Diffusion of Linear and Branched Polystyrenes in Tetrahydrofuran in the Dilute and Semidilute Regimes

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ABSTRACT: Photon correlation spectroscopy of four linear polystyrene standards ($M_w = 1.8 \times 10^5$, $M_w = 3.9 \times 10^5$, $M_w = 3 \times 10^6$, and $M_w = 10^7$) and a uniform nine-branch star ($M_w = 9.6 \times 10^5$) in a good solvent, tetrahydrofuran, is described. For each polymer, the apparent z-average translational diffusion coefficient $D_{t,z}$ computed from the first moment $\bar{\Gamma}$ of the correlation functions $D_{t,z} = \bar{\Gamma}/q^2$ was determined over a wide range of scattering vector $\mathbf{q}$ and at concentrations ranging from very dilute to substantially in excess of the value at which molecular overlap occurs. While the two linear polymers of high molecular weight exhibit properties in agreement with the theoretical description of de Gennes, a breakdown of the scaling description is observed in semidilute solutions of the low molecular weight linear sample and in the branched polymer. In these systems, three distinct regimes of behavior are observed in $D_{t,z}$: (1) a region of dilute solution behavior for $c < c^*$, the overlap concentration; (2) an apparent pseudogel regime when $c > c^{**}$, a characteristic concentration which appears close to the value c_e at which the entanglement transition is predicted in the zero-shear viscosity; (3) a transition region when $c^* < c < c^{**}$ in which anomalously small scaling exponents are determined. It is observed that the measured values of $D_{t,z}$ also exhibit a small but significant angle dependence in the semidilute regime in the latter region even though $\mathbf{q}\cdot R_g \ll 1.0$. Evidence is presented to indicate bimodal relaxation behavior of the correlation functions in the transition region. It is therefore proposed that in the transition regime the theoretical description must incorporate the finite relaxation time for interchain entanglements.

Introduction

Quasi-elastic light scattering techniques provide a useful means of investigating the transport properties of molecular fluids.[1,2] In particular, in our laboratory, we are interested in applying photon correlation spectroscopy to probe the molecular dynamics of concentrated solutions of polymers and polymer melts.[3,4] Recently, de Gennes[5,6] has described a theoretical interpretation of what is termed the semidilute concentration regime, viz., $c \gtrsim c^*$, where c^* is a characteristic concentration at which overlap of the individual macromolecular domains begins. When $c < c^*$, the dilute regime, the polymer coils behave rather like a dilute gas of weakly interacting hard spheres; above c^* intermolecular entanglements are expected to produce cooperative dynamic modes characteristic of a network. Below c^*, the kinetic unit is the entire chain and photon correlation spectroscopy detects center-of-mass translational diffusion at smaller scattering angles[7] and relaxation times characteristic of the intramolecular Rouse–Bueche–Zimm modes, if the condition $\mathbf{q}\cdot R_g > 1$ can be satisfied,[8] where $\mathbf{q}$ is the scattering vector and R_g is the root-mean-square radius of gyration of the polymer coil. When $c > c^*$, de Gennes[5,6] interprets the network dynamics by analogy with those of a permanently cross-linked gel.[9] The kinetic unit is defined to be a "blob" whose characteristic dimension is ξ, the range of the monomer–monomer correlation function, proportional to the mean density between chain entanglements. In this regime, quasi-elastic light scattering at $\mathbf{q}\cdot R_g \sim 1.0$ is predicted to observe[5,6,10] a cooperative translational diffusion mode characterized by a diffusion coefficient

$$D_c = kT/6\pi\eta_0\xi \tag{1}$$

where η_0 is the solvent viscosity. At larger scattering angles, when $k\xi > 1$, it is to be anticipated that the light scattering technique is sensitive to subchain dynamics characteristic of the "blob".[10]

Subsequently, Klein[11] has pointed out some inconsistencies in the de Gennes molecular dynamic model for reptative diffusion. In particular, in the de Gennes model, relaxation of the entanglement constraints on a test chain are dominated by the motions of surrounding chains rather than those of the test chain. This point was independently recognized by Daoud and de Gennes in a later paper.[12] As a consequence of this, Klein finds[11] a cooperative transition in the configurational dynamics of semidilute polymer solutions at a higher concentration than the overlap concentration. The transition occurs at a value which we label c^{**}, when the number of entanglements (or blobs) per chain is $3\pi\sqrt{2}$.[11] Recently, we have pointed out some possible consequences of this result for quasi-elastic light scattering from semidilute solutions.[13] For example, a transition to dynamic behavior reminiscent of a permanent network is to be expected at $c = c^{**}$ rather than $c = c^*$. When $c^* < c < c^{**}$, interchain entanglements must still severely perturb the unhindered translational diffusion of coils manifested in the dilute regime; however, relaxation of the chains is Rouse-like rather than reptative in character, and properties characteristic of a transient network are to be expected. This point was clearly espoused by Lee et al.,[14] who described a coupled rotational–translational diffusion model applicable to congested polymer solutions, i.e., $c \sim c^*$. Subsequently, Reihanian and Jamieson[13] noted that a modification of a transient network formalism of Brochard and de Gennes[15] leads to prediction of bimodal relaxation behavior in the quasi-elastic light scattering spectrum similar to that deduced by Lee et al.[14] These predictions are in qualitative agreement with some independent light scattering data on semidilute DNA and polynucleotide solutions.[13,14] It should be emphasized that the latter data are of a rather preliminary nature; however, it is to be expected that the manifestation of "permanent" network dynamics will be delayed by long-range electrostatic repulsions or an increase in chain stiffness. Such effects will oppose the intermolecular entanglement coupling of chains.

In this paper we are concerned with the behavior of semidilute solutions of polynonelectrolytes. It is pertinent to note that the above considerations should apply to such systems also. Thus we anticipate observing three distinct hydrodynamic regimes in semidilute solutions separated by c^* and c^{**}. Experimental tests of the accuracy of the de Gennes theory in the semidilute regime have noted apparent inconsistencies, particularly when dealing with

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Table I
Structural Parameters of Star Polystyrene in Cyclohexane at 35 °C

M_w(GPC)	M_w(LS)	$[\eta]_b/[\eta]_{l,\theta}$	$[\eta]_b/[\eta]_l$ (z/k)	$R_{s,\theta}$, Å	R_g, Å
9.6×10^5	$(9.5 \pm 0.4) \times 10^5$	0.58 ± 0.01	0.59	162 ± 4	243 ± 12

comparatively small molecular weights. In a good solvent, the statistical scaling theories predict that, for flexible coils,

$$D_c \sim c^\delta \tag{2}$$

where the exponent $\delta = \nu/(3\nu - 1)$ and the parameter ν scales the molecular weight dependence of the radius of gyration

$$R_g \sim N^\nu \tag{3}$$

For $\nu = 0.6$, $\delta = 0.75$. Quasi-elastic light scattering experiments by Adam and Delsanti[10] on a series of linear polystyrene standards with benzene as solvent produced very close agreement with theory. A transition to logarithmic dependence of D_c on c was observed at higher concentrations such that $\delta = 0.67 \pm 0.02$. On the other hand, Bailey et al.,[17] in a similar study of linear polystyrenes in butanone, again observed a transition from dilute-solution characteristics at $c \sim c^*$ but determined $\delta \sim 0.3$. Schaefer[18] noted certain deficiencies in the experimental and analytical methods of Adam and Delsanti[10] and also discovered exceedingly low values of δ for linear polystyrene standards in several solvent systems. It is interesting to note that in most of these studies the molecular weights of the polymer species were comparatively low ($M < 5 \times 10^5$).

Recently, we have carried out a photon correlation spectroscopy study of several linear polystyrene standards and also a nine-branch uniform star polystyrene in tetrahydrofuran at 30 °C, which is a good solvent for polystyrene. A preliminary report of these investigations has been given elsewhere.[19,20] We present here a more detailed description. These data are interpreted to indicate that in each system at least three hydrodynamic regimes are evident in the light scattering data, in accord with the discussion of Reihanian et al.[13] The characteristic concentrations c^*(exptl) and c^{**}(exptl) which separate these regimes are consistent with admittedly crude theoretical estimates based on chain overlap and the characteristic concentration of Klein, respectively. It is further noted that these data provide a possible rationale for reports of anomalously small values of δ. These are observed when $c^* < c < c^{**}$.

Materials and Methods

Four linear polystyrenes ($M_w = 1.8 \times 10^5$, $M_w = 3.9 \times 10^5$, $M_w = 3 \times 10^6$, $M_w = 10^7$) of narrow molecular weight distribution ($M_w/M_n < 1.1$) and a nine-branch uniform star polystyrene ($M_w = 9.6 \times 10^5$, $M_w/M_n = 1.06$) were obtained from Polysciences Inc. Spectroscopic grade tetrahydrofuran from the Aldrich Chemical Co. was utilized (refractive index, $\bar{n}^{20}{}_D = 1.407$; density, $\rho^{20}{}_0 = 0.887$ cP).

The following procedure was developed to prepare optically clean solutions of the polystyrenes in tetrahydrofuran at a series of concentrations in the semidilute regime, viz., at concentrations above the characteristic concentration c^* at which overlap of the hydrodynamic domains of the coils occurs.[19,20] First, dilute solutions were prepared by gravity filtration through Millipore filters (FHLP 01300, pore size 0.5 μm) directly into the scattering cuvette. The cuvette was capped with a seal containing a 0.5-μm Millipore filter to permit evaporation of the solvent but exclude airborne particulates. The solvent was slowly evaporated in a hood at room temperature over a period of several weeks to produce a series of optically clean concentrated solutions. Solute concentrations were then determined by gravimetric determination of the solvent loss.

Quasi-elastic light scattering experiments were performed by using a photon correlation spectrometer described elsewhere.[21] This instrument incorporates a Saicor autocorrelator and determines the full photon correlation function of the scattered light. All experiments were performed in the homodyne mode. Analyses of the correlation functions were performed by the method of moments,[22] using the weight procedure of Brown et al.[23] This generates the first moment $\bar{\Gamma}$ from which the z-average translational diffusion coefficient is computed

$$\bar{\Gamma} = D_{t,z}q^2 \tag{4}$$

where $\mathbf{q} = (4\pi/\lambda) \sin(\theta/2)$ is the scattering vector, λ is the wavelength of incident laser light in the medium, and θ is the scattering angle. Also computed is the normalized second moment $\mu_2/\bar{\Gamma}^2$, which provides a crude measure of the nonexponentiality of the correlation functions. For dilute solutions, we found that the correlation functions are very close to single exponentials ($\mu_2/\bar{\Gamma}^2 < 0.05$). At higher concentrations, we observed systematic departure from exponentiality. A similar behavior was reported by Schaefer.[18] For such systems, first moments were evaluated by the extrapolation method of Brown et al.[23]

Results

We first note that the structural characteristics of the polymer standards and the lack of molecular weight degradation by ultrafiltration procedures were confirmed by light scattering and viscometric experiments. Characterization of the linear polymers was reported previously.[19,20]

In Table I, we summarize results of analysis of the star polymer in cyclohexane at $T = 35$ °C, i.e., the Θ temperature. The weight-average molecular weight was determined by conventional light scattering; $(M_wM_z)^{1/2}$ was measured from the Flory–Mandelkern relation;[24,25] $[\eta]_b/[\eta]_l$(exptl) was determined by the Mark–Houwink relation reported elsewhere;[26,27] $[\eta]_b/[\eta]_l$(theor) was computed for a nine-branch uniform star ($f = 9$) by using the result derived by Zimm and Kilb[28]

$$[\eta]_b/[\eta]_l = (2/f)^{3/2}[0.390(f-1) + 0.196]/0.586 \tag{5}$$

In the dilute-solution regime, in tetrahydrofuran, the concentration dependence of $D_{t,z}$ is linear and is found to be in reasonable agreement with the theoretical predictions of Yamakawa[29]

$$D_t = D_t^0(1 + k_Dc) \tag{6}$$

where

$$k_D = 0.8A_2M - \frac{N_AV_h}{M} - \bar{v}_2 \tag{7}$$

and of Pyun and Fixman[30]

$$k_D = 2A_2M - k_f - \bar{v}_2 \tag{8}$$

where

$$k_f = [7.16 - K(A)]\frac{N_AV_h}{M} \tag{9}$$

In eq 9, $K(A)$ is a monotonically decreasing function of A which is related to A_2. At $T = \Theta$, $K(A) = 4.93$ and $k_f = 2.23\ N_AV_h/M$. A comparison of experiment with theory is given in Table II. It should be noted that in this good solvent, the last two terms in eq 7 are small compared with the first. In fact, the solute partial specific volume $\bar{v}_2 \sim$

Table II
Translational Diffusion of Polystyrenes in Dilute Solution: Theory vs. Experiment

solvent	MW	D_t^0, cm²/s	A_2, cm³/g	$10^{-2}k_D$(exptl), cm³/g	$10^{-2}k_D$(Y), cm³/g	k_D(PF), cm³/g
			A. Linear Polymers			
THF, 30 °C	1.8×10^5	3.25×10^{-7}		0.36 ± 0.08	0.22 ± 0.02	
	3.9×10^5	2.48×10^{-7}		0.96 ± 0.07	0.75 ± 0.03	
	3.0×10^6	8.13×10^{-8}		3.9 ± 0.09	3.9 ± 0.01	
	1.0×10^7	4.35×10^{-8}		6.2 ± 0.3	10.3 ± 0.3	
			B. Star Polymer			
THF, 30 °C	9.6×10^5	$(1.71 \pm 0.04) \times 10^{-4}$	$(1.4 \pm 0.1) \times 10^{-4}$	51 ± 5	39 ± 8	
cyclohexane, 35 °C	9.6×10^5	$(1.66 \pm 0.04) \times 10^{-7}$	$-(2.1 \pm 0.8) \times 10^{-6}$	-41 ± 4	-11 ± 0.6	-2.6 ± 0.6

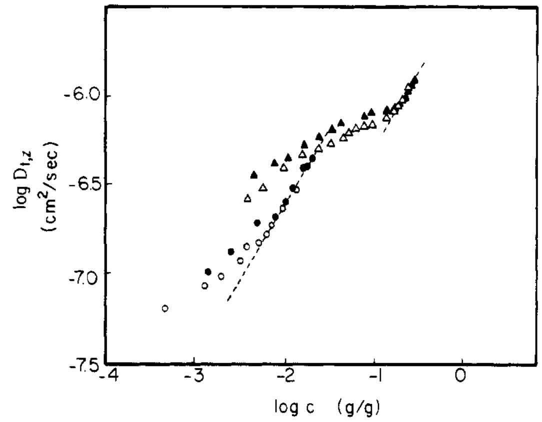

Figure 1. Plot of log $D_{t,z}$ vs. log concentration for linear polystyrenes: (●) $M = 10^7$, $q{\cdot}R = 0.856$; (○) $M = 3 \times 10^6$, $q{\cdot}R = 0.659$; (△) $M = 3.9 \times 10^5$, $q{\cdot}R = 0.215$; (▲) $M = 1.8 \times 10^5$, $q{\cdot}R = 0.155$.

1 mL/g and is neglected. Vrentas and Duda[31] argue that the term in eq 7 containing the hydrodynamic volume should be omitted. This would produce small changes in the numerical values of k_D(theor) in Table II. For these calculations, the experimental value of the second virial coefficient A_2 of the branched polymer was determined by conventional light scattering experiments. The A_2 values for the linear polymers were calculated from the experimental relation deduced by Schulz and Baumann[32]

$$A_2M = (0.0102 \pm 0.0001)M^{0.749\pm0.005}\ \mathrm{cm}^3 \qquad (10)$$

At higher concentrations, nonlinear concentration dependence of $D_{t,z}$ is found. In Figure 1 we show a plot of log $D_{t,z}$ vs. log c for the four linear polystyrenes, determined at small scattering angles, viz., $q{\cdot}R_g < 1.0$. For the two samples of higher molecular weight ($M = 3 \times 10^6$ and $M = 10^7$), we note at this point that the results are in good agreement with the pseudogel model of de Gennes.[5,6] Thus, above a transition concentration, which we label here c^{**} for reasons which will be discussed later, the $D_{t,z}$ values are in accord with eq 2, the exponent δ having the value 0.82 ± 0.05. Further, we note that, for $q{\cdot}R_g < 1$, the $D_{t,z}$ values are independent of scattering angle and, in the pseudogel concentration regime, the light scattering properties appear to be independent of molecular weight. On the other hand, the results for the low molecular weight samples plainly depart dramatically from the scaling prediction of the de Gennes theory.

This behavior is more dramatically depicted in a linear plot of the diffusion data as shown in Figure 2. Here we compare the results shown on the previous figure for the low molecular weight sample, determined at $\theta = 60°$, with values determined at $\theta = 40°$ and $\theta = 20°$. Additional results were obtained at intermediate angles and show the same trends but are omitted for clarity. Evidently, the $D_{t,z}$ values evidence three concentration regimes of behavior. First, we observe the low-concentration regime, where the $D_{t,z}$ data are angle independent and in reasonable agreement with dilute-solution theory as detailed earlier. At higher concentrations, the $D_{t,z}$ values become angle dependent, and we note, as shown in Figure 3, a systematic increase in the values of the normalized second moments at each angle. There is evidently an intermediate regime, defined by characteristic concentrations $c^* < c < c^{**}$, where the apparent values of $D_{t,z}$ scale according to eq 2, with δ assuming increasing values from 0.2 to 0.35 as the scattering angle increased to $\theta = 60°$. At higher scattering angles, a second transition effect is observed at c^{**}, where we can describe the data by using eq 2 with $\delta = 0.82 \pm 0.25$. In this regime $D_{t,z}$ apparently is again independent of molecular weight; however, as is evident from Figure 1, this "pseudogel" behavior cannot be identified with that seen in the high molecular weight samples. Three regimes of hydrodynamic behavior, with similar properties to those manifested in the linear samples of low molecular weight,

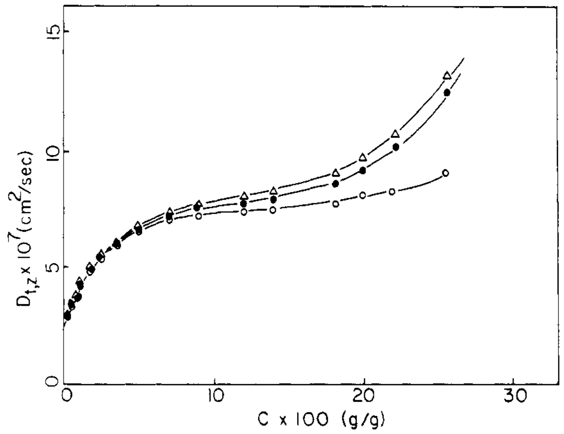

Figure 2. Linear plot of $D_{t,z}$ vs. concentration for linear polystyrene ($M = 3.9 \times 10^5$): (○) $q{\cdot}R = 0.144$; (●) $q{\cdot}R = 0.284$; (△) $q{\cdot}R = 0.415$.

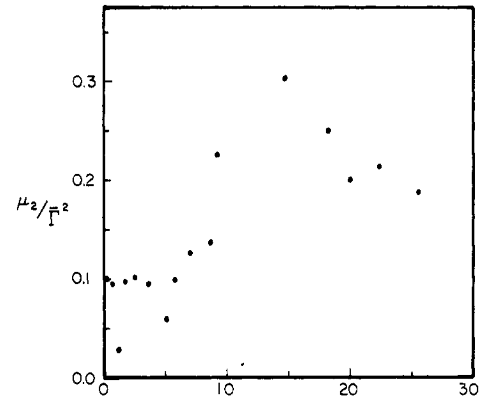

Figure 3. Concentration dependence of the normalized second monent μ_2/Γ^2 for linear polystyrene ($M = 3.9 \times 10^5$, $q{\cdot}R = 0.284$).

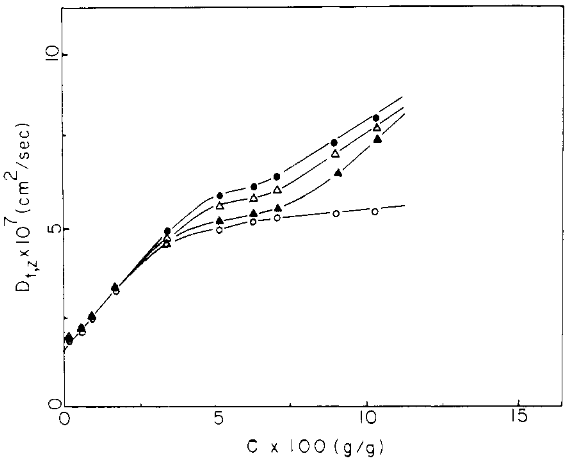

Figure 4. Linear plot of $D_{t,z}$ vs. concentration for nine-branch star polystyrene at several scattering angles: (○) $\theta = 20°$; (▲) $\theta = 40°$; (△) $\theta = 60°$; (●) $\theta = 80°$.

are also observed in the scattering properties of the star polystyrene, as shown in Figure 4.

Discussion

The above light scattering results on four linear polystyrenes indicate a breakdown of the scaling theories for flexible coil molecules in good solvents in the semidilute concentration regime as the molecular weight decreases. In the low molecular weight samples, a wide transition regime separates the dilute regime from a regime where $D_{t,z}$ scales as η^δ with $\delta = 0.81 \pm 0.25$. At this point we note that in an earlier communication, we presented evidence[20] that a narrow transition regime exists in the high molecular weight results and determined values c^* and c^{**} delineating the region of intermediate behavior. We further noted that the molecular weight dependence of c^* and c^{**} for all four samples is consistent with the notion that c^* corresponds to the overlap of the hydrodynamic spheres of individual molecules and that c^{**} is in approximate agreement with theoretical[11] and the experimental[33] results for the properties of the transition concentration where intermolecular entanglements are manifest in the zero-shear viscosity[20] of polystyrene solutions in good solvents.

For example, for polystyrene with $M = 3.9 \times 10^5$, in tetrahydrofuran, defining

$$c^* = \frac{2^{1/2}}{8} \frac{M}{N_A R_s^3} \text{ g/mL} \qquad (11)$$

we calculate c^*(theor) = 0.015 g/mL, since the Stokes radius R_s = 198 Å and ρ_{THF} = 0.88 g/mL. This compares with c^*(exptl) = 0.022 ± 0.002 g/mL, estimated from the results in Figure 2. Further from the result of Klein,[11] the transition in shear viscosity can be defined by

$$c^{**} = \left(\frac{(18\pi^2)^{1/2}}{A} \frac{M_0}{M} \right)^{4/5} \qquad (12)$$

where M_0 is the monomer molecular weight, and, for chains with a C–C backbone, the coefficient A is given by

$$A = (0.83)^2 j(\bar{v})^{5/4}/C_\infty \qquad (13)$$

with j as the backbone units per monomer, $\bar{v}$ the monomer partial specific volume, and C_∞ the characteristic ratio. Using, for polystyrene, $j = 1$, $\bar{v} = 1/\rho_m$, where the monomer density of styrene is ρ_m = 0.9060 g/mL, and C_∞ = 10.0, we calculate A = 0.078. Then, eq 12 leads to c^{**}(theor) = 0.10 g/mL for comparison with c^{**}(exptl) ~ 0.14 ± 0.02 g/mL from Figure 2.

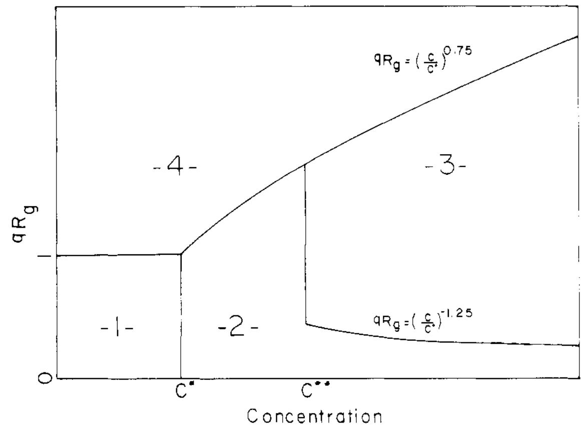

Figure 5. Relaxation diagram for dynamic light scattering from polymer solutions in the dilute and semidilute regimes at finite concentration. Regime 1: independent diffusion of weakly interacting coils. Regime 2: bimodal relaxation; onset of reptative diffusion of coils, blob diffusion of network. Regime 3: pseudogel behavior; severely restricted coil diffusion ($D_t \rightarrow 0$), blob diffusion mode is dominant. Regime 4: Subchain dynamics.

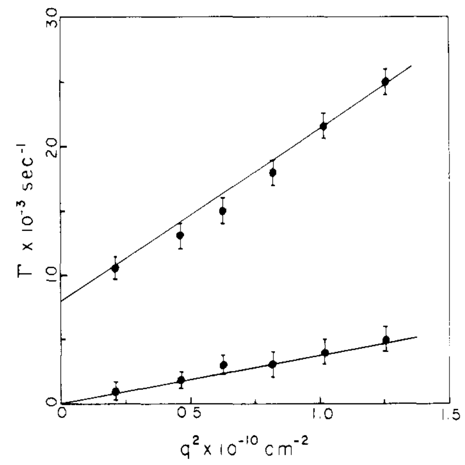

Figure 6. Plot of angle-dependent relaxation frequencies of a bimodal analysis of photon correlation spectroscopy data for the linear polystyrene ($M = 3.9 \times 10^5$) at $c = 12.5 \times 10^{-2}$ g/g. Lines are a theoretical fit, based on ref 13, as discussed in the text.

We note that at the transition concentration defined by eq 12, the hydrodynamic model of Klein[11] predicts a rapid increase in the relaxation time for entanglements ($\tau_e \rightarrow \infty$). This results in a precipitous slowing down of center-of-mass diffusion and, presumably, the appearance of the rapid "blob" diffusion mode in the light scattering spectrum. Indeed theoretical analysis[13] of the quasi-elastic light scattering properties of semidilute solutions predicts that bimodal relaxation is to be anticipated in the crossover regime between the overlap concentration where entanglement coupling begins and the concentration where $\tau_e \rightarrow \infty$. The relative amplitudes of fast to slow modes (A_1/A_2) is strongly angle dependent:[13] at wide angles, $A_1/A_2 \rightarrow \rho = N/g$, the ratio of the number of monomers per chain to the number of monomers per entanglement length; at small angles, the bulk of the relaxation amplitude shifts into the slow mode ($A_1/A_2 \rightarrow 0$). A relaxation map based on this theoretical model is depicted schematically in Figure 5.

We have found that the quasi-elastic light scattering data in the transition regime are consistent with this interpretation. In Figure 6, we show the angle-dependent relaxation frequencies of a bimodal fit to photon correlation spectroscopy data for the linear polystyrene (M = 3.9 × 10^5) at $c = 12.5 \times 10^{-2}$ g/g. Solid lines are a fit to this

Table III
Angle Dependence of the Relative Amplitudes of Fast to Slow Modes in Photon Correlation Spectroscopy Data for Polystyrene ($M = 3.9 \times 10^5$) at $c = 12.5 \times 10^{-2}$ g/g

	scattering angles (θ), deg					
	50	45	40	35	30	20
A_1/A_2	0.72	0.65	0.53	0.30	0.28	0.23

data with the characteristic parameters $D_c \sim D_t = 6.75 \times 10^{-7}$ cm^2/s, $\rho \sim 1.0$, and $\tau_e = 0.12$ ms. The angle dependence of the relative amplitudes of fast to slow modes (A_1/A_2) is given in Table III. It is suggested that this effect is the origin of the increase in second moment of the correlation functions in the semidilute regime evident in Figure 3 and of the apparent anomalous angle dependence of the first moment seen in Figures 2 and 4. The analysis represented in Figure 6 suggests that in the crossover region, the contraction of the chain as concentration increases[34] maintains $N/g \sim 1$ until c^{**} is reached.

The data presented in Figure 1 suggest the existence of two different "pseudogel" regimes where the $D_{t,z}$ values are independent of molecular weight. The implications of this result are not yet clear. We have observed elsewhere[19,20] that the crossover regime in the quasi-elastic light scattering experiments is paralleled closely by the crossover region in zero-shear viscosity of the solution. It may be, therefore, that a suitable superposition of the $D_{t,z}$ values can be achieved by using an appropriate shift factor, presumably incorporating a concentration-dependent chain expansion parameter.[35] However, it is pertinent to note that Daoud and Jannink[36] have theoretically deduced a second crossover regime in semidilute polymer solutions to a tricritical regime where the correlation length ξ scales as c^{-1}. This is predicted to occur at a characteristic concentration $c^{**} \sim \tau$, where $\tau = (T - \Theta)/\Theta$ and Θ is the theta temperature. Our results (Figure 1) for $M = 3.9 \times 10^5$ and 1.8×10^5 are in agreement with this theory if we identify $c^{**} \sim c_\theta^{**}$ for these samples. More recently, Schaefer et al.[37] have formulated a statistical theory for solutions of semiflexible chains. This analysis predicts[37] a breakdown of scaling theory at a concentration $c^\dagger > c^*$ and a crossover to a mean-field regime where $\xi \sim c^{-1/2}$; a third crossover to a Θ pseudogel regime ($\xi \sim c^{-1}$) is again predicted at a higher concentration c_Θ^{**}. Our results are also consistent with this theory. Clarification of these questions will require a more complete study of the molecular weight dependence of the quasi-elastic light scattering properties and a more detailed examination of the relaxational characteristics of the correlation functions in the semidilute regime. In this connection, we note the recent application of histogram analysis methods by Nose and Chu[38] to demonstrate bimodal relaxation behavior in photon correlation spectroscopy data from semidilute polystyrene solutions at the Θ temperature.

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References and Notes

(1) Chu, B. "Laser Light Scattering"; Academic Press: New York, 1974.
(2) Berne, B. J.; Pecora, R. "Dynamic Light Scattering"; Wiley: New York, 1976.
(3) Jamieson, A. M.; McDonnell, M. E. *Adv. Chem. Ser.* **1979**, *No. 174*, 163.
(4) Lee, H.; Jamieson, A. M.; Simha, R. Proceedings, IUPAC 26th International Symposium on Macromolecules, Mainz, West Germany, 1979; Vol. 3, p 1228.
(5) de Gennes, P. G. *Macromolecules* **1976**, *9*, 587.
(6) de Gennes, P. G. *Macromolecules* **1976**, *9*, 594.
(7) Pecora, R. *J. Chem. Phys.* **1964**, *40*, 1604.
(8) Pecora, R. *J. Chem. Phys.* **1968**, *49*, 1032.
(9) Tanaka, T.; Hocker, L.; Benedek, G. B *J. Chem. Phys.* **1973**, *59*, 5151.
(10) Adam, M.; Delsanti, M. *Macromolecules* **1977**, *10*, 1229.
(11) Klein, J. *Macromolecules* **1978**, *11*, 852.
(12) Daoud, M.; de Gennes, P. G. *J. Polym. Sci.* **1979**, *17*, 1971.
(13) Reihanian, H.; Jamieson, A. M *Macromolecules* **1979**, *12*, 684.
(14) Lee, W. I.; Schmitz, K. S.; Lin, S.-C.; Schurr, J. M. *Biopolymers* **1977**, *16*, 583.
(15) Brochard, F.; de Gennes, P. G *Macromolecules* **1977**, *10*, 1157.
(16) Southwick, J. G.; McDonnell, M. E.; Blackwell, J.; Jamieson, A. M. *Macromolecules* **1979**, *12*, 305.
(17) Bailey, D.; King, T. A.; Pinder, D. N. *Chem. Phys.* **1976**, *12*, 161.
(18) Schaefer, D. W. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1978**, *19*, 733.
(19) Yu, T. L. M.S. Thesis, Case Western Reserve University, 1979.
(20) Yu, T. L.; Reihanian, H.; Southwick, J. G.; Jamieson, A. M. *J. Macromol. Sci.*, in press.
(21) Lee, H. S.; Jamieson, A. M.; Simha, R. *Macromolecules* **1979**, *12*, 329.
(22) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.
(23) Brown, J. C.; Pusey, P. N.; Dietz, R. *J. Chem. Phys.* **1975**, *62*, 1136.
(24) McDonnell, M. E.; Jamieson, A. M. *Biopolymers* **1976**, *15*, 1283.
(25) McDonnell, M. E.; Jamieson, A. M. *J. Appl. Polym. Sci.* **1977**, *21*, 3261.
(26) McDonnell, M. E.; Jamieson, A. M. *J. Macromol. Sci.—Phys.* **1977**, *B13*, 67.
(27) Coleman, M. M.; Fuller, R. E. *J. Macromol. Sci.—Phys.* **1975**, *B11*, 419.
(28) Zimm, B. H.; Kilb, R. W. *J. Polym. Sci.* **1959**, *37*, 19.
(29) Yamakawa, H. *J. Chem. Phys.* **1962**, *36*, 2995.
(30) Pyun, C. W.; Fixman, M. *J. Chem. Phys.* **1964**, *41*, 973.
(31) Vrentas, J. S.; Duda, J. L. *J. Polym. Sci.—Phys.* **1976**, *14*, 101.
(32) Schultz, G. V.; Baumann, H. *Makromol. Chem.* **1968**, *114*, 122.
(33) Ferry, J. D. "Viscoelastic Properties of Polymers"; Wiley: New York, 1970; p 536.
(34) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, C.; Picot, C.; de Gennes, P. G. *Macromolecules* **1975**, *8*, 804.
(35) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.
(36) Daoud, M.; Jannink, G. *J. Phys.* (*Paris*) **1976**, *37*, 1973.
(37) Schaefer, D. W.; Joanny, J. F.; Pincus, P. *Macromolecules*, in press.
(38) Nose, T.; Chu, B. *Macromolecules* **1979**, *12*, 590.