060	6.1746	2.0093	1.1990	1.8198	6.9424	1.3305	2.0583
31.0	3.4787	5.9870	2.0244	1.1585	1.9368	7.4136	1.2473	1.9978
32.0	3.2630	5.8104	2.0168	1.1208	2.0625	7.9016	1.1706	1.9408
33.0	3.0605	5.6439	1.9957	1.0851	2.1974	8.4062	1.1000	1.8869
34.0	2.8770	5.4866	1.9806	1.0513	2.3368	8.9275	1.0356	1.8360
35.0	2.7151	5.3379	1.9839	1.0194	2.4758	9.4655	$9.7726^{(-3)}$	1.7877
36.0	2.5714	5.1969	2.0007	$9.8950^{(-3)}$	2.6134	$1.0020^{(+2)}$	9.2437	1.7419
37.0	2.4390	5.0632	2.0151	9.6162	2.7538	1.0592	8.7575	1.6984
38.0	2.3129	4.9363	2.0149	9.3538	2.9020	1.1180	8.3046	1.6569
39.0	2.1926	4.8155	2.0018	9.1044	3.0598	1.1784	7.8811	1.6175
40.0	2.0807	4.7004	1.9884	8.8659	3.2236	1.2406	7.4879	1.5799

[a] Numbers in parentheses stand for the powers of 10; for example, $3.3333^{(-2)}$ means 3.3333×10^{-2}. They are omitted except when their value changes.

trum much less sensitive to the polymer concentration than the depolarized one.

The apparent rotational diffusion coefficient, $\Gamma_{\mathrm{VH}}/f_1(kL,\vartheta)$, is expressed as a weighted sum of the diffusion coefficients $^*D_i$ for $i = \parallel, \perp$, and r. Though the weight $W_{\parallel}$ for the lengthways translation is always at least 1 order of magnitude smaller than W_r, there is a possibility that the lengthways term $(12/L^2)^*D_{\parallel}W_{\parallel}$ can dominate Γ_{VH}/f_1 if Doi-Edwards' conjecture that $D_{\parallel} \simeq D_{\parallel,0}$, $D_{\perp} \simeq 0$, $D_r \simeq \beta D_{r,0}(\nu L^3)^{-2}$ holds in the highly entangled state.

Reanalyzing Zero and Pecora's data[5] of the depolarized DLS of PBLG in the semidilute regime, we estimated D_r from the observed $^*D_r$ values. The estimated D_r was inversely proportional to the ninth-power of the rod length, which is just the power law predicted by the Doi–Edwards theory.

The dynamical structure factors, $g(\mathbf{k},t)$ and $g_{\mathrm{VH}}(\mathbf{k},t)$, derived in 1 and the present paper would be useful for studying the excluded-volume effect among rodlike polymers and concentration dependence of the self-diffusivities in the strongly entangled state.

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Appendix

A. Scattering Factors for $kL \ll 1$. We shall derive in this section analytical forms of scattering factors $\{\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}}\}^{(m)}$ $\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{T}\hat{\mathbf{d}}\}^{(m)}$ $\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{R}\hat{\mathbf{d}}\}^{(m)}$, and $\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{\Phi}^{-1}\hat{\mathbf{d}}\}^{(m)}$ for $kL \ll 1$.

Since the lth order spherical Bessel function $j_l(x)$ is approximated by $j_l(x) \simeq x^l/(2l + 1)!!$ for $x \ll 1$, we have from eq 10

$$b_l(K) \simeq \frac{K^l}{(l + 1)(2l + 1)!!}$$

where $K = kL/2$. When $K \ll 1$, all $b_l(K)$, except for $l = 0$, are negligibly small. Substituting this fact into eq 19 and using the formula[16] for $C(220;m,-m,0)$, we easily have an expression for vector element $\hat{d}_{lm}$

$$\hat{d}_{lm} = (-1)^m/(30)^{1/2} \quad \text{for } l = 2$$
$$= O(K^l) \quad \text{otherwise} \qquad \text{(A.1)}$$

for $m = 1$ and 2.

Column vector $\hat{\mathbf{d}}^{(m)}$ having only one nonzero component $\hat{d}_{2m}$ for $K = 0$, it is evident that we only need $\langle 2m|\mathbf{T}|2m\rangle$, $\langle 2m|\mathbf{R}|2m\rangle$, and $\langle 2m|\mathbf{\Phi}^{-1}|2m\rangle$ to compute scattering factors $\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{T}\hat{\mathbf{d}}\}^{(m)}$, $\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{R}\hat{\mathbf{d}}\}^{(m)}$, and $\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{\Phi}^{-1}\hat{\mathbf{d}}\}^{(m)}$. Using eq 24 and a formula for the C coefficient $C(222;m0m)$, we easily have $\langle 2m|\mathbf{T}|2m\rangle = (11 - 2m^2)/7$. It is almost self-evident that $\langle 2m|\mathbf{R}|2m\rangle = 6$. In order to compute $\langle 2m|\mathbf{\Phi}^{-1}|2m\rangle$, we have to know the form of matrix $\mathbf{W}$ for $K \ll 1$. From eq 26 to eq 28, we know that matrix $\mathbf{W}^{(m)}$ is diagonal for $K \to 0$, the lth diagonal element of which is $\langle lm|\mathbf{W}|lm\rangle = -\langle lm|\mathbf{Q}|lm\rangle$. Matrix $\mathbf{\Phi}$ $(=\mathbf{E} + \pi\nu bL^2\mathbf{W})$ is diagonal and so also is its inverse. We thus have the lth diagonal element of $\{\mathbf{\Phi}^{(m)}\}^{-1}$ as

$$\langle lm|\mathbf{\Phi}^{-1}|lm\rangle = \frac{1}{1 - \pi\nu bL^2\langle lm|\mathbf{Q}|lm\rangle} \quad \text{for } m = 1 \text{ and } 2$$

From these considerations, we have the scattering factors for $kL \ll 1$ as

$$\{\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}}\}^{(m)} = 1/30 \qquad \text{(A.2)}$$

$$\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{T}\hat{\mathbf{d}}\}^{(m)} = (11 - 2m^2)/(7)(30) \qquad \text{(A.3)}$$

$$\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{R}\hat{\mathbf{d}}\}^{(m)} = 6/30 \qquad \text{(A.4)}$$

$$\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{\Phi}^{-1}\hat{\mathbf{d}}\}^{(m)} = 1/\{30(1 - \nu/\nu^*)\} \qquad \text{(A.5)}$$

where $\nu^* = 16/\pi\nu bL^2$.

B. Scattering Factors for $kL \gg 1$. Though we can easily guess from Figures 2 and 4–6 the exponent of the kL dependence of the scattering factors $\{\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}}\}^{(m)}$, $\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{T}\hat{\mathbf{d}}\}^{(m)}$, $\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{R}\hat{\mathbf{d}}\}^{(m)}$, and $\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{\Phi}^{-1}\hat{\mathbf{d}}\}^{(m)}$ for $kL \gg 1$, we shall derive in this section asymptotic forms for the first three of these scattering factors. (We have not yet succeeded in doing so for the last.) These scattering factors written in the matrix representation being not suitable for our purpose, we start from analytical expressions for these quantities.

Since it is clear from eq 18 that $d_{\mathbf{k}}(\mathbf{u}) = i(4\pi)^{1/2}\cdot\sum_{lm} d_{lm} Y_{lm}{}^*(\mathbf{u})$, we know the depolarized particle structure factor, $\mathbf{d}^{\mathrm{T}}\mathbf{d}$, is expressed as $\mathbf{d}^{\mathrm{T}}\mathbf{d} = (1/4\pi)\int \mathrm{d}\mathbf{u}\, d_{\mathbf{k}}{}^*(\mathbf{u})\, d_{\mathbf{k}}(\mathbf{u})$. Substituting eqs 6 and 8 and an explicit form of $\hat{\alpha}_{\mathrm{VH}}(\mathbf{u})$ into $d_{\mathbf{k}}(\mathbf{u})$, we can easily carry out the integration with respect to ϕ

$$\frac{1}{4\pi}\int \mathrm{d}\mathbf{u}\, d_{\mathbf{k}}{}^*(\mathbf{u})\, d_{\mathbf{k}}(\mathbf{u}) = I_{\mathrm{cc}}\cos^2\frac{\vartheta}{2} + I_{\mathrm{ss}}\sin^2\frac{\vartheta}{2} \qquad \text{(B.1)}$$

$$I_{\mathrm{cc}} = \frac{1}{4K^3}\int_{-K}^{K}\mathrm{d}x\left(1 - \frac{x^2}{K^2}\right)\sin^2 x \qquad \text{(B.2)}$$

$$I_{\mathrm{ss}} = \frac{1}{16K}\int_{-K}^{K}\mathrm{d}x\left(1 - \frac{x^2}{K^2}\right)^2 j_0(x)^2 \qquad \text{(B.3)}$$

where $K = kL/2$. Using a formula[17] for $\int \mathrm{d}x\, j_0(x)^2$, we have

$$I_{\mathrm{cc}} = \frac{1}{2K^3}\left\{\frac{K}{3} - \frac{1}{2}j_1(2K)\right\} \qquad \text{(B.4)}$$

$$I_{\mathrm{ss}} = \frac{1}{16K}\left[\mathrm{Si}(2K) + \frac{1}{8K^4}\{(2K^2 + 1)\sin 2K + 2K(2K^2 - 1)\cos 2K\}\right] \qquad \text{(B.5)}$$

where $\mathrm{Si}(x)$ is the sine integral defined by $\mathrm{Si}(x) = \int_0^x \mathrm{d}t\, \sin t/t$. Since $\mathbf{d}^{\mathrm{T}}\mathbf{d} = 2[\{\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}}\}^{(1)}\cos^2(\vartheta/2) + \{\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}}\}^{(2)}\sin^2(\vartheta/2)]$, it is evident that $\{\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}}\}^{(1)} = I_{\mathrm{cc}}/2$ and $\{\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}}\}^{(2)} = I_{\mathrm{ss}}/2$. We thus know the asymptotic forms of $\{\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}}\}^{(1)}$ and $\{\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}}\}^{(2)}$ for $kL \gg 1$ as

$$\lim_{kL\to\infty}\{\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}}\}^{(1)} = \frac{1}{3}(kL)^{-2} \qquad \text{(B.6)}$$

$$\lim_{kL\to\infty}\{\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}}\}^{(2)} = \frac{\pi}{16}(kL)^{-1} \qquad \text{(B.7)}$$

Since matrix $\mathbf{T}$ comes from the term $(D_{\parallel} - D_{\perp})(\mathbf{k}\cdot\mathbf{u})^2$ in eq 15, we compute $\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{T}\hat{\mathbf{d}}\}^{(m)}$ from $(1/4\pi)\int \mathrm{d}\mathbf{u}\, d_{\mathbf{k}}{}^*(\mathbf{u})\cos^2\theta\, d_{\mathbf{k}}(\mathbf{u})$.

$$\frac{1}{4\pi}\int \mathrm{d}\mathbf{u}\, d_{\mathbf{k}}{}^*(\mathbf{u})\cos^2\theta\, d_{\mathbf{k}}(\mathbf{u}) = T_{\mathrm{cc}}\cos^2\frac{\vartheta}{2} + T_{\mathrm{ss}}\sin^2\frac{\vartheta}{2} \qquad \text{(B.8)}$$

$$T_{\mathrm{cc}} = \frac{1}{4K^5}\int_{-K}^{K}\mathrm{d}x\left(1 - \frac{x^2}{K^2}\right)x^2\sin^2 x \qquad \text{(B.9)}$$

$$T_{\mathrm{ss}} = \frac{1}{16K^3}\int_{-K}^{K}\mathrm{d}x\left(1 - \frac{x^2}{K^2}\right)^2\sin^2 x \qquad \text{(B.10)}$$

Similarly to I_{cc} and I_{ss}, we compute T_{cc} and T_{ss}, from which we obtain $\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{T}\hat{\mathbf{d}}\}^{(m)}$ for $m = 1$ and 2. Retaining only the leading term in K, we have the asymptotic forms of $\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{T}\hat{\mathbf{d}}\}^{(1)}$ and $\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{T}\hat{\mathbf{d}}\}^{(2)}$ for $kL \gg 1$ as follows:

$$\lim_{kL\to\infty}\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{T}\hat{\mathbf{d}}\}^{(1)} = (1/15)(kL)^{-2} \qquad \text{(B.11)}$$

$$\lim_{kL\to\infty}\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{T}\hat{\mathbf{d}}\}^{(2)} = (1/12)(kL)^{-2} \qquad \text{(B.12)}$$

Since the origin of matrix $\mathbf{R}$ is the term $D_{\mathrm{r}}\mathcal{R}^2$ in eq 15, we compute $\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{R}\hat{\mathbf{d}}\}^{(m)}$ from $(1/4\pi)\int \mathrm{d}\mathbf{u}\, d_{\mathbf{k}}{}^*(\mathbf{u})\,\mathcal{R}^2\, d_{\mathbf{k}}(\mathbf{u})$, the computation of which is tedius but straightforward. Asymptotic forms of $\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{R}\hat{\mathbf{d}}\}^{(1)}$ and $\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{R}\hat{\mathbf{d}}\}^{(2)}$ thus obtained are

$$\lim_{kL\to\infty}\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{R}\hat{\mathbf{d}}\}^{(1)} = 1/15 \qquad \text{(B.13)}$$

$$\lim_{kL\to\infty}\{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{R}\hat{\mathbf{d}}\}^{(2)} = (\pi/192)kL \qquad \text{(B.14)}$$

Using eqs B.6, B.7, B.11, and B.12, we have

$$\lim_{kL\to\infty}\left\{\frac{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{T}\hat{\mathbf{d}}}{\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}}}\right\}^{(1)} = 1/5 \qquad \text{(B.15)}$$

$$\lim_{kL\to\infty}\left\{\frac{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{T}\hat{\mathbf{d}}}{\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}}}\right\}^{(2)} = (4/3\pi)(kL)^{-1} \qquad \text{(B.16)}$$

Similarly

$$\lim_{kL\to\infty}\left\{\frac{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{R}\hat{\mathbf{d}}}{\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}}}\right\}^{(1)} = (1/5)(kL)^2 \qquad \text{(B.17)}$$

$$\lim_{kL\to\infty}\left\{\frac{\hat{\mathbf{d}}^{\mathrm{T}}\mathbf{R}\hat{\mathbf{d}}}{\hat{\mathbf{d}}^{\mathrm{T}}\hat{\mathbf{d}}}\right\}^{(2)} = (1/12)(kL)^2 \qquad \text{(B.18)}$$

C. Relationships with Zero and Pecora's Theory. Zero and Pecora presented a theory of the depolarized dynamic light scattering of rodlike polymers.[5] We shall show in this section that, except for a constant numerical factor, their polarizability time autocorrelation function, $I_{\mathrm{VH}}{}^{\alpha}(\mathbf{k},t)$, is equivalent to our $g_{\mathrm{VH}}(\mathbf{k},t)$ for $kL \ll 1$ and $\nu/\nu^* \ll 1$.

The polarizability time autocorrelation function,

$I_{\rm VH}{}^{\alpha}(\mathbf{k},t)$, in the present notation, is defined as

$$I_{\rm VH}{}^{\alpha}(\mathbf{k},t) = \langle N\rangle(\Delta\alpha)^2\int {\rm d}\mathbf{u}_0\int {\rm d}\mathbf{u}_t\, \hat{\alpha}_{\rm VH}{}^*(\mathbf{u}_0)\, G_{\rm s}(\mathbf{k},t)\, \hat{\alpha}_{\rm VH}(\mathbf{u}_t) \quad \text{(C.1)}$$

where $\langle N\rangle$ is the average number of molecules in the scattering volume and $\mathbf{u}_0$ and $\mathbf{u}_t$ are, respectively, the orientation unit vector of a rod at times 0 and t. $G_{\rm s}(\mathbf{k},t)$ is the spatial Fourier transform of the joint probability function $G_{\rm s}(\mathbf{r},\mathbf{u}_t,t;0,\mathbf{u}_0,0)$ for the rod to be at position $r = 0$ with orientation $\mathbf{u} = \mathbf{u}_0$ at time $t = 0$ and at position $r = r$ with orientation $\mathbf{u} = \mathbf{u}_t$ at time t.

Expanding $G_{\rm s}(\mathbf{k},t)$ in spherical harmonics $Y_{lm}{}^*(\mathbf{u}_t)$, we have

$$G_{\rm s}(\mathbf{k},t) = \frac{1}{4\pi}\sum_{lm} C_{lm}(\mathbf{k},t)\, Y_{lm}{}^*(\mathbf{u}_t) \quad \text{(C.2)}$$

Let $\mathbf{c}(t)$ be a column vector, the lmth element of which is $C_{lm}(\mathbf{k},t)$. Since $G_{\rm s}(\mathbf{k},t)$ obeys the diffusion equation, $\partial G_{\rm s}/\partial t = -\Theta_{\mathbf{k}} G_{\rm s}$, we have a kinetic equation for vector $\mathbf{c}(t)$ as

$$\partial \mathbf{c}(t)/\partial t = -\boldsymbol{\Theta}\mathbf{c}(t) \quad \text{(C.3)}$$

where matrix $\boldsymbol{\Theta}$ is given by eq 21. (If we write eq C.3 in the component representation, we can easily find out that eq C.3 is equivalent to eq III.2 in ref 5.) Using the diagonality of matrix $\boldsymbol{\Theta}$ with respect to m, Zero and Pecora separated eq C.3 for each m, truncated the size of submatrix $\boldsymbol{\Theta}^{(m)}$ to 2 × 2, and analytically solved the kinetic equation for subvector $\mathbf{c}^{(m)}$. Our method, on the other hand, at first solves the matrix eigenvalue problem $\boldsymbol{\Theta}\mathbf{U} = \mathbf{U}\boldsymbol{\Lambda}$, computes the solution vector as $\mathbf{c}(t) = \mathbf{U}\cdot\exp(-\boldsymbol{\Lambda}t)\cdot\mathbf{U}^{-1}\mathbf{c}(0)$, and writes the Green function $G_{\rm s}(\mathbf{k},t)$ as

$$G_{\rm s}(\mathbf{k},t) = \frac{1}{4\pi}\sum_{lm}\sum_{l'm'} Y_{lm}{}^*(\mathbf{u}_t)\, \langle lm|\mathbf{L}(t)|l'm'\rangle\, Y_{l'm'}(\mathbf{u}_0) \quad \text{(C.4)}$$

where matrix $\mathbf{L}(t)$ ($\equiv\mathbf{U}\exp(-\boldsymbol{\Lambda}t)\mathbf{U}^{-1}$) describes the time evolution of the system, and we used the initial condition that $\mathbf{c}(0) = \sum_{l'm'} Y_{l'm'}(\mathbf{u}_0)$.

Substituting eqs 7 and C.4 into eq C.1 and integrating with respect to $\mathbf{u}_0$ and $\mathbf{u}_t$, we have[18]

$$\begin{aligned} I_{\rm VH}{}^{\alpha}(\mathbf{k},t) &= \langle N\rangle\frac{(\Delta\alpha)^2}{30}\times \\ &\quad \Big[\{\langle 21|\mathbf{L}(t)|21\rangle + \langle 2,-1|\mathbf{L}(t)|2,-1\rangle\}\cos^2\frac{\vartheta}{2} + \\ &\quad \{\langle 22|\mathbf{L}(t)|22\rangle + \langle 2,-2|\mathbf{L}(t)|2,-2\rangle\}\sin^2\frac{\vartheta}{2}\Big] = \\ &\quad \langle N\rangle(\Delta\alpha)^2\mathbf{z}^{\rm T}\mathbf{L}(t)\mathbf{z} \end{aligned} \quad \text{(C.5)}$$

where $\mathbf{z}$ is a column vector, the lmth element of which is

$$\begin{aligned} z_{lm} &= -\frac{1}{(30)^{1/2}}\cos\frac{\vartheta}{2} \qquad \text{if } l = 2 \text{ and } m = \pm 1 \\ &= \pm\frac{1}{(30)^{1/2}}\sin\frac{\vartheta}{2} \qquad \text{if } l = 2 \text{ and } m = \pm 2 \\ &= 0 \qquad \text{otherwise} \end{aligned} \quad \text{(C.6)}$$

Using eqs A.1 and 20, we know that vector $\mathbf{z}$ is nothing but vector $\mathbf{d}$ for $kL \ll 1$. Since $\boldsymbol{\Phi} = \mathbf{E}$ for $\nu = 0$, we have from eqs C.5 and 31 the relationship between Zero and Pecora's $I_{\rm VH}{}^{\alpha}(\mathbf{k},t)$ and our $g_{\rm VH}(\mathbf{k},t)$ as

$$I_{\rm VH}{}^{\alpha}(\mathbf{k},t) = \frac{\langle N\rangle(\Delta\alpha)^2}{L}\lim_{\substack{kL\to 0\\ \nu\to 0}} g_{\rm VH}(\mathbf{k},t) \quad \text{(C.7)}$$

D. Scattering Factors as Functions of *kL*. For the purpose of practical use, we present here Table IV that lists $S_t{}^{(m)}$, $R_t{}^{(m)}$, $R_{\rm r}{}^{(m)}$, and $\mathbf{m}^{(m)}(kL)$ for $m = 1$ and 2 for $kL = 0$–40. Using Table IV, we can compute the initial decay rate, $\Gamma_{\rm VH}$, for $0 \le kL \le 40$ and $0 \le \nu/\nu^* < 1$. (As for $\Gamma_{\mathbf{k}}$, use Table I of ref 3 and Table II of ref 1.)

Supplementary Material Available: A source program, written in Microsoft FORTRAN V.4.1, that computes $g_{\rm VH}(\mathbf{k},t)$ at delay times of 0 s and 1 μs to 0.5 s in steps of 1, 2, and 5, test input data, and results of computation (98 pages). Ordering information is given on any current masthead page. See also ref 13.

References and Notes

(1) Maeda, T. *Macromolecules* **1989**, *22*, 1881. Equation A.7 in this paper should read as

$$\lim_{kL\to\infty} A(kL,\nu) \simeq 1 + (\pi\nu bL^2/2)\mathbf{s}^{\rm T}\mathbf{s}O(1)$$

(2) Berne, B. J.; Pecora, R. *Dynamic Light Scattering*; John Wiley & Sons: New York, 1976.

(3) Maeda, T.; Fujime, S. *Macromolecules* **1984**, *17*, 1157.

(4) Doi, M.; Shimada, T.; Okano, K. *J. Chem. Phys.* **1988**, *88*, 4070.

(5) Zero, K. M.; Pecora, R. *Macromolecules* **1982**, *15*, 87.

(6) Doi, M.; Edwards, S. F. *J. Chem. Soc. Faraday Trans. 2* **1978**, *74*, 560.

(7) The polar axis being antiparallel to the z axis, the arguments of the trigonometric functions in eq 4 are not θ and ϕ but $\pi - \theta$ and $-\phi$.

(8) Doi, Shimada, and Okano defined the (isotropic) dynamical structure factor as $g(\mathbf{k},t) = (1/\nu LV)\langle c_{\mathbf{k}}(t)\, c_{-\mathbf{k}}(0)\rangle$. Our definition for the depolarized one is slightly different from theirs in our using $c_{\mathbf{k}}{}^*(0)$ in place of $c_{-\mathbf{k}}(0)$. This difference comes from the fact that $\hat{\alpha}_{\rm VH}(\mathbf{u})$ in eq 6 does not include $\mathbf{k}$ but is expressed in terms of $Y_{2m}(\mathbf{u})$.

(9) If we put $m = m' = 0$ in eqs 21 and 26 and use Racah's expression[12] for $C(l_1l_2l_3;000)$, we have matrices $\boldsymbol{\Theta}$ and $\mathbf{W}$ for the isotropic scattering.

(10) These properties can be derived from the symmetry of the C coefficient. See ref 12.

(11) We completely neglect elements of vectors and matrices having odd l or l', because of the properties of matrix $\boldsymbol{\Omega}$ that $\langle lm|\boldsymbol{\Omega}|l'm'\rangle = 0$ unless l and l' have the same parity. [There is no parity mixing for l and l'.]

(12) Rose, M. E. *Elementary Theory of Angular Momentum*; John Wiley & Sons: New York, 1957.

(13) The program, written on a 5.25-in., 1.2-Mbyte diskette in PC-DOS format, is available on request to the author.

(14) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.

(15) Russo, P. S.; Karasz, F. E.; Langley, K. H. *J. Chem. Phys.* **1984**, *80*, 5312.

(16) Abramowitz, M.; Stegun, I. A. *Handbook of Mathematical Functions—with Formulas, Graphs, and Mathematical Tables*; Dover: New York, 1972.

(17) See, for example, Chapter 8 of ref 2.

(18) There are typographical errors in eq III.7 of ref 5, in which the position of $\sin^2(\theta/2)$ and $\cos^2(\theta/2)$ be exchanged.