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Rotational and Translational Diffusion in Semidilute Solutions of Rigid-Rod Macromolecules

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ABSTRACT: Dynamic light scattering studies were done on solutions of poly(γ-benzyl L-glutamate) (PBLG) in 1,2-dichloroethane. In this solvent, PBLG exists as a rigid α helix with a length per residue of 1.5 Å and a diameter of 15 Å. The concentration of the solutions ranged between 4 and 50 mg/mL, and the molecular weights of the PBLG were between 150 000 and 210 000. The rotational diffusion coefficients were inversely proportional to the concentration squared and to about the eighth power of the length for concentrations above 5 mg/mL and roughly equivalent to the infinite-dilution values below 5 mg/mL. The translational diffusion coefficients had little concentration dependence and were roughly two-thirds of the predicted infinite-dilution value.

I. Introduction

For dilute solutions, the overall dimensions of a polymer can be related to the translational and rotational diffusion coefficients by simple equations derived from hydrodynamics.[1-5] Thus, any technique, such as dynamic light scattering, which can measure these diffusion coefficients should also yield information about molecular dimensions. However, because the intensity of scattered light is relatively low, the diffusion coefficients for truly dilute solutions are difficult to measure. This is especially true for the rotational diffusion coefficients, which usually require the measurement of extremely weak depolarized scattered light intensity fluctuations. In addition, some particles may change shape with concentration (as in certain micellar systems) and thus cannot be studied in dilute solutions. The effect of concentration on the motions of flexible polymers has been thoroughly investigated by numerous authors.[6-8] However, the motions of semiflexible and rigid polymers have large, complicated concentration dependences, particularly for long rodlike molecules, which have not been extensively investigated. In this article we present a study of the translation and rotation of rodlike macromolecules of known size and compare the time constants obtained with theory in the hope that a well-defined relationship between their motions and concentration can be established.

II. Rotation and Translation in the Semidilute Region

In this section, we present a brief synopsis of the Doi–Edwards theory of the concentration dependence of the rotational and translational diffusion coefficients of long rigid rods in the semidilute region.[9-11] In the next section, we present a theory of polarized and depolarized light scattering from these systems in the limit in which the rods are long but still short enough so that destructive intramolecular interference is of no importance in determining the scattered light time correlation function.

At infinite dilution, the rotational diffusion coefficient (Θ) and the translational diffusion coefficient (D) can be calculated for long rigid rods from Broersma's relations[2-4]

$$\Theta = (3kT/\pi\eta_s L^3)(\delta - \zeta)$$

$$\delta = \ln (2L/d)$$

$$\zeta = 1.45 - 7.5(1/\delta - 0.27)^2 \qquad \text{(II.1)}$$

$$D = (kT/3\pi\eta_s L)(\delta - (1/2)(\gamma_\parallel + \gamma_\perp)) \qquad \text{(II.2)}$$

$$\gamma_\parallel = 1.27 - 7.4(1/\delta - 0.34)^2$$

$$D_\parallel = (kT/2\pi\eta_s L)(\delta - \gamma_\parallel) \qquad \text{(II.3)}$$

$$\gamma_\perp = 0.19 - 4.2(1/\delta - 0.39)^2$$

$$D_\perp = (kT/4\pi\eta_s L)(\delta - \gamma_\perp) \qquad \text{(II.4)}$$

where L is the length of the rod, d is the diameter of the rod, and η_s is the viscosity of the solvent. These relations assume that the rods are large enough so that stick boundary conditions hold; i.e., they behave as macroscopic rods in a viscous medium.

For much more concentrated solutions, one would expect a decrease in these values due to hindrance by neighboring rods. Doi and Edwards[9-11] have presented a theory of restricted rotational diffusion for number concentrations of rods ranging from greater than $1/L^3$ to $2\pi/dL^2$, i.e., where the solutions are still isotropic but exhibit strong steric repulsions between rods. In this treatment, the translational motion of each rod parallel to its axis is assumed to be unhindered while motion perpendicular to its axis is restricted to about the distance to the nearest neighboring rod, which we shall call a_c. For small values of a_c ($1/L^3 \ll c$), translational diffusion perpendicular to the rod axis is assumed to be forbidden. Thus, the rotational motion is restricted to a small solid angle $\Omega = a_c/L$ for a time of order τ_0. In order for a particular "test" rod (A) to rotate (see Figure 1), the neighboring rod (B) must translate a distance on the order of its length, thus releasing the constraint on the test rod. If $D_\parallel$ is the translational diffusion coefficient parallel to the rod's axis, this means that $\tau_0 \approx L^2/D_\parallel$ and the rotational diffusion coefficient would be given by the equation

$$\Theta = (\Omega)^2/\tau_0 \approx (a_c/L)^2/\tau_0 = D_\parallel a_c^2/L^4 \qquad \text{(II.5)}$$

Assuming an isotropic distribution of rods ($c < 1/dL^2$), Doi and Edwards[10] have shown that $a_c \approx 1/cL^2$, where c is the number concentration of rods. In addition, assuming $D_\parallel$ is unrestricted and is equal to its infinite-dilution value, we have from eq II.3

$$D_\parallel \propto kT \ln (L/d)/\eta_s L$$

The resulting equation for the concentration dependence of the rotational diffusion coefficient is

$$\Theta = \beta' kT \ln (L/d)/\eta_s L^9 c^2 \qquad \text{(II.6)}$$

where β' is a proportionality constant (expected to be within an order of magnitude of 10). This theory also predicts that the translational diffusion coefficient in the semidilute region is about half its infinite-dilution value. This follows from the fact that since $D = (1/3)(D_\parallel + 2D_\perp)$ and $D_\perp = 0$ in the semidilute region, $D = (1/3)D_\parallel$, where $D_\parallel$ is still equal to its infinite-dilution value. But at infinite

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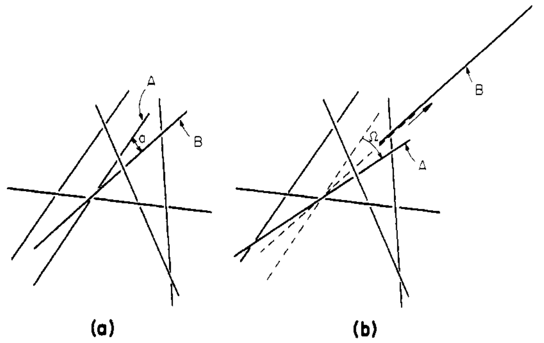

Figure 1. Schematic representation of a semidilute solution of rodlike macromolecules: (a) before rod A rotates; (b) after rod A rotates.

dilution $D_\perp = (1/2)D_\parallel$ so $D = (2/3)D_\parallel$, which is just twice the semidilute value.

Since the solution viscosity (η) is inversely proportional to the rotational diffusion coefficient (as for dilute solutions), Doi and Edwards also derived an expression for the viscosity of semidilute solutions of rods.[11] For dilute solutions, the theoretical relations are [11,12]

$$\eta = \alpha' ckT/\Theta = \nu\Phi\eta_s$$
$$\nu = (8x^2/45)\ln(x)$$
$$x = L/d \tag{II.7}$$

where Φ is the volume fraction and α' is a proportionality constant. For polymer density ρ and molecular weight MW, $c = \rho\Phi N/(\text{MW})$, where N is Avogadro's number. Thus, assuming $\Theta \approx 3kT\ln(x)/\pi\eta_s L$ (long rods), the expression for α' becomes

$$\alpha' = 24(\text{MW})/45\pi d^2\rho NL = 8M_0/15\pi d^2 L_0\rho N \tag{II.8}$$

where, for rodlike macromolecules, M_0 is the molecular weight per residue and L_0 is the length per residue. For semidilute solutions, the expression for the viscosity is[11,12]

$$\eta = \alpha' ckT/\Theta = \alpha' c^3 L^9 \eta_s/\beta' \ln(x) = k'[\ln(x)]^2(\nu\Phi)^2\eta_s \tag{II.9}$$

where k' is a proportionality constant. After some algebra, the equation for β' in terms of k' is found to be

$$\beta' = (3/\pi k')(45\rho Nd^2L_0/8M_0) \tag{II.10}$$

Assuming a molecular weight per residue of 219, a density of 1.32 g/mL and a length per residue of 1.5 Å, the value of β' for poly(γ-benzyl L-glutamate) (PBLG) should be about $45/k'$, within an order of magnitude.

III. Theory of Light Scattering in the Semidilute Region

Polarized dynamic light scattering (I_{VV}) is a common technique for measuring the translational diffusion coefficient of macromolecules in solution. Less common, but of increasing interest, is the measurement of rotational diffusion coefficients using depolarized light scattering (I_{VH}).[1,14-16] For dilute solutions of relatively small rods ($qL \leq 3$), the homodyne autocorrelation functions are[1]

$$I_{\text{VV}}(t) = A\exp(-2q^2Dt) + B \tag{III.1}$$

$$I_{\text{VH}}(t) = A'\exp(-12\Theta t - 2q^2Dt) + B' \tag{III.2}$$

where A, B, A', and B' are constants for a given scattering vector length q [$q = (4\pi n/\lambda)\sin(\theta/2)$] and incident light intensity, t is the time, and θ is the scattering angle. For longer rods ($qL \geq 3$), additional exponentials begin to arise due to intramolecular interference.[1] However, up to about $qL = 5$, the combined amplitudes of the additional exponentials are still less than 10% of the total and, except for extremely precise work, can be neglected.

These relations assume that the translational and rotational motions of the rods are statistically independent. A large anisotropy in the translational diffusion of the rod would in fact result in translational–rotational coupling. Such coupling could occur even in very dilute solution if the rod were long and thin enough.[17-23] It is clear, however, that if the translational anisotropy in the semidilute region postulated in the Doi–Edwards theory described above is correct, then semidilute solutions of long thin rods should exhibit important translational–rotational coupling effects which should modify relations III.1 and III.2. Doi and Edwards have presented a theory of the polarized light scattering time correlation functions for the semidilute rod solutions.[10] They, however, make approximations which are inapplicable to the systems that we are studying. Lee et al.[19] have presented a theory for polarized light scattering from concentrated DNA solutions which assumes that the DNA molecules are "rodlike" and cannot travel perpendicular to their long axis because of the hindrance of neighboring DNA molecules. This theory assumes negligible intramolecular and intermolecular interference in the light scattering spectra. We present here a slightly more general version of the Lee et al. theory. Both intramolecular and intermolecular interference are neglected. The rods are, as in the previous theories,[17-23] assumed to exhibit anisotropic translational diffusion which couples the translational and rotational motions (see eq III.8). Our version of the theory allows easy calculation of the depolarized light scattering time correlation functions in the semidilute region.

The homodyne autocorrelation function of scattered light is proportional to the square of the polarizability time autocorrelation function, given by the expression (assuming only self-correlations of molecules need be considered)[1]

$$I_{\text{if}}^{\alpha}(q,t) = \langle N\rangle\langle\alpha_{\text{if}}^*(0)G_s(q,t)\alpha_{\text{if}}(t)\rangle \tag{III.3}$$

N is the number of molecules in the scattering volume. $G_s(q,t)$ is the spatial Fourier transform of the joint probability function $G_s(R,\Omega_t,t;0,\Omega_0,0)$ for the polymer to be at position $R = 0$ with orientation $\Omega = \Omega_0$ at time $t = 0$ and at position $R = R$ with orientation $\Omega = \Omega_t$ at time t. The quantity α_{if} is the projection of the polarizability tensor $\tilde{\alpha}$ onto the initial ($\hat{n}_i$) and final ($\hat{n}_f$) polarization directions of the light wave; that is

$$\alpha_{\text{if}} = \hat{n}_i\cdot\tilde{\alpha}\cdot\hat{n}_f$$

The polarizability tensor in a molecule-fixed system for a cylindrically symmetric molecule can be represented by a diagonal tensor where $\alpha_\parallel$ is the polarization parallel to its optic axis (assumed to be the symmetry axis) and $\alpha_\perp$ is the polarization perpendicular to this axis. Choosing our laboratory axes so that the scattering vector **q** lies along the z axis, we write the pertinent expressions for I_{VV} and I_{VH}:

$$I_{\text{VV}}^{\alpha}(q,t) = \langle N\rangle\langle\alpha_{yy}^*(0)G_s(q,t)\alpha_{yy}(t)\rangle \tag{III.4}$$

$$I_{\text{VH}}^{\alpha}(q,t) = \langle N\rangle\left\langle\left(\alpha_{yx}^*(0)\sin\left(\frac{\theta}{2}\right) + \alpha_{yz}^*(0)\cos\left(\frac{\theta}{2}\right)\right)\times G_s(q,t)\left(\alpha_{yz}(t)\sin\left(\frac{\theta}{2}\right) + \alpha_{yz}(t)\cos\left(\frac{\theta}{2}\right)\right)\right\rangle \tag{III.5}$$

These expressions can be rewritten in terms of the spherical harmonics ($Y_{lm}(\Omega_t)$), the average molecular polarizability ($\alpha = (1/3)(\alpha_\parallel + 2\alpha_\perp)$), and the molecular anisotropy ($\beta = \alpha_\parallel - \alpha_\perp$):

$$I_{\mathrm{VV}}{}^{\alpha}(q,t) = \langle N\rangle(4\pi)[\alpha^2\langle Y_{00}{}^*(\Omega_0)G_{\mathrm{s}}(q,t)Y_{00}(\Omega_t)\rangle + \frac{\alpha\beta}{3}\left(\frac{1}{5}\right)^{1/2}[\langle Y_{00}{}^*(\Omega_0)G_{\mathrm{s}}(q,t)Y_{20}(\Omega_t)\rangle + \langle Y_{20}{}^*(\Omega_0)G_{\mathrm{s}}(q,t)Y_{00}(\Omega_t)\rangle] + \frac{\beta^2}{30}[\langle Y_{2-2}{}^*(\Omega_0)G_{\mathrm{s}}(q,t)Y_{2-2}(\Omega_t)\rangle + \langle Y_{22}{}^*(\Omega_0)G_{\mathrm{s}}(q,t)Y_{22}(\Omega_t)\rangle] + \frac{\beta^2}{40}[\langle Y_{20}{}^*(\Omega_0)G_{\mathrm{s}}(q,t)Y_{20}(\Omega_t)\rangle] \tag{III.6}$$

$$I_{\mathrm{VH}}{}^{\alpha}(q,t) = \langle N\rangle\frac{(4\pi)\beta^2}{30}\left[(\langle Y_{21}{}^*(\Omega_0)G_{\mathrm{s}}(q,t)Y_{21}(\Omega_t)\rangle + \langle Y_{2-1}{}^*(\Omega_0)G_{\mathrm{s}}(q,t)Y_{2-1}(\Omega_t)\rangle)\sin^2\left(\frac{\theta}{2}\right) + (\langle Y_{22}{}^*(\Omega_0)G_{\mathrm{s}}(q,t)Y_{22}(\Omega_t)\rangle + \langle Y_{2-2}{}^*(\Omega_0)G_{\mathrm{s}}(q,t)Y_{2-2}(\Omega_t)\rangle)\cos^2\left(\frac{\theta}{2}\right)\right] \tag{III.7}$$

All terms $\langle Y_{lm}{}^*(\Omega_0)G_{\mathrm{s}}(q,t)Y_{l'm'}(\Omega_t)\rangle$ where $m \neq m'$ were dropped, since fuuther considerations will show them to be zero. As shown by numerous authors,$^{17-20}$ $G_{\mathrm{s}}(q,t)$, assuming a random distribution of rods, is given by the diffusion equation

$$\frac{\mathrm{d}}{\mathrm{d}t}[G_{\mathrm{s}}(q,t)] = [-q^2D - q^2\Delta D(\cos^2\psi - 1/3) - \Theta\hat{I}^2]G_{\mathrm{s}}(q,t) \tag{III.8}$$

where ψ is the angle between the laboratory z axis and the rod axis, $\mathbf{q}$ lies along the z axis, $D = (1/3)(D_{\parallel} + 2D_{\perp})$, as stated above, $\Delta D = D_{\parallel} - D_{\perp}$ (the anisotropy in the translational diffusion coefficient), and $\hat{I}^2$ is the rotational diffusion operator:

$$\hat{I}^2 = -\frac{1}{\sin^2\psi}\left[\sin\psi\frac{\partial}{\partial\psi}\left(\sin\psi\frac{\partial}{\partial\psi}\right) + \frac{\partial^2}{\partial\phi^2}\right]$$

This equation can be solved by expanding $G_{\mathrm{s}}(q,t)$ in spherical harmonics:

$$G_{\mathrm{s}}(q,t) = \frac{1}{4\pi}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}C_{lm}(q,t)Y_{lm}{}^*(\Omega_t) \tag{III.9}$$

With the boundary condition $G_{\mathrm{s}}(R,\Omega_t,t;0,\Omega_0,0) = (1/4\pi)\cdot\delta(R)\delta(\Omega_t - \Omega_0)$ we obtain

$$C_{lm}(q,0) = Y_{lm}(\Omega_0) \tag{III.10}$$

Substituting the expansion for $G_{\mathrm{s}}(q,t)$ into the differential equation III.8, multiplying both sides by $Y_{lm}(\Omega_t)$, and integrating over all angles, we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}[C_{lm}(q,t)] = [-q^2D + 1/3q^2\Delta D - l(l+1)\Theta]C_{lm}(q,t) - q^2\Delta D\sum_{l',m'}\left[\int Y_{lm}(\Omega_t)\cos^2\psi\, Y_{l'm'}{}^*(\Omega_t)\,\mathrm{d}\Omega_t\right]C_{l'm'}(q,t)$$

Expressing $\cos^2\psi$ in terms of $Y_{20}(\Omega_t)$, we may rewrite this equation as

$$\frac{\mathrm{d}}{\mathrm{d}t}[C_{lm}(q,t)] = [-q^2D - l(l+1)\Theta]C_{lm}(q,t) - \left(\frac{4}{3}\right)\left(\frac{\pi}{5}\right)^{1/2}q^2\Delta D \times \sum_{l',m'}\left[\int Y_{lm}(\Omega_t)Y_{20}(\Omega_t)Y_{l'm'}{}^*(\Omega_t)\,\mathrm{d}\Omega_t\right]C_{l'm'}(q,t) \tag{III.11}$$

Formulas for finding the numerical values of the integral of three spherical harmonics are given by Edmonds.^{24}

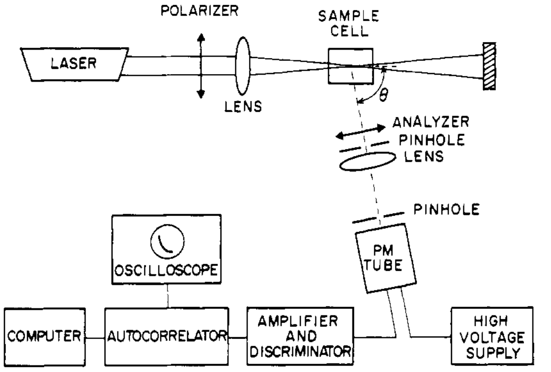

Figure 2. Schematic diagram of the light scattering apparatus.

These integrals are zero for $l = l' = 0$, $l \geq l' + 2$ (note: the roles of l and l' are interchangeable), and $m \neq m'$. Thus, eq III.11, including only the nonzero terms, becomes

$$\frac{\mathrm{d}}{\mathrm{d}t}[C_{lm}(q,t)] = \left[-q^2D - l(l+1)\Theta - \left(\frac{4}{3}\right)\left(\frac{\pi}{5}\right)^{1/2}q^2\Delta D \times \left(\int Y_{lm}(\Omega_t)Y_{20}(\Omega_t)Y_{lm}{}^*(\Omega_t)\,\mathrm{d}\Omega_t\right)\right]C_{lm}(q,t) - q^2\Delta D\left(\frac{4}{3}\right)\left(\frac{\pi}{5}\right)^{1/2} \times \left[\left(\int Y_{lm}(\Omega_t)Y_{20}(\Omega_t)Y_{l-2,m}{}^*(\Omega_t)\,\mathrm{d}\Omega_t\right)C_{l-2,m}(q,t) + \left(\int Y_{lm}(\Omega_t)Y_{20}(\Omega_t)Y_{l+2,m}{}^*(\Omega_t)\,\mathrm{d}\Omega_t\right)C_{l+2,m}(q,t)\right] \tag{III.12}$$

Numerical calculations show that the contribution of $C_{40}(t)$ is relatively small, as is the contribution of $C_{6,\pm1}(t)$ and $C_{6,\pm2}(t)$ to the expressions for $C_{4,\pm1}(t)$ and $C_{4,\pm2}(t)$; thus, these terms will be ignored when solving for the time dependence of these coefficients. After taking the Laplace transform of eq III.12, we solved the resulting pairs of simultaneous equations in $C_{lm}(t)$ and $C_{l+2,m}(t)$ for $l = 0$, 2, the terms of importance for light scattering:

$$\begin{aligned}C_{00}(q,t) &= C_{00}(0)[A_{00}\exp\{-\Gamma_0{}^-t\} + B_{00}\exp\{-\Gamma_0{}^+t\}] + C_{20}(0)D_{00}[\exp\{-\Gamma_0{}^-t\} + \exp\{-\Gamma_0{}^+t\}]\\ C_{20}(q,t) &= C_{20}(0)[B_{00}\exp\{-\Gamma_0{}^-t\} + A_{00}\exp\{-\Gamma_0{}^+t\}] + C_{00}(0)D_{00}[\exp\{-\Gamma_0{}^-t\} + \exp\{-\Gamma_0{}^+t\}]\\ C_{2,\pm1}(q,t) &= C_{2,\pm1}(0)[A_{21}\exp\{-\Gamma_{21}{}^-t\} + B_{21}\exp\{-\Gamma_{21}{}^+t\}] + C_{4,\pm1}(0)D_{21}[\exp\{-\Gamma_{21}{}^-t\} + \exp\{-\Gamma_{21}{}^+t\}]\\ C_{2,\pm2}(q,t) &= C_{2,\pm2}(0)[A_{22}\exp\{-\Gamma_{22}{}^-t\} + B_{22}\exp\{-\Gamma_{22}{}^+t\}] + C_{4,\pm2}(0)D_{22}[\exp\{-\Gamma_{22}{}^-t\} + \exp\{-\Gamma_{22}{}^+t\}]\end{aligned} \tag{III.13}$$

where

$$\begin{aligned}\Gamma_0{}^{\pm} &= q^2D + 3\Theta + \frac{2}{21}q^2\Delta D \pm \frac{1}{2}\left[\left(6\Theta + \frac{4}{21}q^2\Delta D\right)^2 + \frac{16}{45}(q^2\Delta D)^2\right]^{1/2}\\ \Gamma_{21}{}^{\pm} &= q^2D + 13\Theta - \frac{4}{33}q^2\Delta D \pm \frac{1}{2}\left[\left(14\Theta - \frac{4}{77}q^2\Delta D\right)^2 + \frac{32}{147}(q^2\Delta D)^2\right]^{1/2}\\ \Gamma_{22}{}^{\pm} &= q^2D + 13\Theta - \frac{2}{33}q^2\Delta D \pm \frac{1}{2}\left[\left(14\Theta + \frac{20}{77}q^2\Delta D\right)^2 + \frac{16}{147}(q^2\Delta D)^2\right]^{1/2}\end{aligned} \tag{III.14}$$

$$A_{00} = \left(q^2D + 6\Theta + \frac{4}{21}q^2\Delta D - \Gamma_0^-\right) \Big/ (\Gamma_0^+ - \Gamma_0^-)$$

$$B_{00} = 1 - A_{00}$$

$$A_{21} = \left(q^2D + 20\Theta - \frac{34}{231}q^2\Delta D - \Gamma_{21}^-\right) \Big/ (\Gamma_{21}^+ - \Gamma_{21}^-)$$

$$B_{21} = 1 - A_{21}$$

$$A_{22} = \left(q^2D + 20\Theta + \frac{16}{231}q^2\Delta D - \Gamma_{22}^-\right) \Big/ (\Gamma_{22}^+ - \Gamma_{22}^-)$$

$$B_{22} = 1 - A_{22}$$

$$D_{00} = \left(\frac{2}{3}\right)\left(\frac{1}{5}\right)^{1/2} q^2\Delta D/(\Gamma_0^+ - \Gamma_0^-)$$

$$D_{21} = \left(-\frac{4}{21}\right)\left(\frac{3}{2}\right)^{1/2} q^2\Delta D/(\Gamma_{21}^+ - \Gamma_{21}^-)$$

$$D_{22} = \left(\frac{2}{21}\right)(3)^{1/2} q^2\Delta D/(\Gamma_{22}^+ - \Gamma_{22}^-) \qquad \text{(III.15)}$$

Combining eq III.6, III.7, III.9, III.10, and III.13 and using the orthonormality property of spherical harmonics[1]

$$\langle Y_{lm}^*(\Omega_0) Y_{l'm'}(\Omega_0) Y_{l''m''}(\Omega_t) Y_{l'''m'''}(\Omega_t) \rangle = \delta_{ll'}\delta_{l''l'''}\delta_{mm'}\delta_{m''m'''}$$

we write the polarizability autocorrelation functions:

$$\begin{aligned} I_{\text{VV}}{}^{\alpha}(q,t) = \langle N \rangle \Bigg[& \alpha^2(A_{00} \exp\{-\Gamma_0^- t\} + B_{00} \exp\{-\Gamma_0^+ t\}) + \\ & \left(\frac{2}{3}\right)\left(\frac{1}{5}\right)^{1/2} \alpha\beta D_{00}(\exp\{-\Gamma_0^- t\} + \exp\{-\Gamma_0^+ t\}) + \\ & \frac{\beta^2}{15}(A_{22} \exp\{-\Gamma_{22}^- t\} + B_{22} \exp\{-\Gamma_{22}^+ t\}) + \\ & \frac{\beta^2}{45}(A_{00} \exp\{-\Gamma_0^+ t\} + B_{00} \exp\{-\Gamma_0^- t\}) \Bigg] \end{aligned} \qquad \text{(III.16)}$$

$$\begin{aligned} I_{\text{VH}}{}^{\alpha}(q,t) = {} & \\ \langle N \rangle \frac{\beta^2}{15} \Bigg[& (A_{22} \exp\{-\Gamma_{22}^- t\} + B_{22} \exp\{-\Gamma_{22}^+ t\}) \sin^2\left(\frac{\theta}{2}\right) + \\ & (A_{21} \exp\{-\Gamma_{21}^- t\} + B_{21} \exp\{-\Gamma_{21}^+ t\}) \cos^2\left(\frac{\theta}{2}\right) \Bigg] \end{aligned} \qquad \text{(III.17)}$$

Expanding the square roots in terms of the parameter $\gamma = q^2\Delta D/\Theta$, one obtains for the time constants and amplitude factors (keeping terms to order γ^2)

$$\Gamma_0^- = q^2D - \frac{2}{135}\Theta\gamma^2 - \ldots$$

$$\Gamma_0^+ = q^2D + \frac{4}{21}q^2\Delta D + 6\Theta + \frac{2}{135}\Theta\gamma^2 + \ldots$$

$$\Gamma_{21}^- = q^2D - \frac{2}{21}q^2\Delta D + 6\Theta - \frac{4}{1029}\Theta\gamma^2 - \ldots$$

$$\Gamma_{21}^+ = q^2D - \frac{34}{231}q^2\Delta D + 20\Theta + \frac{4}{1029}\Theta\gamma^2 + \ldots$$

$$\Gamma_{22}^- = q^2D - \frac{4}{21}q^2\Delta D + 6\Theta - \frac{2}{1029}\Theta\gamma^2 - \ldots$$

$$\Gamma_{22}^+ = q^2D + \frac{16}{231}q^2\Delta D + 20\Theta + \frac{2}{1029}\Theta\gamma^2 + \ldots \qquad \text{(III.18)}$$

$$A_{00} = \left(1 + \frac{2}{63}\gamma + \frac{2}{135}\gamma^2 + \ldots\right) \Big/ \left(1 + \frac{2}{63}\gamma + \frac{4}{135}\gamma^2 + \ldots\right)$$

$$B_{00} = \left(\frac{2}{135}\gamma^2 + \ldots\right) \Big/ \left(1 + \frac{2}{63}\gamma + \frac{4}{135}\gamma^2 + \ldots\right)$$

$$A_{21} = \left(1 - \frac{2}{539}\gamma + \frac{4}{1029}\gamma^2 + \ldots\right) \Big/ \left(1 - \frac{2}{539}\gamma + \frac{8}{1029}\gamma^2 + \ldots\right)$$

$$B_{21} = \left(\frac{4}{1029}\gamma^2 + \ldots\right) \Big/ \left(1 - \frac{2}{539}\gamma + \frac{8}{1029}\gamma^2 + \ldots\right)$$

$$A_{22} = \left(1 + \frac{10}{539}\gamma + \frac{2}{1029}\gamma^2 + \ldots\right) \Big/ \left(1 + \frac{10}{539}\gamma + \frac{4}{1029}\gamma^2 + \ldots\right)$$

$$B_{22} = \left(\frac{2}{1029}\gamma^2 + \ldots\right) \Big/ \left(1 + \frac{10}{539}\gamma + \frac{4}{1029}\gamma^2 + \ldots\right) \qquad \text{(III.19)}$$

The terms containing β^2 and $\alpha\beta$ in eq III.16 are usually negligible compared to those containing α^2 and so may usually be ignored. With this approximation, we note that in the limit of no translational–rotational coupling, $\gamma = 0$, the squares of eq III.16 and III.17 are proportional to eq III.1 and III.2, respectively. In the semidilute region, ΔD would be equal to $D_{\parallel}$ ($\Delta D = D_{\parallel} - D_{\perp}$ and $D_{\perp} = 0$), D would be equal to $(1/3)D_{\parallel}$ ($D = (1/3)(D_{\parallel} + 2D_{\perp})$), and $\gamma = q^2\Delta D/\Theta = q^2D_{\parallel}/\Theta$. As the concentration increases, Θ decreases and thus the coupling between translation and rotation (as indicated by γ) should increase.

It should be emphasized that these equations were expanded in γ to order γ^2 and should be valid for $\gamma \lesssim 10$. Note that the theory of Doi and Edwards[10] applies in the limit $\gamma \rightarrow \infty$ (i.e., where the rotational diffusion coefficient is almost zero), which is not appropriate for the PBLG systems studied in this work. Also, for the systems studied, γ should be small enough so that B_{21} and B_{22} are essentially zero and $\Gamma_{21}^- \approx \Gamma_{22}^- \approx q^2D + 6\Theta$, within experimental error.

IV. Experimental Section

A schematic of the dynamic light scattering apparatus is shown in Figure 2. The sample cells used were 10-mm-square fused-glass fluorimeter cells (Savant, Type 23). The scattering was done at a scattering angle of 90° using argon ion lasers (Spectra-Physics Model 165 and Lexel Model 95) at the 4880-Å line. The photomultiplier tubes used were an EMI 9502-RF and an ITT FW130 (particularly low after-pulsing). The output of the EMI tube was digitized by an SSR Model 1120 amplifier–discriminator system while the output of the ITT tube was digitized by a Mech-Tronics Model 511 amplifier–discriminator. A Malvern 48-channel autocorrelator (clipped) was used to collect the data, which were then transferred to a Data General Nova 3 computer and stored on floppy disks.

The output of the autocorrelator was fit by nonlinear least-squares analysis to the equation

$$C(t) = A + B \exp(-2t/\tau) \qquad \text{(IV.1)}$$

where A and B are constants, τ is the decay time constant, and t is the time. Typical laser power was 1 W for the depolarized data and 0.2–1 W for the polarized data. The acquisition time for each polarized data set was a few minutes, while that for each depolarized data set was 5–10 h. Due to after-pulsing, the first 5 μs were ignored for experiments performed with the EMI tube, and the first 1 or 2 μs were ignored in those experiments performed with the ITT tube. Since the actual data sets are not perfect

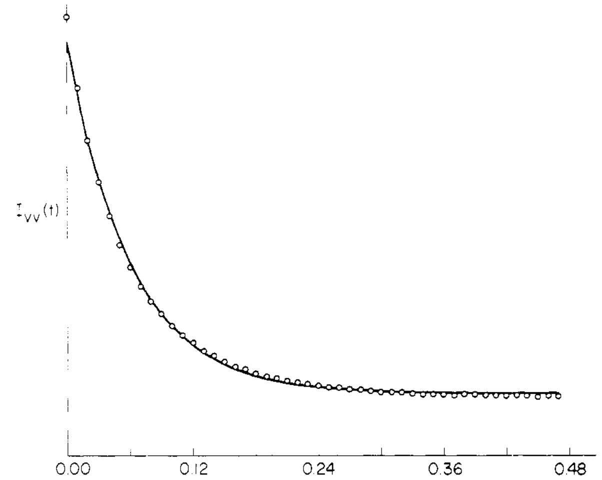

Figure 3. Autocorrelation function of the intensity of the polarized scattered light ($I_{VV}(t)$, arbitrary units) for a 5.1 mg/mL solution of PBLG in 1,2-dichloroethane (MW = 170 000).

exponentials, all comparisons between different concentrations and molecular weights were made at the same time scales (10 μs/channel for the polarized data and 1 μs/channel for the depolarized data).

The PBLG was purchased from Sigma (Type IIA). The molecular weights were determined by Sigma, using viscosity measurements in dichloroacetic acid, and ranged from 150 000 to 210 000. Within 1–5%, our measurements of the viscosity in 1,2-dichloroethane yielded the same molecular weights. Furthermore, measurements in our laboratory of the infinite-dilution diffusion coefficients in various solvents (1,2-dichloroethane, dimethylformamide, and mixtures of dichloroacetic acid and 1,2-dichloroethane) are compatible with rodlike molecules of these molecular weights. We did not measure the polydispersity. From the method of preparation, the theoretical ratio of weight-average to number-average molecular weight is less than 1.1.[25] The actual polydispersity may be much higher than this.[26] Without more precise knowledge of the molecular weight distribution function, it is difficult to determine the quantitative effect of polydispersity on the results. We suspect, however, that it does not drastically change the main trends of the data. The low signal-to-noise ratio of the depolarized correlation functions (see section V) is perhaps a larger source of error. The samples were dissolved in 1,2-dichloroethane (Aldrich, 99+%) and filtered through 0.2 μm, 13-mm-diameter Fluoropore filters (Teflon filters from Millipore). Ultraviolet absorption measurements showed that filtering did not change the concentrations. Additional concentrations of solutions were made after filtering by evaporation or addition of solvent. Since freshly filtered solutions exhibit large refractive index anisotropies, the solutions were usually allowed to equilibrate for a few days before data were collected. Relatively reproducible results were normally obtainable over a period of months, although the polarized decay times did tend to increase slightly with time, possibly due to long relaxation toward equilibrium. All data were taken at 20 °C.

V. Results

Sample correlation functions are shown in Figures 3 and 4. The rotational diffusion coefficient is plotted vs. $1/c^2$ in Figure 5, while the reciprocal decay time for the polarized intensity ($1/\tau_p$) is plotted vs. concentration in Figure 6. The size of the symbols does not indicate the experimental precision; the actual precision is a few percent for the polarized data and about 10% for the depolarized data.

The region defined by Doi and Edwards would range from about 0.1 to 10 mg/mL; however, the actual onset of the region appears to be a little greater than 5 mg/mL ($c \gg 1/L^3$, as expected). Beyond this concentration, the plots of Θ vs. $1/c^2$ are linear. For the molecular weights

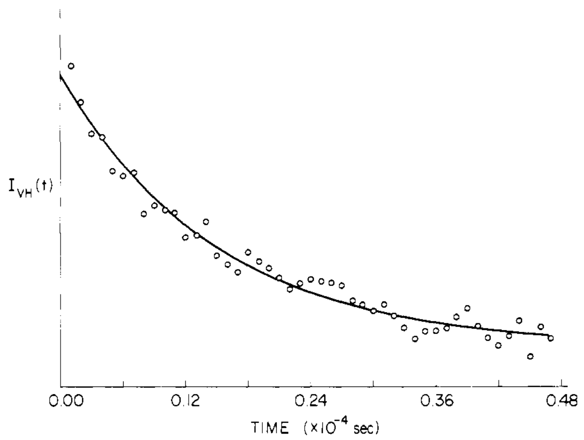

Figure 4. Autocorrelation function of the intensity of the depolarized scattered light ($I_{VH}(t)$, arbitrary units) for a 20.3 mg/mL solution of PBLG in 1,2-dichloroethane (MW = 170 000).

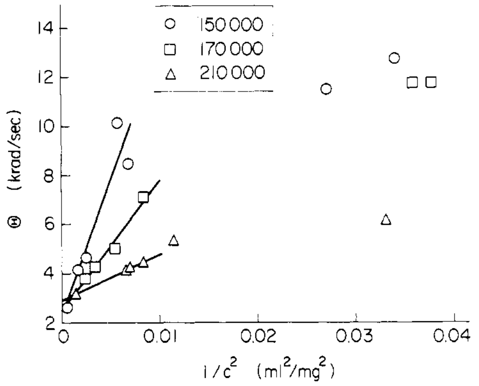

Figure 5. Plot of the rotational diffusion coefficient (Θ) vs. reciprocal concentration squared for three different molecular weights of PBLG in 1,2-dichloroethane solutions. The lines are linear least-square fits of Θ vs. $1/c^2$ for $1/c^2 < 0.02$.

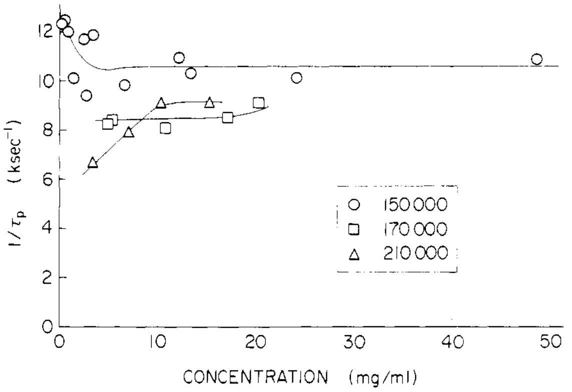

Figure 6. Plot of reciprocal polarized decay time ($1/\tau_p$) vs. concentration for three different molecular weights of PBLG in 1,2-dichloroethane solutions. The lines are not fits but merely emphasize the trend of the data.

150 000, 170 000, and 210 000, comparison of the slopes with Doi and Edwards' relation yields β' values of 1070, 1170, and 1768, respectively. Thus, β' is several orders of magnitude larger than predicted. From Doi and Edwards' theory, the ratio ($R_{2:1}$) of the slopes (A_2, A_1) for two different lengths should fit the relation (assuming c is in units of mg/mL)

$$R_{2:1} = A_2/A_1 = (L_1/L_2)^x[\ln (L_2/d_2)/\ln (L_1/d_1)][(\mathrm{MW})_2/(\mathrm{MW})_1]^2$$

where x is predicted to be 9 and L_i, d_i, and $(\mathrm{MW})_i$ are, respectively, the length, diameter, and molecular weight for molecule i. Experimentally, the values found for x are 8.2, 7.5, and 7.1, where the value 8.2 is obtained from comparing the two shortest PBLG rods. The average for a comparison of all three lengths is 7.6 ± 0.6. Considering the precision of the data points, this value, though slightly lower than predicted, is reasonably close to 9. One possible explanation, other than the precision of the data, for the increase in β' value (or decrease in x) with length may be flexibility, resulting in a smaller hydrodynamic length for the longer rods (estimates of the persistence length for PBLG range from 900 to 1400 Å).[27] Transient electric birefringence experiments on long, rodlike viruses were performed by Maguire et al.[28] They also observed a $1/c^2$ dependence for Θ but obtained a value of 5.7 for x, using only two different viruses. However, their rods are an order of magnitude longer than ours and may flex considerably at high concentrations.

Below about 5 mg/mL, the values for Θ have leveled off and become concentration independent. For the molecular weights 150 000, 170 000, and 210 000, the values obtained for Θ below 5 mg/mL are, respectively, 13 ± 3, 12 ± 2, and 6.1 ± 0.2 krad/s. With experimental error, these values correspond well with the values predicted from Broersma's relations for infinite dilution (15.5, 11.2, and 6.25 krad/s, respectively).

The $1/\tau_p$ values, on the other hand, show relatively little concentration dependence in this region, as expected from Doi and Edwards' theory[9-11] (the lines on Figure 6 are meant merely to guide the eyes; they are not fits). However, the values are about two-thirds the infinite-dilution value rather than the predicted one-half. This discrepancy can be qualitatively explained by the two-exponential nature of the curves (as observed experimentally and predicted by the theory presented in section III). Unfortunately, the quality of the data is not good enough to give a consistent fit to eq III.16 (ignoring the terms containing β). Although a double-exponential fit can yield a reasonably good value for the slower exponential (i.e., corresponding to a diffusion coefficient about $(1/3)D_{\|}$), the difference in time scales between the two exponentials and the low amplitude of the fast exponential make a quantitative determination of the value of the time constants impossible for the lower end of the concentration range. The higher concentrations do show a reasonably strong contribution from the rotational time and fit eq III.16 at least semiquantitatively. Qualitatively, the contribution from the faster mode could cause the apparent rise in the polarized decay time (as determined from a single-exponential fit) seen in Figure 6.

For Doi and Edwards' initial theory, one would expect the intercept of these plots in Figure 5 to be zero (i.e., no rotation at infinite concentration). However, the actual intercepts are fairly substantial (2–3 krad/s). This discrepancy arises from the finite thickness of the rods. At the higher concentrations, one would expect translational diffusion parallel to the axis to no longer be completely unhindered as the distance between rods becomes comparable to their diameters. Consequently, the rate of rotational diffusion should begin to drop faster than the $1/c^2$ dependence and a fit to $1/c^2$ would yield a false intercept. A simple, tentative treatment[9-12] for this effect is to simply correct the size of a_c for the diameter; i.e., let $a_c = \langle r_c \rangle - d$ and $\langle r_c \rangle = \alpha_c / cL^2$, where α_c is some numerical factor. The new equation obtained for Θ is

$$\Theta = \beta' kT \ln (L/d)(\alpha_c - cdL^2)^2/\alpha_c^{\,2}\eta_s L^9 c^2 \qquad \text{(V.1)}$$

Although the data are not precise enough to fit to this form, the magnitude of the intercepts is consistent with this equation.

Matheson has obtained a value for k' from viscosity data ($k' = 0.002 \pm 0.001$). This yields a β' value of $(2 \pm 1) \times 10^4$, which is about an order of magnitude greater than the value found here; considering the experimental error and theoretical approximations, this agreement is reasonably close.

VI. Conclusions

We have found that, at least semiquantitatively, the Doi–Edwards theory describes the hydrodynamics of PBLG rods in semidilute solution. In the semidilute region a $1/c^2$ behavior and an inverse eighth-power dependence on the rod length are found for the rotational diffusion coefficient. Considering the possible errors in the experiment, this value is consistent with the theoretical exponent of -9 for the length. We note that the proportionality constant β' is about 2 orders of magnitude higher than predicted so the value of the rotational diffusion coefficient in the semidilute region is much higher than predicted.

More work on the rotation and translation of rodlike molecules should be done in order to further test the theory and the limits of its applicability. Experiments on polyelectrolytes would be important for future applications to the study of rodlike micellar and biological systems. It would be especially important, for instance, to have a theory for β' and also for the intercept. More precise light scattering data would also give a more severe test of eq III.16 and III.17 and, perhaps, explicit extraction of ΔD directly from the data.

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Note Added in Proof. Maguire et al.[28] have reinterpreted their data on long rodlike viruses (*Phys. Rev. Lett.* **1981**, *47*, 148). Their value for x (7.7) is now in accord with ours.

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Simulation of Polymer Network Formation by the Monte Carlo Method

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ABSTRACT: A Monte Carlo method for simulation of the stepwise polyreaction generating treelike polymer structures and admitting intramolecular reactions inside the largest particle (identified with the gel) has been developed. The method is equivalent to the kinetic theory of network formation applied to finite systems. The limiting properties of an infinite system are obtained by extrapolation; among those best accessible are the critical conversion of gelation and weight fractions of sol and gel. Polymerization of a trifunctional monomer with a first-shell substitution effect was used as an example to demonstrate that, with the exception of some special cases, the results obtained by the kinetic method are virtually identical with those provided by the statistical method based on the treelike model and cascade substitution.

Introduction

Network models are essentially graphlike and network formation from smaller building units is simulated either by percolation in D-dimensional space using Monte Carlo methods or by formation of (perturbed) treelike structures in $D = 1$, equivalent to percolation on the Cayley tree, which is usually given an anlytical solution.

The treelike models are based on the Flory–Stockmayer[1,2] approach, but the network formation can be treated in two different ways: either statistically (theory of branching processes (TBP) developed mainly by Gordon; cf., for example, ref 3 and 4), when the final assembly of molecules is generated from the building units, in which different numbers of functional groups have been converted into chemical bonds, or kinetically (kinetic theory), when the growth of molecules is considered as a chemical reaction occurring between two functional groups of any pair of existing molecules. Both methods are statistically nonequivalent because in the kinetic approach the integrity of the existing structures, and so information on the formation history, is preserved, while it is not so in the statistical TBP. This difference is irrelevant for equilibrium-controlled reaction (both approaches are equivalent) but may become serious in the case of kinetically controlled reactions.

To make the situation clearer, let us consider a simple case of a step polyaddition of a f-functional monomer with all functional groups of the same type but with a first-shell substitution effect (FSSE). FSSE means that the reactivity of an unreacted group depends on the number of reacted groups in the same monomer unit (called the reaction state of the unit) but not on reaction states of other units in the system.

The fractions of units in different reaction states (later called the distribution of units) are determined by kinetic differential equations based on the mass action law. If additivity of contributions to the activation energy is valid, the number of kinetic equations is $f + 1$. The distribution of units is thus a function of time and depends on the respective rate constants.

As shown below, it is to our advantage to express the fractions of units as a function of overall conversion of functional groups; the conversion is then an implicit function of time. Note that in the calculation of the distribution of units only their molar concentrations, i.e., the mass action law, are operative and not any other constraints coming, for example, from ring closure determined by chain flexibility or space embedding. Such constraints would alter the distribution of reaction states, although nothing changes from the point of view of chemical reactivity of the functional groups.

Up to this point, there is no difference between the methods (TBP and kinetic) and the distributions of units are identical.

In the theory of branching processes, the treelike molecules are generated from the distribution of units by applying the so-called cascade substitution procedure and generating functions (or an equivalent recursive procedure when the language of conditional probabilities is preferred[5]) which generates all possible treelike molecules with proper weighting compatible with random combination of reacted functional groups to form a bond. An example of detailed application of this procedure can be found, for example, in the paper by Gordon and Scantlebury.[6] It is important to note that the molecules are generated from monomer units at any extent of reaction anew. It is clear that there is no information stored on sequence order in the generated structures. To make the situation clearer, imagine that the monomer is colored and its color is time (conversion) dependent. In kinetically controlled reactions, the sequences of colors (although subjected to statistical fluctuations) must evidently depend on reactivities of functional groups. A strong positive substitution effect, for example, would yield long sequences of the same color.

The question is whether this lack of memory inherent in TBP may affect the distribution of sizes (masses) of the generated molecules, gelation, and sol–gel relation.

In the kinetic method, first used by Stockmayer[1] and later developed for a number of polymerization problems,[7,8] the distribution of units is not input information but is generated implicity in the course of the growth process. Instead of the $f + 1$ differential equations, one writes an inifinite number of differential equations, corresponding to a bimolecular reaction (without substitution effect)

$$Z_{ij} + Z_{kl} \rightarrow Z_{i+k,j+l-2}$$

where Z_{ij} represents a molecule composed of i monomer units and bearing j unreacted functional groups. The

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