1. Note the sharp increase at lower angles in $f(\theta)$ that is obtained by the inclusion of the P_4 term. This is in contrast to the case shown in Figure 7 for the low molecular weight nematic liquid crystal *N*-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline, MBBA, where $\langle P_2(\cos\theta)\rangle >> \langle P_4(\cos\theta)\rangle$, and reinforces our initial postulate that for highly ordered systems, it would be necessary to experimentally obtain information about the higher order terms in eq 1 in order to obtain a valid picture of the orientational distribution function, $f(\theta)$. The negative values of $f(\theta)$ obtained at some angles are presumably due to the truncation of the series expansion. Information about the higher moments of the distribution would be necessary to faithfully reproduce the form of $f(\theta)$ for all θ.

Finally, the fact that the above determinations can be performed on a naturally fluorescent polymer precludes a valid criticism often leveled at probe studies: namely, that the presence of the probe might create a significant local perturbation of the structure and that ensemble averages for the probe do not adequately reflect those of the polymer chains, the real subject of study.

Conclusion

It is possible to use the fluorescence depolarization method to obtain the orientational distribution function to second order for highly oriented ultrahigh-modulus fibers.

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Appendix

The Polarization of the Absorption Transition Moment in Kevlar 49. The justification for assuming that the transition for Kevlar 49 is long-axis polarized, i.e., $\alpha = 0°$, lies in the fact that a reasonable and self-consistent numerical solution to the equations for r' and r'' is readily deduced. If the transition were short-axis polarized, i.e., $\alpha = 90°$, the following set of equations analogous to eq 10 and 11 derived from the tensor elements of ref 14 would apply:

$$r' = \frac{3(2x+1)\langle\cos^4\theta\rangle - 2(6x+1)\langle\cos^2\theta\rangle + (6x-1)}{8(1-\langle\cos^2\theta\rangle)} \quad \text{(A1)}$$

$$r'' = \frac{5(2x+1)\langle\cos^4\theta\rangle - 6(6x-5)\langle\cos^2\theta\rangle + (10x-11)}{2(2x+1)\langle\cos^4\theta\rangle + 12(2x-3)\langle\cos^2\theta\rangle + (4x-14)} \quad \text{(A2)}$$

where $x = \cos^2\delta$.

One can readily see that $r'' < 0$ for highly oriented fiber samples, i.e., small values of θ. For perfect orientation, $\theta \equiv 0$, $r'' = -1/2$. Note that the data here clearly show that $r'' > 0$. Additionally, an attempt to solve eq A1 and A2 using the experimentally determined values of r' and r'' shows that it is impossible irrespective of the choices of δ to obtain θ equal to a small angle as indicated from the X-ray results[4] and the generally accepted physics of these materials.

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Quasielastic Light Scattering from Entangled Polymer Solutions

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ABSTRACT: The theoretical interpretation of the quasielastic light scattering properties of entangled polymer solutions is discussed. A modified version of the theory of Brochard and deGennes, based on an entanglement network with finite lifetime, is found to be in accord with recent experimental results on certain macroion solutions. This leads to the suggestion that an intermediate regime of hydrodynamic properties exists between that concentration corresponding to the onset of entanglements, described by the "congested diffusion" model of Lee et al., and the characteristic concentration defined by Klein in which a cooperative transition to a reptative diffusion mode occurs. The analysis described here appears to have potential for a more detailed interpretation of the hydrodynamic structure of entangled polymer solutions from light scattering experiments.

Following the theoretical treatment by deGennes[1,2] of the hydrodynamic properties of entangled solutions of flexible polymers in good solvents, there has been recent interest in experimental tests of the accuracy of the theoretical predictions utilizing quasielastic light scattering techniques.[3-5] In summary, the deGennes theory[1,2] concludes that, at concentrations below c^*, a critical value at which interchain entanglements are manifest, the relaxation of concentration fluctuations proceeds by the usual Fickian mechanism, characterized by the mutual trans-

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lational diffusion coefficient, the behavior of which is conventionally modeled by appropriate modification of an early analysis of Pyun and Fixman;[6,7] above c^*, the hydrodynamic properties of the gel are considered[1,2] to be analogous to those of a permanently cross-linked gel,[8] and the relaxation of concentration fluctuations is described by a cooperative diffusion coefficient for the pseudogel structure, $D_c = E_g/\Phi$, where E is the longitudinal elastic modulus of the pseudogel and Φ is a frictional coefficient characterizing the relative translatory motion of polymer chain segments and solvent. The experimental work appears to have confirmed the essential features of the theory, but it has been noted that, attendant to the onset of entanglement behavior, there is evidently a transition from a more or less single exponential relaxation behavior in the correlation function of scattered photons to a nonexponential behavior which is suggestive of multiple relaxation modes.[5]

In solutions of macroions above c^*, nonexponential relaxation behavior in light scattering correlation functions is particularly striking and has been interpreted as consisting of two well-separated exponential decays.[9,10] This phenomenon is particularly well-documented in DNA solutions,[11,12] and a theoretical treatment has been given by Lee et al.[13] which successfully describes the qualitative behavior of the light scattering properties. The theory of Lee et al.[13] is based on the notion that in macroion solutions, at c^*, since the chains are instantaneously nonspherical, there will be a coupling of the internal modes of motion of the chains and anisotropic external diffusion. The dynamic characteristics of the two relaxation modes which result from this analysis are framed in terms of the longest relaxation time for internal motions, and $D_{||}$, the diffusion coefficient for translational motion parallel to the longest axis of the aspherical chain, modeled as a prolate ellipsoid.

The purpose of this note is to point out that a theoretical interpretation by Brochard and deGennes[14] of the quasielastic light scattering properties of Θ solutions of flexible polymers above c^*, when suitably modified, provides an alternative route to interpreting the bimodal relaxation behavior of concentration fluctuations in congested or entangled polymer solutions. Further, in combination with a recent hydrodynamic model for such systems by Klein,[15] the revised formalism may offer a basis for interpreting the concentration and/or molecular weight dependence of the relaxation spectrum of concentration fluctuations.

Theory

The basic hydrodynamic model utilized is that of an equivalent Rouse–Bueche–Zimm chain comprising N kinetic units or segments. We begin by proposing a slightly modified form of the equation of motion of Brochard and deGennes[14] for longitudinal displacements of the polymer chain segments:

$$\xi_0(\dot{r} - u) = \frac{m_0}{c}\frac{\partial}{\partial x}(S) - \partial W/\partial x \tag{1}$$

where ξ_0 is the segmental frictional coefficient which includes the effects of intersegmental hydrodynamic interactions,[2] m_0 is the mass of the segment, c is the solute concentration in g/mL, S is the thermally stimulated stress per unit volume, $(\dot{r} - u)$ represents the motion of a chain segment at position r relative to the solvent, and W is an external perturbation which is introduced to facilitate computation of the light scattering spectrum.[14] The stress S is represented as the sum of a constant component σ_0, the osmotic stress per chain segment, operating on a time scale long in comparison to τ_r, the characteristic lifetime of interchain entanglements, and a time-dependent term σ_1, the segmental viscoelastic stress relevant to the pseudogel, which operates on a time scale comparable to τ_r.

Thus we write

$$S = \sigma_0 + \sigma_1(t) \tag{2}$$

where σ_0 is the osmotic stress per unit volume,[14]

$$\sigma_0 = E_0(\partial r/\partial x) \tag{3}$$

$E_0 = c\ (\partial\pi/\partial c)$ is the isothermal osmotic rigidity which scales with concentration as c/N, where N is the number of segments per chain; $\sigma_1(t)$ is the time-dependent elastic stress of the pseudogel structure per unit volume. Following Brochard and deGennes,[14] σ_1 is evaluated from a simple Maxwell model

$$E_{gel}^{-1}\dot{\sigma}_1 + \sigma_1/\eta = d\dot{r}/dx \tag{4}$$

where E_{gel} is the longitudinal elastic modulus of the pseudogel, which scales as c/g, where g is the average number of chain segments between entanglements, and η is the macroscopic viscosity such that $\eta = E_{gel}\tau_r$. The Fourier–Laplace transform of eq 1, subject to eq 2–4, leads to the result

$$r(q,\omega) = iq\chi(q,\omega)W \tag{5}$$

where

$$\chi^{-1}(q,\omega) = i\omega\xi_0 + E_0q^2 + E_{gel}q^2\left(\frac{i\omega\tau_r}{1 + i\omega\tau_r}\right) \tag{6}$$

and $W = W_0 \exp[i(qx - \omega\tau)]$. Defining:

$$\xi_0 = \left(\frac{m_0}{c}\right)E_{gel}/D_c$$

where D_c is the cooperative diffusion coefficient of the pseudogel network,[1,2,8]

$$\rho = E_{gel}/E_0$$

$$\omega\tau_r = \alpha$$

$$D_c\tau_rq^2 = \mu$$

We derive:

$$\chi(q,\omega) = \frac{(1 + i\alpha)}{E_0q^2(1 + \alpha\rho\mu^{-1} - \alpha^2\rho\mu^{-1} + 1 + i\alpha + i\alpha\rho)} \tag{7}$$

The light scattering spectrum may be computed from the relation[14]

$$S(q,\omega) = -\frac{Tcq^2}{\pi\omega}\,\mathrm{Im}\{\chi(q,\omega)\} \tag{8}$$

To simplify the analysis, it is convenient to write:[14]

$$S(\mu,\alpha) = S(q,\omega)\frac{\pi E_0}{cT\tau_r} = -\alpha^{-1}\,\mathrm{Im}\left\{\frac{1 + i\alpha}{D(\alpha)}\right\} \tag{9}$$

where

$$D(\alpha) = 1 + i\alpha(1 + \rho + \rho\mu^{-1}) - \alpha^2\rho\mu^{-1} = -\rho\mu^{-1}(\alpha - iS_1)(\alpha - iS_2) \tag{10}$$

with

$$S_1 \sim (1 + \rho + \rho\mu^{-1})^{-1} \tag{11a}$$

$$S_2 = (1 + \rho + \rho\mu^{-1})\rho^{-1}\mu \tag{11b}$$

Using eq 8–10, we obtain finally

$$S(\mu,\alpha) = \frac{\pi\mu\rho^{-1}}{(S_2 - S_1)}\left\{\left(1 - \frac{1}{S_2}\right)L_2(\alpha) + \left(\frac{1}{S_1} - 1\right)L_1(\alpha)\right\} \tag{12}$$

where $L_i(\alpha)$ defines a Lorentzian function of the form

$$L_i(\alpha) = \frac{1}{\pi}\frac{S_i}{\alpha^2 + S_i^2} \tag{13}$$

with S_i defined by eq 10. This analysis consequently leads to the conclusion that the light scattering spectrum is a superposition of two single Lorentzian components with line widths

$$\Delta\omega_1 = \frac{D_c q^2}{\rho + (\rho + 1)D_c\tau_r q^2} \tag{14}$$

$$\Delta\omega_2 = \frac{1}{\tau_r} + (\rho^{-1} + 1)D_c q^2 \tag{15}$$

If we define the center of mass diffusion of the polymer coils as $D_t = (m_0/c)E_0/\xi_0 = \rho^{-1}D_c$, we may rewrite eq 14 and 15 in the form

$$\Delta\omega_1 = \frac{D_t q^2}{1 + (D_c + D_t)q^2\tau_r} \tag{16}$$

and

$$\Delta\omega_2 = \frac{1}{\tau_r} + (D_c + D_t)q^2 \tag{17}$$

The relative amplitudes of these components are given by

$$\frac{A_2}{A_1} = \frac{1 - 1/S_2}{1/S_1 - 1} = \frac{\mu(1 + \rho^{-1})}{\rho(1 + \mu^{-1})(1 + \mu + \rho^{-1}\mu)} \tag{18}$$

Discussion

Equations 14–16 are significantly different from those derived by Brochard and deGennes.[14] However, for the particular case considered by these authors of a Θ solution ($\rho \gg 1$), our results also lead to the conclusions that the amplitude of the fast mode (A_2) is insignificant in comparison with that of the slow mode (A_1) at all experimentally accessible wave vectors and, in addition, that the line width of the slow mode becomes extremely narrow. Consequently, only the slow mode can be observed in Θ solutions. For smaller values, $\rho \sim 1$, eq 18 predicts the relative amplitude of the slow and fast component will approach the limit ρ^{-1} at large wave vectors. However, at small q values, the bulk of the relaxation amplitude shifts into the slow mode. The angle dependence of the linewidth parameters corresponding to eq 14 and 15 is shown in Figure 1. There is a difference in the precise definition of the parameter τ_r between our equations and those of deGennes.[1,2,14] In accordance with the discussion of Klein,[15] we have defined τ_r as the mean lifetime of the chain lengths between transient cross-links of the pseudogel. The concentration dependence of the parameters of eq 14–16 is, in principle, predicted by the analysis of Klein.[15] Thus the value of τ_r is expected to increase as the concentration increases above a value c^* corresponding to $(N/g) \sim 18$. Anticipating some of the experimental data on polynucleotide solutions to be discussed below, however, we note that an intermediate regime of hydrodynamic behavior may exist for concentration values between $c^{**} < c < c^*$, where c^{**} corresponds to $N/g \sim 1$. In this regime, τ_r may decrease from a value approximately equivalent to that of the longest internal Rouse–Zimm mode of the complete chain at c^{**} as the chain length between entanglements decreases. As the concentration increases toward c^*, we realize that screening of the intersegmental hydrodynamic interactions will increase.[16] At c^*, τ_r begins to increase rapidly as the cooperative transition to a true reptative mode of diffusion occurs (i.e., snakelike motion through essentially a fixed entanglement structure[15]); below c^{**}, isotropic translational diffusion is observed; for $c^{**} < c < c^*$, diffusion is anisotropic, but not reptative as defined by Klein.[15] Interestingly, in a recent study of the hydrodynamic properties of solutions of xanthan polysaccharide,[17] it was remarked that the transition corresponding to the onset of entanglements was observed at a lower concentration in the quasielastic light scattering spectrum in comparison with that evident in viscometric experiments.

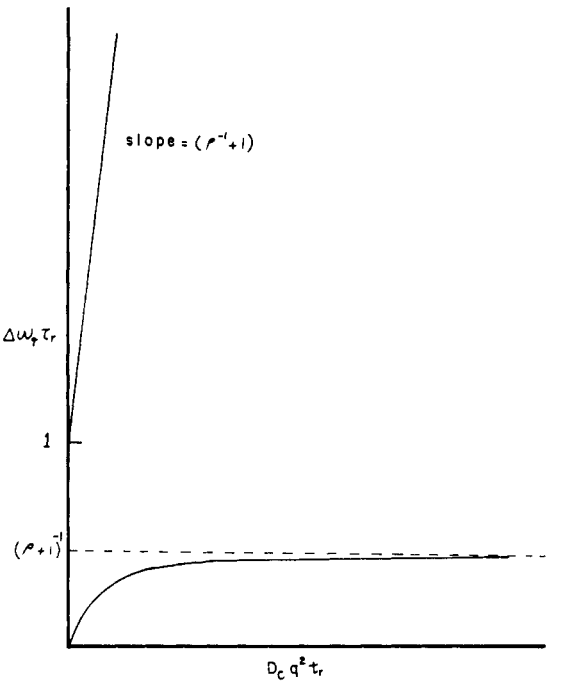

Figure 1. Angle dependence of the fast and slow decay modes as predicted by eq 14 and 15.

At this point, we note that these properties of the relaxation processes shown in Figure 1 are very similar to those of the fast and slow modes deduced by the analysis of Lee et al.[13] In view of this similarity, it is to be expected that eq 14–18 can be applied to interpret quasielastic light scattering data from DNA solutions. We have selected two experimental studies from the literature to illustrate the application of these equations. First, we note that the theoretical formalism noted above can be used to obtain a good fit to the angle-dependent relaxational parameters characterizing the quasielastic light scattering[10] from N 1 DNA ($M = 31 \times 10^6$, $c = 25$ μg/mL) in 1.0 M NaCl/0.01 M Tris/0.01 M EDTA at pH 8.0 with the choice of parameters $D_c = 0.72 \times 10^{-8}$ cm²/s, $\tau_r = 8$ ms, $\rho = 1.9$, $D_t = 0.38 \times 10^{-8}$ cm²/s. The quality of the fit is shown in Figure 2. Unfortunately, no detailed reports of concentration dependence of the quasielastic light scattering properties of DNA solutions appear to be available. A recent study of the polynucleotide poly(adenylic acid) in 0.1 M NaCl, 0.01 M Na Cacodylate at pH 7.4 includes both angle-dependent and concentration-dependent quasielastic light scattering studies in the entanglement regime.[18] Table I summarizes the parametric fit to these results. Again a close correspondence between theory and the angle-dependent experimental relaxational parameters is observed. Further, we note that eq 18 correctly predicts the experimentally observed variation of the relaxation ampli-

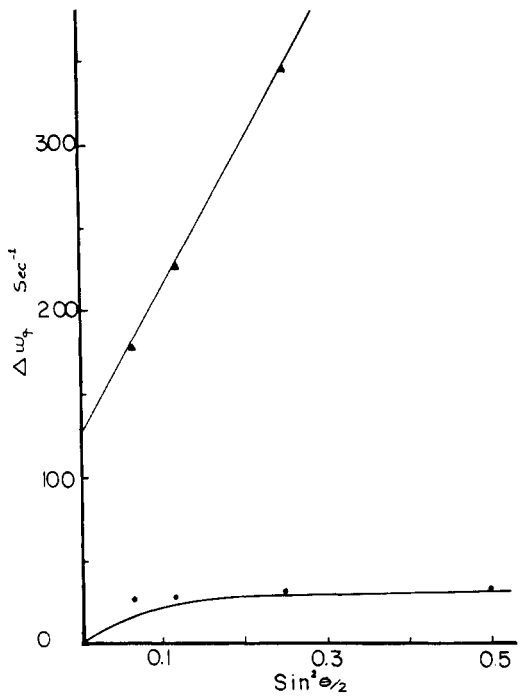

Figure 2. Line width parameters vs. $\sin^2 \theta/2$ for fast and slow modes in the light scattering spectrum of N1 DNA (mol wt ~ 31×10^6). The points (▲) and (●) are the data of Schmidt.[10] The solid lines are computed from eq 14 and 15 with $D_c = 0.72 \times 10^{-8}$ cm²/s, $\tau_r = 8.0$ ms, and $\rho = 1.9$.

Table I
Hydrodynamic Structure of Entangled Poly(adenylic acid) Solutions

system, poly(adenylic acid)[a]	concn, g/L	mol wt × 10^6	$D_c \times 10^8$, cm²/s	$\tau_r \times 10^3$, s	ρ	$D_t \times 10^8$, cm²/s
0.1 M NaCl	4.8	3.5	8.4	9.0	1.7	5.0
0.01 M Na Cacodylate pH 7.4	2.4	3.5	3.8	13.3	0.7	5.4
	0.12	3.5	1.0	28.6	0.2	5.0

[a] Reference 18.

tudes with sin $\theta/2$: at small angles $A_1/A_2 \gg 1$; at large angles, the ratio A_1/A_2 varies as ρ^{-1}. Also, we observe that the theoretical interpretation discussed above provides a simple rationale for the fact that τ_r can be smaller than the longest internal relaxation time for the entire chain.[13] Two unexpected aspects of the results on the polynucleotide systems are worthy of comment. First, the numerical value of τ_r decreases with increasing concentration in contrast to the prediction of Klein.[15] We suggest that this may reflect the fact that the concentrations studied are in a regime $c^{**} < c < c^*$ where τ_r essentially corresponds to the longest Rouse–Zimm relaxation time for the section of the chain between entanglements.

If the effect of hydrodynamic screening is ignored, we would expect τ_r to scale as $(N/g)^{-3\nu}$ in this regime, where the exponent ν characterizes the molecular weight dependence of the hydrodynamic radius $R_g \sim N^\nu$. Because of the long-range character of interchain repulsive interactions, this concentration zone might reasonably be expected to be wider for macroion solutions than for solutions of uncharged polymers. Second, we note that at lower concentrations the value of ρ decreases below unity. Since one might anticipate that

$$\rho = E_g/E_0 \sim N/g \tag{19}$$

and if we adopt the most simple model that c^{**} corresponds to $N/g \sim 1$ and $E_0 \sim E_g$, we would conclude $\rho = 1$ at c^{**}. As the concentration increases above c^{**}, N/g certainly increases more or less rapidly, depending on the structural properties of the polymer. A value of $\rho < 1$ implies $E_g/E_0 < 1$. The reason for this discrepancy is presently unclear. One possibility is that near c^{**}, at long times, the average interchain electrostatic repulsions contributing to E_0 are greater than those at short times relevant to the computation of E_g when considerable overlap of the chain domains is present. We also note the possibility of numerical error in the experimental decomposition of fast and slow modes due to the possible influence of sample polydispersity. Finally, as the concentration increases beyond c^*, according to Klein,[15] τ_r must begin to increase rapidly. Under this circumstance, the two relaxation modes predicted by eq 14–18 rapidly coalesce, and one obtains the original result of deGennes.[2] Obviously, the hydrodynamic model described above is oversimplified and can be expected to elucidate only the salient features of the relaxation spectrum of entangled polymer solutions.

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