Quasielastic Light Scattering Investigation of Concentration Fluctuations and Coupling to Stress Relaxation in a Polymer Solution: Polystyrene in CCl₄

C. H. Wang* and X. Q. Zhang

Department of Chemistry, University of Nebraska–Lincoln, Lincoln, Nebraska 68588-0304

Received February 7, 1994; Revised Manuscript Received January 23, 1995[®]

ABSTRACT: A detailed light scattering study of the polystyrene (PS) in carbon tetrachloride (CCl₄) solution at various scattering angles and PS concentrations has been carried out. Both static and dynamic light scattering measurements have been made on the solution covering dilute, semidilute, and concentrated concentration regimes. The dynamic light scattering measurement spans a time scale of 10^{-6}–10^2 s. The static light scattering measurement provides osmotic modulus and static correlation length data at various PS concentrations. The homodyne intensity–intensity time correlation function is single exponential in the dilute concentration regime, but it deviates from single exponential in the semidilute and concentrated concentration regimes. The deviation is interpreted as due to the coupling of the concentration fluctuation to longitudinal stress relaxation modes. With the help of a theory, recently developed in this laboratory, information concerning the cooperative diffusion coefficient, longitudinal stress modulus, the distribution of stress relaxation times, dynamic correlation length, and friction coefficient associated with the concentration fluctuation is obtained as a function of PS concentration. Much of the experimental data for the PS/CCl₄ system is new.

I. Introduction

Quasielastic light scattering (QELS) is an effective method for the study of polymer solutions. A dilute polymer solution of flexible chains may be characterized by the radius of gyration, R_g, of the polymer chain and by the amplitude of the scattering vector, given by $q = (4\pi n/\lambda) \sin(\theta/2)$, where λ is the wavelength in vacuum, n is the medium's refractive index, and θ is the scattering angle. When $qR_g \ll 1$, the QELS experiment probes the translational motion of the coil; when $qR_g \gg 1$, information concerning both the translational and internal motion of the coil is obtained. Thus, for a nearly monodisperse polymer sample ($\overline{M}_w/\overline{M}_n \sim 1.0$), the dynamic structure factor, $S(q,t)$, observed in the QELS experiment is single exponential if the coil size, R_g, is less than q^{-1} and is the sum of exponentials when R_g is much greater than q^{-1}. However, even in the latter case, unless the molecular weight of the polymer is extremely large and the experiment is carried out at a large scattering angle, the deviation from the single-exponential decay for $S(q,t)$ is small.[1]

As the polymer concentration increases beyond the overlap concentration C^*, given by $M_w/4/3)\pi R_g^3 N_A$, where M_w is the molecular weight of the polymer and N_A is Avogadro's number, the single-exponential decay is generally not observed. For high molecular weight polymer, the overlap concentration is reached at low polymer concentration. Solutions in which polymer coils strongly overlap, yet the solution concentration is still low, are called semidilute. In contrast to the dilute solution for which $S(q,t)$ is characterized by single-exponential decay, significant deviation from the single exponential is noted in the semidilute solution.

Previous studies of the dynamic structure factor $S(q,t)$ have shown that deviations from the single-exponential decay were prominent in semidilute polymer solutions with θ-solvents.[2-4] It was thought that the deviation was due to poor or marginal solvent quality. However,

recent work also detected the deviation in polymer solutions consisting of good solvents.[5,6]

Brochard and de Gennes[7] were first to analyze the dynamic structure factor of the semidilute solution using an approach originated by Tanaka et al.[8] for permanent gels. They treated the semidilute solution of entangled chains as a transient gel. Adam and Delsanti further modified the deviation.[9] It is assumed that the transient gel is characterized by a lifetime τ_r. For times shorter than τ_r the coils are entangled, and the usual polymer diffusion occurs only for times longer than τ_r. Brochard and de Gennes have argued, however, that concentration fluctuations are present always, and mutual diffusion can occur in a time shorter than τ_r because within such time the concentration fluctuations may diffuse over a distance scale q^{-1}. They have predicted the presence of fast and slow relaxation modes using the transient gel model. The fast mode is associated with mutual diffusion whose rate constant is given by $\Gamma_f = D_c q^2$, where D_c is known as the cooperative diffusion coefficient given by $D_c = (M_\pi + N_0)/\zeta$. Here M_π is the osmotic modulus, N_0 is the longitudinal mechanical modulus of the transient gel formed by the entangled polymer chain, and ζ is the friction coefficient. The slow mode is given by the rate constant $\Gamma_s = D_c/(D_g\tau_r)$, where D_g is equal to N_0/ζ, which also contributes to the cooperative diffusion coefficient. Recent measurements[2-4] of $S(q,t)$ using a multi-τ correlator have, however, shown that these theoretical results are at best only in qualitative agreement with experiments. In addition, viscoelastic modes are also present in solutions with polymer molecular weight less than the critical entangled molecular weight.[6] For the solutions with small molecular weight, the polymer chain entanglement mechanism does not play a role, and as a result the Brochard–de Gennes theory does not apply. To help clarify the nature of dynamic light scattering spectra of binary polymer solutions, we have recently carried out a theoretical analysis in which the effect of the stress relaxation or viscoelasticity of the polymer solution is incorporated.[10,11] Hydrodynamic and nonequilibrium thermodynamic equations were used in carrying out the

analysis; no assumption of polymer entanglement was made in the calculation. Our theoretical result shows that a difference in the partial specific volume of the polymer and that of the solvent component must exist in order to allow concentration fluctuations to couple to the stress relaxation modes of the polymer solution. In other words, the extent of coupling of concentration fluctuations to the solution stress relaxation modes depends on a coupling parameter, β, proportional to $(\partial \varrho / \partial \varrho_2)_{T,p}$, which is the density increment owing to an increase in the polymer concentration. Here ϱ represents the total solution density (g/mL), and ϱ_2 is the polymer concentration (g/mL). When β does not vanish, a significant mixing of the dynamics of concentration fluctuations and solution stress relaxation may result. The mixing could give rise to an increment in the effective diffusion rate and an appearance of additional modes in the quasielastic light scattering spectrum. At large scattering angles the relaxation times associated with the additional modes do not depend on the amplitude of the scattering vector q. These q-independent modes are the stress relaxation or viscoelastic modes associated with the polymer solution.

We have used this theory to interpret light scattering experimental results of a binary polymer solution consisting of polystyrene (PS) in diethyl phthalate (DEP), which is a good solvent for PS at room temperature.[5] We have shown that all results from static and dynamic light scattering can be interpreted according to this theory. To provide a further test of the theory, we have studied another binary system consisting of PS in CCl$_4$, in which CCl$_4$ is a very good solvent for PS. Due to the high density of CCl$_4$, the coupling parameter β of the PS/CCl$_4$ system is large and, therefore, the stress relaxation or viscoelastic modes should be very pronounced. We have indeed found this to be the case. In this paper we show that the nonequilibrium thermodynamic theory can also provide a consistent interpretation of the PS/CCl$_4$ dynamic and static light scattering results at various concentrations from dilute to semidilute and concentrated ranges.

The outline of this paper is as follows: In section II we review the theoretical background needed for the interpretation of the experimental data. We also point out recent new theoretical development on this topic in this section. Experimental details are described in section III. A discussion of experimental results are given in section IV, followed by a summary and conclusion of this work.

II. Theoretical Background

To provide a summary of the theoretical results needed for analysing the experimental data, we now give a brief discussion of the equations and hypothesis introduced in the development of the theory. We shall also point out recent developments on this yet unclarified topic.

Since the change in the refractive index due to solution density in dilute and semidilute concentration regimes is smaller than that due to polymer concentration by at least an order of magnitude, to a good approximation the QELS intensity from a binary polymer solution can be written as[1]

$$I(q,t) = \left(\frac{\partial n}{\partial c}\right)^2 \langle c(q,t)\, c^*(q)\rangle \qquad (1)$$

where $c = \varrho_2/\varrho_1$, with ϱ_1 and ϱ_2 being the concentrations (in g/mL) of the solvent and solute (polymer), respec-

tively. Angular brackets indicate an ensemble average. The quantity $c(q,t)$ in eq 1 is the spatial Fourier transform of concentration fluctuation $\delta c(r,t)$ given by

$$c(q,t) = \int \delta c(\mathbf{r},t)\, e^{-i\mathbf{q}\cdot\mathbf{r}}\, d^3 r \qquad (2)$$

Here $\mathbf{q}$ is the scattering vector introduced previously. In linearized form, $\delta c(r,t) = (\varrho_{20}/\varrho_{10})\,[\delta\varrho_2/\varrho_{20} - \delta\varrho_1/\varrho_{10}]$; the subscript 0 indicates the equilibrium value. Here $\delta\varrho_i$ is the fluctuation of the concentration of component i from its equilibrium value. Since the solvent particle fluctuation is much faster than that of polymers, the dynamics of $\delta c(r,t)$ in times longer than 10^{-6} s are essentially decided by polymers as indicated by $\delta\varrho_2$.

To study the time correlation function of $c(q,t)$ given in eq 1, also known as the dynamic structure factor $S(q,t)$, we need an equation of motion for $\delta\varrho_2$. For this we have used the Bearman–Kirkwood equation given in linearized form as[12]

$$\varrho_{20}\frac{\partial}{\partial t}\mathbf{v}_2 = \nabla\cdot\boldsymbol{\sigma}_2 - \varrho_{20}\nabla\mu_2 + \varrho_{20}\mathbf{F}_2 \qquad (3)$$

where the velocity of particle 2 is connected to the concentration fluctuation $\delta\varrho_2$ via the equation of continuity

$$\frac{\partial}{\partial t}\delta\varrho_2 = -\varrho_{20}\nabla\cdot\mathbf{v}_2 \qquad (4)$$

Similar equations can also be written for the solvent particles, but we focus our attention on polymer particle 2. Using thermodynamics, it is straightforward to obtain an expression relating the gradient of chemical potential, $\nabla\mu_2$, to the solution density fluctuation $\delta\varrho$ and to the polymer concentration fluctuation $\delta\varrho_2$. Further, nonequilibrium thermodynamics can be used to provide an expression for the frictional force $\mathbf{F}_2$ in terms of the frictional coefficient and the time rate of change of $\delta\varrho_2$. However, no progress is made unless the stress tensor for the polymer component, σ_2, is specified. Bearman and Kirkwood did not provide an expression for σ_2; nevertheless, they showed that for low-viscosity molecular mixtures, $\boldsymbol{\sigma}_\alpha$, the stress tensor on component α can be written as

$$\nabla\cdot\boldsymbol{\sigma}_\alpha = (k_\alpha + \eta_\alpha/3)\nabla(\nabla\cdot\mathbf{v}) + \eta_\alpha\nabla^2\mathbf{v} \qquad (5)$$

where η_α and k_α are the *partial* coefficients of shear and bulk viscosity, respectively. One should note that they use the solution velocity $\mathbf{v}$, rather than particle velocity $\mathbf{v}_\alpha$ in eq 5. Since the solution viscosity is connected to the density fluctuations of the whole solution by the equation of continuity,

$$\frac{\partial}{\partial t}\delta\varrho = -\varrho_0\nabla\cdot\mathbf{v} \qquad (6)$$

one needs to relate the density fluctuations to the concentration fluctuations. This is the origin of the concentration-density coupling parameter β.

In contrast to the result of Bearman and Kirkwood, Doi and Onuki[13] have expressed σ_2 in terms of polymer velocity $\mathbf{v}_2$ in their investigation of the coupling of concentration to stress relaxation. If this assumption is made, then the polymer viscoelasticity has a direct influence on concentration fluctuations and the coupling parameter β would always be equal to 1. Doi and Onuki

have, however, not given a derivation to justify the assertion; recent theoretical efforts carried out in this laboratory, which are elaborated upon elsewhere,[14] do not support the Doi−Onuki hypothesis.

If one follows Bearman and Kirkwood and relates σ_2 to the velocity of the polymer solution, then one can incorporate the theory of linear viscoelasticity of the polymer solution into the equation for σ_2 by

$$\nabla \cdot \sigma_2 = \int_0^t du \left\{ \left[K_2 \cdot (t - u) + \frac{1}{3} G_2(t - u) \right] \nabla(\nabla \cdot \mathbf{v}) + G_2(t - u) \nabla^2 \mathbf{v} \right\} \quad (7)$$

where $\mathbf{v}$ depends on time and space, but for brevity of the notation they are not explicitly expressed. Like k_α and η_α in eq 5, K_2 and G_2 are respectively the partial compressional and shear modulus associated with the polymer component. Exactly how the partial longitudinal modulus is related to the longitudinal modulus of the solution needs to be further investigated. Considering the fact that polymer chains play an important role in determining the mechanical modulus of the polymer solution, it has been assumed that K_2 and G_2 are equal to those for the whole polymer solution.[10] In ref 14, it is found, however, that $M_2 (=K_2 + {}^4/_3 G_2)$ is proportional to βM_0, where M_0 is the magnitude of the solution longitudinal stress modulus.

Having clarified each term on the right-hand side of eq 3, one can use eq 4 and go on to express the velocity variable $\mathbf{v}_2$ in terms of $\delta \varrho_2$. Afterward, one then takes the spatial Fourier transform on both sides of the equation and obtains

$$\frac{\partial^2}{\partial t^2} \delta \varrho_2(q,t) = -\frac{q^2}{\varrho_0} \int_0^t du\, M_2(t - u) \dot\varrho(q,u) - q^2 \left\{ \phi_2 C_L{}^2 \varrho(q,t) + \left[\phi_1 \left(\frac{\partial \pi}{\partial \varrho_2} \right)_{P,T} - C_L{}^2 \phi_2 \left(\frac{\partial \varrho}{\partial \varrho_2} \right)_{P,T} \right] \delta \varrho_2 (q,t) \right\} - \zeta \frac{\partial}{\partial t} \delta \varrho_2(q,t) \quad (8)$$

where M_2 is the longitudinal modulus of the polymer component equal to $K_2 + ({}^4/_3) G_2$, ϕ_α is the volume fraction of component α, C_L is the isothermal sound velocity, π is the osmotic pressure, and finally ζ is the friction coefficient. Equation 8 contains both concentration and density variables; strictly it can be solved only when another equation relating the polymer concentration to the solution density fluctuation is also available. However, since the dynamics of concentration fluctuations occurs at a time scale much longer than the sound-wave propagation, to describe the diffusion process, one may neglect the inertia term, i.e., the term on the left-hand side of eq 8. Further, one may also consider the medium to be under an isobaric condition. These simplifications then allow one to adiabatically eliminate the fast variable associated with the pressure fluctuation. Thus, under the isobaric condition, one writes

$$\delta \varrho = \left(\frac{\partial \varrho}{\partial \varrho_2} \right)_{P,T} \delta \varrho_2 = (\varrho_0/\varrho_{02})_{P,T} \beta\, \delta \varrho_2 \quad (9)$$

where the coupling parameter β defined according to eq 9 is given by[15] $(\varrho_0/\varrho_{20})(\partial \varrho/\partial \varrho_2)_{P,T}$. It is easy to show that β is proportional to $|\bar V_1 - \bar V_2|$, the difference in the specific volumes of polymer and solvent components.

Thus, by adapting eq 7 one concludes that there must exist a nonvanishing β; i.e., there must exist a difference

in the specific volumes of polymer and solvent molecules for the stress relaxation or viscoelasticity of the solutions to have any effect on the concentration fluctuation dynamics. Akcasu, Klein, and Wang (AKW) have recently employed the projection operator technique using a set of dynamic variables including a nonconserved diffusion current to describe the coupling of concentration fluctuations to viscoelastic modes.[16] AKW have found an extra term in the viscosity kernel and suggest that the solution viscoelastic effect could still be present when $\beta = 0$. However, the extra term is due to the non-Markovian hypothesis introduced in the derivation of the polymer diffusion coefficient and is not related to the coupling of the concentration fluctuation to the stress relaxation considered here.[14]

With the help of eq 9, eq 8 becomes an equation involving only $\delta \varrho_2$. In this simplified form one can proceed to solve the equation, using the Laplace transform technique to obtain

$$\delta \hat\varrho_2(q,\omega) = \frac{[\hat m(\omega) + \zeta]}{\Delta(q,\omega)} \delta \varrho_2(q) \quad (10)$$

where

$$\delta \hat\varrho_2(q,\omega) = \int \int d^3 r\, dt\, e^{i(q\cdot\mathbf{r} - \omega t)}\, \delta \varrho_2(\mathbf{r},t) \quad (11)$$

$$\hat m(\omega) = \frac{q^2}{\varrho_2} \beta \int_0^\infty dt\, e^{-i\omega t} M_2(t) \quad (12)$$

and

$$\Delta(q,\omega) = i\omega \hat m(\omega) + \phi_1 q^2 M_\pi + i\omega \zeta \quad (13)$$

Here M_π is the osmotic modulus given by $\phi_1 \varrho_2 (\partial \pi / \partial \varrho_2)_{P,T}$.[17] To obtain the dynamic structure factor $S(q,t)$, one multiplies the result of $\delta \varrho_2(q,\omega)$ by $\delta \varrho_2{}^*(q)$ and then takes an ensemble average. One may also invert it to time by taking the inverse Laplace transform of eq 10 to obtain $\delta \varrho_2(q,t)$. However, except for the simple case corresponding to a single-exponential decay for $M_2(t)$, i.e., only one stress relaxation mode, one cannot obtain an analytical solution for the general case. Nevertheless, an approximate solution for $\delta \varrho_2(q,t)$ can be obtained by treating the quantity $\beta[M_2(t) - M_{20}]/(M_\pi + \beta M_{20})$ as a perturbation.[11] Here M_{20} is the initial amplitude of $M_2(t)$. The perturbation solution for $S(q,t)$ is also rather involved, but under the condition $D_c q^2 \gg \tau_s{}^{-1}$, it simplifies to

$$S(q,t) \sim \langle \delta \varrho_2(q,t)\, \delta \varrho_2{}^*(q) \rangle = \langle |\delta \varrho_2(q)|^2 \rangle \Big\{ A e^{-D_c q^2 t} + \sum_i B_i e^{-t/\tau_i} \Big\} \quad (14)$$

where τ_s is the shortest relaxation time of $M_2(t)$; D_c is the cooperative diffusion coefficient given by

$$D_c = (M_\pi + \beta M_{20})/\varrho_2 \zeta \quad (15)$$

The amplitude factor A and B_i are given by

$$A = 1 - \frac{\beta M_{20}}{(M_\pi + \beta M_{20})} \quad (16)$$

and

$$B_i = \beta M_i/(M_\pi + \beta M_{20}) \quad (17)$$

The longitudinal stress relaxation modulus is generally given by

$$M_2(t) = \sum_i M_i e^{-t/\tau_i} \tag{18}$$

where τ_i is the relaxation time associated with the mode having amplitude M_i. Equation 18 is a discrete mode representation of the stress relaxation modulus. In the continuous relaxation time representation, $M_2(t)$ is written as

$$M_2(t) = M_{20} \int_0^\infty \varrho(\tau) \, e^{-t/\tau} \, d\tau \tag{19}$$

and the second term on the right-hand side of eq 14 becomes

$$\sum_i B_i e^{-t/\tau_i} = \frac{\beta M_{20}}{(M_\pi + \beta M_{20})} \int_0^\infty \varrho(\tau) \, e^{-t/\tau} \, d\tau \tag{20}$$

where $\varrho(\tau)$ is the normalized distribution function for the longitudinal stress modulus.

The significance of eq 14 is that one can extract information about the longitudinal stress modulus of the polymer solution using QELS. This possibility is due to the mixing of stress relaxation or viscoelastic modes to the dynamics of concentration fluctuations. One notes that, besides the diffusive mode that has a q^2 dependence in the relaxation rate, there are q-independent stress relaxation modes. Thus, in the presence of coupling one would expect the density fluctuations associated with localized segmental motion to be present in the concentration fluctuation spectrum of the polymer solution. It is of interest to point out that, while the present result as given by eq 14 bears a similarity to de Gennes' transient gel model as elaborated by Adam and Delsanti,[9] the two theories are obtained with different premises. Our theory does not assume chain entanglements, while, on the other hand, polymer chain entanglement is the main ingredient of the Brochard–de Gennes' approach. By setting $\beta = 1$ and also restricting the relaxation modulus to only one viscoelastic mode with relaxation time τ_r associated with the disengagement of entangled chains, we obtain in this special case $B = M_{20}/(M_\pi + M_{20})$ and $A/B = M_\pi/M_{20}$, which agrees with their amplitude ratio of the fast to slow mode, provided that the volume fraction is set to $\phi_1 = 1$. The relaxation time of the stress relaxation mode obtained from the present theory in this restricted case is τ_r, whereas the Adam–Delsanti calculation gives $\tau_r M_{20}/(M_\pi + M_{20})$, if the compressional modulus K_2 is neglected and M_{20} is set equal to $(4/3)G$, where G is the shear modulus of the polymer solution. The difference in the relaxation time is due to the assumption $\beta[M_2(t) - M_{20}] \ll M_\pi + \beta M_{20}$, introduced in the perturbation treatment in ref 11. When this assumption is valid, the two relaxation times become practically equal. Therefore, our approach requires only finite values of β and M_{20} and the assumption of polymer chain entanglements is not necessary, despite the fact that the chain entanglement would enhance the importance of the viscoelastic modes.

III. Experimental Section

Polystyrene (PS) samples used in this study were purchased from Toya Soda and had a polydispersity index $\bar{M}_w/\bar{M}_n$ of 1.09, with $\bar{M}_w$ being equal to 2.88×10^6 (Type F-288, TSK standard

polystyrene). Polymer solutions were prepared by dissolving PS into CCl_4 (Fisher Scientific). Dust in solutions with less than 1 wt % concentration was removed by filtering through 0.2-μm Millipore filters into light scattering cells. Solutions with higher concentrations were difficult to filter, and dust in these solutions was removed by centrifugation at 9000 g for over 8 h at elevated temperatures.

Static light scattering measurements were performed at 24 °C by using an apparatus consisting of a Brookhaven 200 SM goniometer and a Spectra-Physics Model 125 He–Ne laser at a wavelength of 632.8 nm with a power of 40 mW. The scattering intensity was measured at scattering angles varying from 30 to 150°. The refractive index increment $dn/d\varrho_2$ of the PS in CCl_4 was obtained from Brandrup's *Polymer Handbook*. The density increment $(\partial\varrho/\partial\varrho_2)$ needed to calculate the coupling parameter β was determined by using a volummetric flask and a balance, accurate to ± 0.0001 g. Volummetric flasks used were size 5 and 10 mL Pyrex class A with Pyrex stoppers. The overlap concentration, C^*, calculated by using $M_w/(4/3\pi R_g^3 N_A)$, was 0.0042 g/cm^3.

Dynamic light scattering measurements were carried out by using an ALV-5000 correlator. Normalized homodyne intensity–intensity correlation functions $G(q,t)$ were measured as a function of polymer concentration and scattering angle. The normalized field correlation function $g(q,t)$, which is proportional to the dynamic structure factor $S(q,t)$, is obtained from $G(q,t)$ via the Sigert relation

$$\alpha g(q,t) = [G(q,t) - 1]^{1/2} \tag{21}$$

where α is the contrast factor due to the finite-sized pinhole used in the experiment. The dynamic light scattering experiments were also carried out at 24 °C.

IV. Results and Discussion

1. Static Intensity. The absolute intensity, expressed by the Rayleigh ratio $R(q)$ at scattering vector **q**, is given by

$$R(q) = KM\varrho_2 S(q) \tag{22}$$

where K is an optical constant equal to $(4\pi^2 n^2/N_A\lambda^4) (dn/d\varrho_2)^2$ and $S(q)$ is the (static) structure factor. The structure factor $S(q)$ depends on q because the correlation length ξ_s for the concentration fluctuations is not negligible. To obtain the correlation length, we fit the angular dependence data for $S(q)$ to the Ornstein–Zernlike equation

$$S(q) = \frac{S(0)}{1 + q^2 \xi_s^2} \tag{23}$$

where $S(0)$ is the static structure factor extrapolated to the zero scattering angle. We have measured $R(q)$ as a function of the scattering angle and polymer concentration ϱ_2 using the light scattering intensity of benzene as the reference. For all samples studied, the depolarized scattering intensity is negligible, and thus the polarized scattering intensity is used to evaluate $R(g)$. Using the $R(q)^{-1}$ versus q^2 plot (Figure 1), we obtain, from the slope and intercept of the plot, the correlation length ξ_s for each polymer concentration studied. In the moderate and high polymer concentration, we have observed an upward curvature in the $R(q)$ versus q plot, similar to that reported by Chen and Berry.[18] This makes the determination of ξ_s at moderate and high concentration difficult. Therefore, the correlation length data above $\varrho_2 = 0.02$ g/mL are subject to large uncertainty. We plot in Figure 2 ξ_s as a function of PS concentration ϱ_2 (in g/cm^3). Clearly ζ_s decreases with increasing ϱ_2. In the semidilute region, ξ_s can be fit to
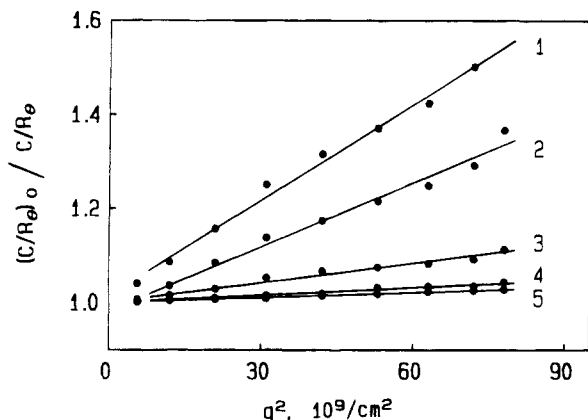
Figure 1. Ornstein–Zernike plot of the Rayleigh ratio of PS in CCl$_4$. C is constant and subscript 0 represents values at zero scattering angle. Line 1 corresponds to $\varrho_2 = 1.67 \times 10^{-3}$ g/cm^3, line 2 to 3.35×10^{-3} g/cm^3, line 3 to 6.71×10^{-3} g/cm^3, line 4 to 13.4×10^{-3} g/cm^3, and line 5 to 24.6×10^{-3} g/cm^3.
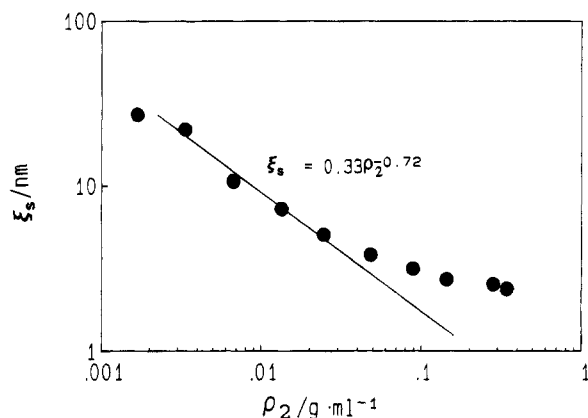

Figure 2. Concentration dependence of the static correlation length for the PS/CCl$_4$ system.

a power law expression given by $0.33\varrho_2^{-0.72}$ nm, which is in good agreement with the result reported for polymer in good solvent.[19] The data above 0.02 g mL^{-1} level off and have positive deviation from the fitted line from the low concentration data. The positive deviation is due to the limitation of the light scattering method, in contrast to small-angle neutron and X-ray scattering which can measure ξ_s to values below 1 nm with accuracy. In fact, using small-angle neutron and small-angle X-ray scattering, Brown, Mortensen, and Floudas[20] have found in polystyrene/toluene that in the semidilute solution ξ_s is the monomer dimension about 0.5 nm.

The quantity $(\partial\pi/\partial\varrho_2)/\varrho_2$ is related to the Rayleigh ratio at zero scattering angle by $RTK/R(0)$. We have measured the quantity $K\varrho_2/R(q)$ as a function of scattering angle and extrapolated the result to $\theta = 0°$ to obtain $(\partial\pi/\partial\varrho_2)$. The result of $(\partial\pi/\partial\varrho_2)$ as a function of ϱ_2 is plotted in Figure 3.

At low concentration, $(\partial\pi/\partial\varrho_2)$ can be expanded in a virial series as[21]

$$(\partial\pi/\partial\varrho_2)/RT = (1/M_w)(1 + 2A_2M_w\varrho_2 + 3A_3M_w\varrho_2^3 + ...) \quad (24)$$

where A_2 and A_3 are second and third virial coefficients, respectively. The second virial coefficient obtained from our data is equal to 2.58×10^{-4} mol·cm^3/g^2. This agrees with the literature result.[22] He et al.[23] have reported $(\partial\pi/\partial\varrho_2)$ data for the PS/CCl$_4$ system up to 2×10^{-3} g/cm^3. Their $(\partial\pi/\partial\varrho_2)$ result shows an anomaly in the
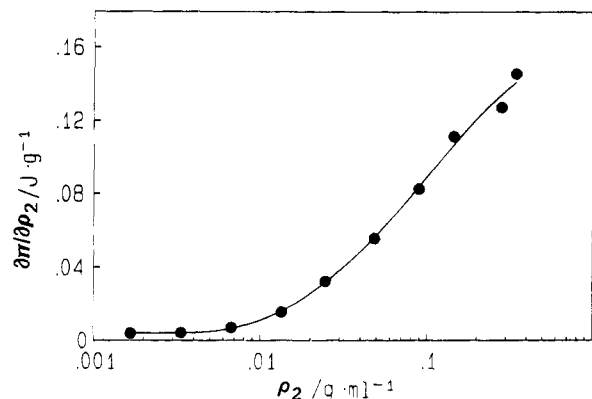

Figure 3. $(\partial\pi/\partial\varrho_2)_{T,P}$ plotted vs ϱ_2 for PS in CCl$_4$.

dilute concentration region, but at $\varrho_2 = 2 \times 10^{-3}$ g/cm^3, it is in qualitative agreement with the present result. The present work has extended the result of $(\partial\pi/\partial\varrho_2)$ to much higher PS concentration, and when ϱ_2 exceeds C^*, the overlap concentration, the virial expansion of $(\partial\pi/\partial\varrho_2)$ is invalid.

Recent theoretical efforts have been directed to describe the concentration dependence of the osmotic pressure at high concentration. For Θ-solvent, Ohta and Oono have worked out an expression using a renormalization group treatment.[24] Using scaling theory,[25] π in the semidilute polymer solution is found to vary with the polymer concentration according to $\sim\varrho_2^y$, where $y = 3\nu/(3\nu - 1)$. The value of ν ranges from 0.5 to 0.6, depending on solvent quality. For Θ-solvent $\nu = 0.5$ and thus $(\partial\pi/\partial\varrho_2)$ varies with the polymer concentration as ϱ_2^2. For good solvents,[26] ν is about equal to 0.6, and this gives $(\partial\pi/\partial\varrho_2) \sim \varrho_2^{1.25}$. While we do not have the ν value for CCl$_4$, due to the good solvent quality of CCl$_4$, we expect ν for the PS/CCl$_4$ system to be close to the good solvent result. In the semidilute concentration regime, our $(\partial\pi/\partial\varrho_2)$ data can be fit to $\varrho_2^{1.16\pm0.06}$, which is not too much off from the scaling prediction, bearing in mind that the scaling theory is an asymptotic result at infinite molecular weight. The scaling result for the osmotic modulus M_π is contrasted with the experimental result of M_{20} in Figure 11.

As shown in eqs 15–17, the osmotic modulus contributes importantly to the cooperative diffusion coefficient D_c and to the amplitude factors A and B_i. We now combine the M_π data from static light scattering with D_c and amplitude factors from the dynamic light scattering data to obtain viscoelastic information on the PS/CCl$_4$ solution in the semidilute and concentrated regime.

2. Dynamic Light Scattering. A representative field–field correlation function $g(q,t)$ obtained for the PS/CCl$_4$ solution with PS equal to 0.0482 g/cm^3 at 90° scattering angle is shown in Figure 4. The correlation function covers 8 decades in time and is not single exponential. The CONTIN program analysis gives a bimodal relaxation time distribution, with one narrow distribution peak at shorter times whose position changes with q and a broad distribution peak at longer times that is independent of q at large q. From the CONTIN result and the result of theoretical analysis outlined in section II, it suggests that the field–field correlation function $g(q,t)$ can be analyzed in terms of two Kohlrausch–Williams–Watts (KWW) functions as

$$g(q,t) = x_1\exp[-(t/\tau_1)^{\beta_1}] + x_2\exp[-(t/\tau_2)^{\beta_2}] \quad (25)$$
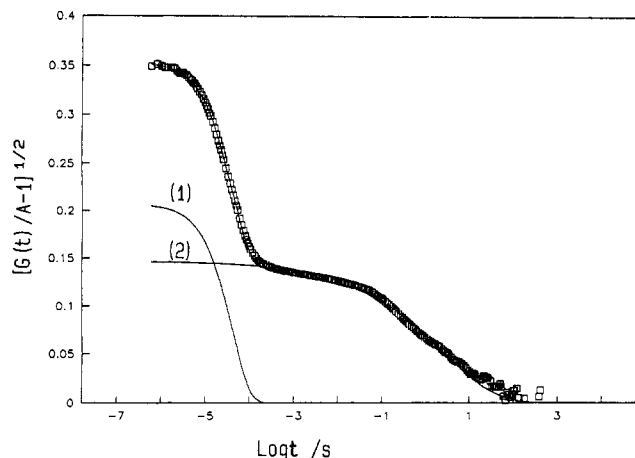
where $x_1 + x_2 = 1$. We have used a multiparameter

Figure 4. Representative field–field correlation function obtained at 90° scattering angle for ϱ_2 equal to 0.0246 g/cm^3 for the PS/CCl$_4$ system and resolution of the correlation function into cooperative diffusion mode (1) and viscoelastic mode (2) by eq 14.
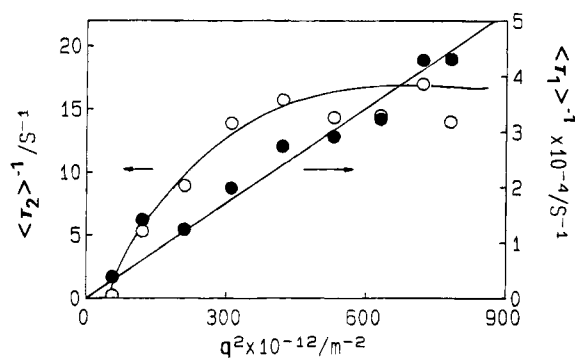

Figure 5. Plots of mean relaxation rates $\langle\tau_1\rangle^{-1}$ and $\langle\tau_2\rangle^{-1}$ for the PS/CCl$_4$ solution ($M_w = 2.88 \times 10^6$, $C = 0.0890$ g·mL^{-1}) as a function of q^2. Here $\langle\tau_1\rangle^{-1}$ shows a q^2 dependence, whereas $\langle\tau_2\rangle^{-1}$ shows no q-dependence for large q.

program to resolve the dynamic light scattering data to eq 25. The results of the fit are also shown in Figure 4. The quality of the fit is satisfactory. The shape parameter obtained from the fit for curve 1 is nearly single exponential ($\beta_1 = 0.97$), whereas for curve 2 it is broad ($\beta_2 = 0.37$) and covers a wide dynamic range from 10^{-6} to 10^2 s. The average relaxation rates calculated from each KWW function are plotted as a function of q^2 in Figure 5. The relaxation rate associated with curve 1 shows a q^2 dependence, thus suggesting a diffusive character, whereas that associated with curve 2 has a complex q dependence at small q and becomes independent of q as q becomes greater than about 2×10^5 cm^{-1}. As discussed in section II, the q-independent result for curve 2 at large q suggests that curve 2 is associated with stress relaxation modes. The fact that, at small q, $\langle\tau_2\rangle^{-1}$ decreases rapidly with decreasing q is due to mixing of diffusive and stress relaxation modes. The mean relaxation times, shown in Figure 5, are calculated according to $\langle\tau_i\rangle = \tau_i\Gamma(1/\beta_i)/\beta_i$, where $\Gamma(x)$ is a gamma function. These results are qualitatively similar to that found in the PS/DEP (diethyl phthalate) system.[5]

Having identified the diffusive mode, we go on to calculate the cooperative diffusion coefficient D_c by using the formula $D_c = (q^2\langle\tau_1\rangle)^{-1}$. The results are shown in Table 1 for various PS concentrations. At 24 °C, the mutual diffusion coefficient of PS in CCl$_4$ is about 10^{-7} cm^2/s, which is about 1 order of magnitude faster than the cooperative diffusion coefficient of PS in DEP. At low concentration, D_c increases rapidly with increasing
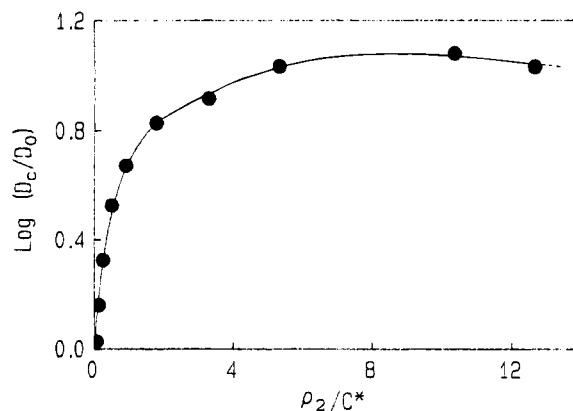

Figure 6. Plot of the cooperative diffusion coefficient D_c as a function of polymer concentration ϱ_2. D_c is calculated from $\langle\tau_1\rangle$ in accordance with the formula $D_c = [q^2\langle\tau_1\rangle]^{-1}$. The D_c data are normalized with respect to D_0, and ϱ_2 is normalized to the overlap concentration C^*.

Table 1. Cooperative Diffusion Coefficient D_c, Osmotic Modulus M_π, Longitudinal Modulus M_0, and M_π/M_0 Ratio of PS in CCl$_4$ at Various Concentrations

ϱ_2 (g/cm^3)	D_c (cm^2/s) $\times 10^8$	M_π (kPa)	M_{20} (kPa)	M_π/M_{20}
1.67×10^{-3}	7.45	0.065	8.67	134.09
3.35×10^{-3}	10.1	0.139	16.62	119.21
6.71×10^{-3}	14.8	0.47	58.51	125.23
1.34×10^{-2}	23.5	2.03	8.42	102.51
2.46×10^{-2}	32.9	7.59	313.1	41.26
4.82×10^{-2}	47.0	25.19	676.0	26.84
8.90×10^{-2}	57.6	66.22	1028.4	15.53
1.44×10^{-1}	75.4	136.11	2340.9	17.20
2.81×10^{-1}	84.1	258.54	2486.7	9.62
3.43×10^{-1}	75.4	332.81	2594.6	7.80

PS concentration. However, the increase levels off at about 5 times the overlap concentration, as shown in Figure 6, where the concentration is normalized to C^* and D_c to D_0. Here D_0 (=7.0 $\times$ 10^{-8} cm^2/s) is D_c extrapolated to infinite dilution, i.e., the tracer diffusion coefficient of PS in CCl$_4$. Above C^*, D_c continues to increase with increasing ϱ_2, but at a slower rate. As ϱ_2 exceeds $10C^*$, D_c starts to decrease. This result is qualitatively similar to the behavior obtained in the PS/DEP system.[5] However, in the PS/DEP system, D_c does not level off at $10C^*$, but instead it reaches a maximum value at $10C^*$ and then starts to decrease at higher concentration.

Consistent with the blob model, one may define a dynamic correlation length ξ_e in accordance with the Stokes–Einstein equation:[25]

$$D_c = \frac{kT}{6\pi\eta_s\xi_e} \qquad (26)$$

where η_s is the solvent viscosity. One may estimate ξ_e from the Kirkwood–Riseman theory[27] provided that a correction due to the finite polymer volume or the blob size is also included. The increase in D_c with concentration indicates that the dynamic correlation length ξ_e decreases with increasing PS concentration. The ξ_e value calculated by using eq 26 is shown in Figure 7 as a function of ϱ_2. For the PS concentration less than 0.02 g/cm^3, ξ_e decreases with a power law concentration dependence given by $0.70\varrho_2^{-0.53}$. One notes that the exponent obtained for ξ_e is a little less than that obtained for ξ_s, and the preexponential factor is about a factor of 2 larger. However, within experimental error, ξ_c and ξ_s are proportional to each other. These results agree with the values reported for PS in other
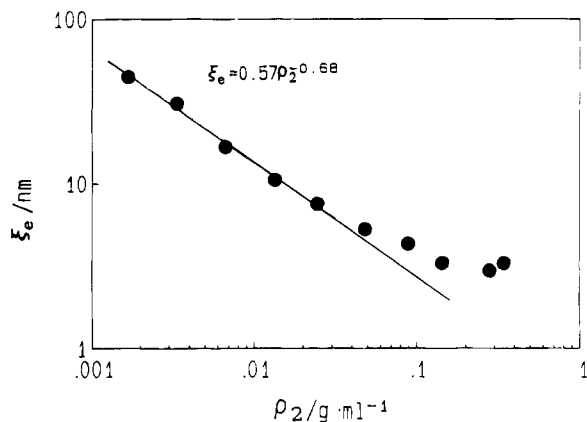
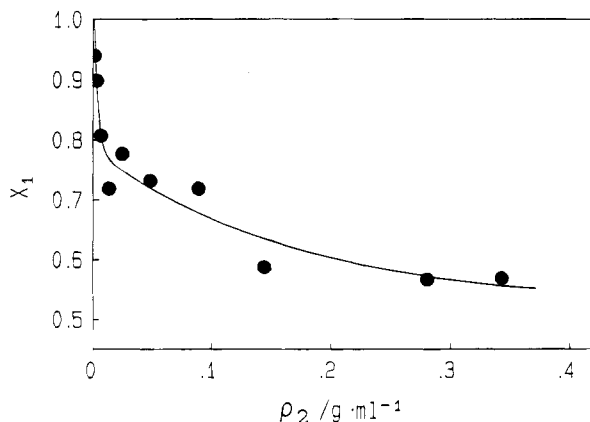**Figure 7.** Concentration dependence of the dynamic correlation length for the PS/CCl$_4$ system.

Figure 8. Amplitude factor x_1, associated with the cooperative diffusion mode plotted as a function of the PS concentration ϱ_2.

Figure 9. Ratio of $M_\pi/\beta M_0$ plotted as a function of concentration ϱ_2.

Figure 10. Coupling parameter β plotted versus concentration ϱ_2 for a PS sample at 24 °C with $M_w = 1.86 \times 10^5$. Over the concentration range from 0 to 0.1 g/mL, β can be represented as $\beta = 0.2847\varrho_2$.

good solvents.[19] Above $\varrho_2 = 0.02$ g/mL, the decrease of ξ_e is considerably less than that predicted by the power law equation. The reason for this is similar to that for the static correlation length ξ_s.

According to eq 15, D_c is determined by both the osmotic modulus and the longitudinal stress modulus. We can obtain the M_π/M_{20} ratio by analyzing the shape of the dynamic structure factor $S(q,t)$. According to eqs 14–17, the amplitude factor of the cooperative diffusion mode is equal to $1 - \beta M_{20}/(M_\pi + \beta M_{20})$. Since we have already obtained M_π from the static light scattering experiment, we can calculate the βM_{20} value from the amplitude factor. The curve-fitting technique described earlier gives the value of x_1, which is shown in Figure 8 as a function of polymer concentration. According to eqs 14 and 16, one can identify x_1 with the amplitude factor A. At low concentration, x_1 is nearly equal to 1, suggesting that the contribution from the viscoelastic modes is negligible. However, it decreases rapidly as the concentration is increased toward C^* and then decreases gradually with further concentration increase. This result thus suggests that viscoelastic modes gradually become prominent as the polymer concentration is increased toward the semidilute and concentrated regime.

From the amplitude factor, we have obtained the α = $M_\pi/\beta M_{20}$ ratio, which is shown in Figure 9 as a function of the polymer concentration. One notes that at low polymer concentrations $M_\pi/\beta M_{20}$ is much greater than 1. However, as the polymer concentration increases, the ratio rapidly decreases. Using the M_π value obtained from static light scattering and the α ($=M_\pi/$
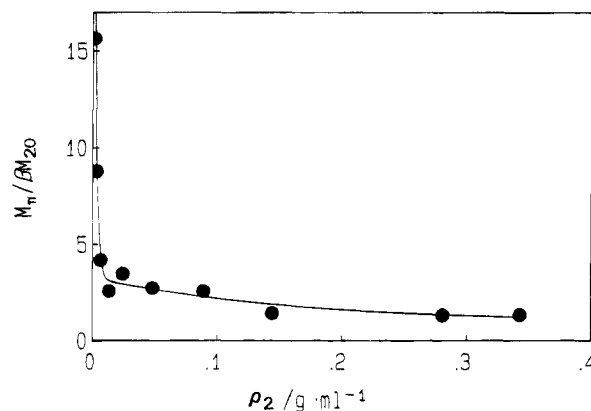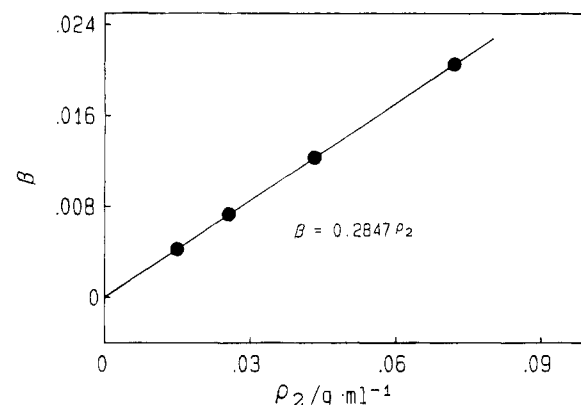
βM_{20}) ratio obtained above, we can obtain the M_{20} value, if the coupling parameter β is also measured. We have determined the β value by measuring the change in the solution density as PS is added to solution. In Figure 10, we show the concentration dependence of the β value. Over the concentration range studied, β increases linearly with increasing ϱ_2 according to the equation $\beta = 0.2847\varrho_2$. The value of β in PS/CCl$_4$ is about 6.8 times larger than that of the PS/DEP system reported previously.[5] Due to a large β, the viscoelastic mode is more prominent in this system than in the PS/DEP system,[5] consistent with the theoretical prediction.

Having obtained the values of β, we can calculate M_{20}, the amplitude of the partial stress modulus of the polymer component $M_2(t)$. Results for M_{20} and M_π are shown in Figure 11 as a function of PS concentration. These values are also given in Table 1. One notes that $M_\pi/M_{20} \ll 1$ at all concentrations; however, as mentioned above, the quantity α ($=M_\pi/\beta M_{20}$) is much larger than 1 at low polymer concentrations, tending to a value of about 1 at high concentration (Figure 9).

It should be emphasized that M_{20} is not the longitudinal modulus of the polymer solution but the partial longitudinal modulus of the polymer component in the solution. Our recent theoretical study has shown that M_{20} is related to the longitudinal stress modulus M_0 according to[14] $M_{20} = \phi_1\beta M_0$. Using this expression, we have calculated the value of M_0 to be 2.1×10^4 kPa at $\varrho_2 = 1.67 \times 10^{-3}$ g/cm^3 and 2.8×10^4 kPa at $\varrho_2 = 3.43 \times 10^{-1}$ g/cm^3. The partial longitudinal modulus M_{20} as determined here by the combined use of QELS and static light scattering corresponds to the value at the
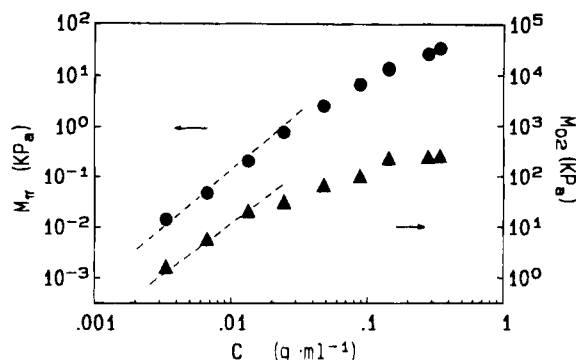
Figure 11. Osmotic modulus M_π and longitudinal stress modulus M_0 plotted versus concentration from PS in CCl_4. Dotted lines are drawn with a slope of $^9/_4$.

Figure 12. Frictional coefficient ζ of PS in CCl_4 plotted as a function of ϱ_2.

frequency of 10^6 Hz, because the shortest delay time of our present correlator is 1 μs; thus, the M_0 value as deduced from the present QELS data also corresponds to the result at about 1 MHz. This value can be compared with the high-frequency longitudinal modulus M_∞ as determined by Brillouin scattering. To carry out the comparison, we have measured the frequency shift, $\Delta\nu_B$ for the PS/CCl_4 solution at the highest and lowest concentrations presently studied. The values of M_∞ are related to the Brillouin shift $\Delta\nu_B$ by $\Delta\nu_B = q(M_\infty/\varrho_0)^{1/2}/2\pi$. At $\varrho_2 = 1.67 \times 10^{-3}$ g/cm^3, M_∞ is found to be 2.69 GPa, and at $\varrho_2 = 3.43 \times 10^{-1}$ g/cm^3, M_∞ is 3.37 GPa. M_∞ is the longitudinal modulus of the polymer solution at 10^9 Hz. The M_∞ values obtained by Brillouin scattering are higher than M_0 by a factor of about 120. While one can attribute the decrease in the longitudinal stress modulus from the value at 10^9 Hz (M_∞) to that at 10^6 Hz (M_0) to relaxation, Brillouin scattering and ultrasonic measurements on the same bulk polymer[28] have shown that the difference in the longitudinal stress modulus at 10^9 Hz and that at 10^6 Hz is only about a factor of 10. However, $M_0 = \Delta K + (^4/_3)G$, where K and G are the compressional and shear modulus, respectively. ΔK is the change of the compressional modulus due to density fluctuations. In general, the compressional modulus is larger than the shear modulus in polymer solution or melt. Nevertheless, because QEL scattering arises from fluctuations from equilibrium, only the change in K from the dynamic value at 10^{-6} s to the equilibrium value is detected in the dynamic light scattering experiment.[29] Since the equilibrium compressional modulus is about 10^8 Pa, ΔK is about 10^2 Pa. Thus, it appears that the shear modulus G makes the dominant contribution to the light scattering M_{20} or M_0. This conclusion is consistent with recent experimental results on polymer gel and polymer solution in the semidilute concentration region by Horkay et al.[30]

One also notes that, from the lowest to highest concentrations, M_∞ only increases by a factor of about 1.2, whereas there is about a 300-fold increase in M_{20} over the same concentration range. The small increase in M_∞ is easy to understand because, at the gigahertz (10^9 Hz) frequency, the system, albeit a polymer solution, appears as a glass, and the change of polymer concentration in the glassy region will not affect the value of M_∞ much. On the other hand, at megahertz frequency, the system is in the liquid or rubbery state, and in this region M_{20} would be a stronger function of polymer concentration.

We now discuss the concentration dependence of M_{20}. For polymer with high molecular weight, scaling theory[25,31] has shown that the plateau shear modulus
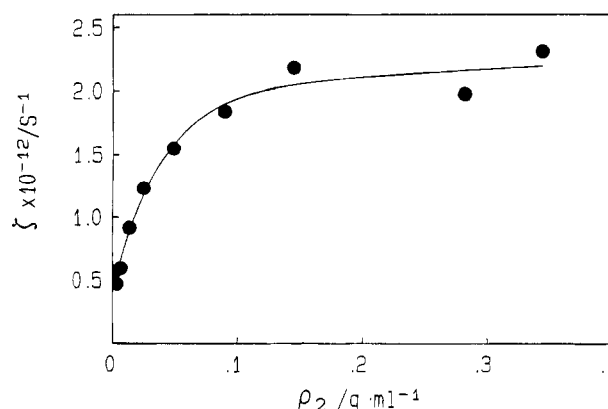
G_N^0 of polymer solution depends on the concentration as $\varrho_2^{9/4}$. Since the PS molecular weight used in this study exceeds the entanglement molecular weight M_e, which equals 3.5×10^4,[32] one is tempted to relate M_{20} to the plateau shear modulus G_N^0. In Figure 11, the dotted line corresponds to a line drawn in the semidilute concentration region with a slope of $^9/_4$. A similar line is also drawn for the osmotic modulus result. Above the semidilute concentration, both M_{20} and M_π data fall below the theoretical lines. Due to the β factor associated with M_0, it should be pointed out that the concentration dependence of M_0 is much weaker. The concentration dependence in M_0 is similar to that of M_∞, associated with Brillouin scattering.

Having obtained M_π, M_{20}, and β values, one can calculate the friction coefficient ζ from the D_c data. The calculated ζ value is plotted as a function of concentration ϱ_2 in Figure 12. The friction coefficient represents the interaction between the solvent molecules with diffusive polymer chain segments. One notes that the friction coefficient is on the order of the 10^{12}/s range for the PS/CCl_4 system, and it increases with increasing PS concentration, but the increase becomes smaller above 4C^*. This is in contrast to the PS/DEP system, in which the polymer experiences a larger friction and continues to increase rapidly even at very high polymer concentration.

In conclusion, we have carried out a detailed light scattering study of the PS/CCl_4 system at various PS concentrations at 24 °C. The study includes static and dynamic light scattering measurements covering a dynamic range of 10^{-6}–10^2 s. From the angular-dependent static light scattering measurements, we have determined the osmotic modulus and the static correlation length associated with concentration fluctuations as a function of PS concentration covering dilute, semidilute, and concentrated concentration regimes. While the time correlation function in the dilute regime has an exponential decay, we have found that it significantly deviates from the single-exponential decay in the semidilute and concentrated concentration regimes. The deviation is interpreted as due to the coupling of the cooperative diffusion mode to stress relaxation modes of the polymer solution. The cooperative diffusion coefficient data have been studied as a function of concentration. These concentration-dependent diffusion data have also been interpreted in terms of the concentration dependence of the dynamic correlation length. The experimental results consisting of static and dynamic light scattering have been consistently interpreted using a theory developed in this

laboratory. With the help of the theory, we are able to obtain not only thermodynamic quantities such as the osmotic modulus but also the longitudinal stress modulus and friction coefficient as a function of polymer concentration from both static and dynamic light scattering data.

References and Notes

(1) Berne, B.; Pecora, R. *Dynamic Light Scattering, with Applications to Chemistry, Biology and Physics*; Wiley: New York, 1976.

(2) Brown, W.; Stepanek, P. *Macromolecules* **1988**, *21*, 1791.

(3) Brown, W.; Johnsen, R. M.; Stepanek, P.; Jakes, J. *Macromolecules* **1988**, *21*, 2859.

(4) Nicolai, T.; Brown, W.; Johnsen, R. M.; Stepanek, P. *Macromolecules* **1990**, *23*, 1165.

(5) Wang, C. H.; Zhang, X. Q. *Macromolecules* **1993**, *26*, 707.

(6) Sun, Z.; Wang, C. H. *Macromolecules* **1994**, *27*, 5667.

(7) Brochard, F.; de Gennes, P.-G. *Macromolecules* **1977**, *10*, 1157.

(8) Tanaka, T.; Hocker, L. U.; Benedek, G. B. *J. Chem. Phys.* **1973**, *59*, 5151.

(9) Adam, M.; Delsanti, M. *J. Phys., Lett. (Paris)* **1984**, *45*, L-279. Adam, M.; Delsanti, M. *Macromolecules* **1985**, *18*, 1760.

(10) Wang, C. H. *J. Chem. Phys.* **1991**, *95*, 3788.

(11) Wang, C. H. *Macromolecules* **1992**, *25*, 1524.

(12) Bearman, R. J.; Kirkwood, J. G. *J. Chem. Phys.* **1958**, *28*, 136.

(13) Doi, M.; Onuki, A. *J. Phys. II Fr.* **1992**, *2*, 1631.

(14) Wang, C. H. *J. Chem. Phys.*, in press.

(15) The absolute value is introduced for convenience for systems with negative $(\partial \varrho/\partial \varrho_2)_{T,P}$ such as the system considered here. Since the effective modulus entering the concentration fluctuation depends on β^2, the introduction of the absolute value does not change the result.

(16) Akcasu, A. Z.; Klein, R.; Wang, C. H. *Macromolecules* **1994**, *27*, 2736.

(17) Although the subscript 0 is used to denote the equilibrium value, we shall drop the subscript 0 except at places where there is confusion. Usually, the osmotic modulus M_π is defined without ϕ_1. However, in order to express the osmotic pressure driven diffusion coefficient D_π as $M_\pi/\zeta\varrho_2$, it is necessary to incorporate ϕ_1 in the expression of M_π.

(18) Chen, S.-J.; Berry, G. C. *Polymer* **1990**, *31*, 793.

(19) Brown, W.; Nicolai, T. *Colloid Polym. Sci.* **1990**, *268*, 977 and references therein.

(20) Brown, W.; Mortensen, K.; Floudas, G. *Macromolecules* **1992**, *25*, 6904.

(21) Yamakawa, H. *Modern Theory of Polymer Solution*; Harper and Row: New York, 1971.

(22) Our A_2 value compares well with the value $(2.6 \times 10^{-4}$ mol·cm^3/g) of Stockmayer et al. (Stockmayer, W. H.; Moore, L. D., Jr.; Fixman, M.; Epstein, B. N. *J. Polym. Sci.* **1955**, *16*, 517) but is lower than the value of 3.58×10^{-4} mol·cm^3/g^2 published by: Wolinski, L.; Wolinski, K.; Tureyuski, R. *Makromol. Chem.* **1979**, *180*, 2399. The difference is due to different molecular weights used. Chu et al. (*Macromolecules* **1982**, *15*, 673) also cited the A_2 value; however, their result suffers from an incorrect unit and cannot be compared.

(23) Chu et al. reported the $\partial\pi/\partial\varrho_2$ data up to C^* in two papers: (1) Chu, B.; He, M.-J.; Kubota, K.; Lin, Y. H. *Macromolecules* **1981**, *14*, 392. (2) He, M.-J.; Kubota, K.; Pope, J.; Chu, B. *Macromolecules* **1982**, *15*, 673. Their $(\partial\pi/\partial\varrho_2)$ results are different in papers 1 and 2; however, our $(\partial\pi/\partial\varrho_2)$ data in the dilute region are in the range of Figure 4 of paper 2.

(24) Ohta, T.; Oono, Y. *Phys. Lett.* **1983**, *79*, 339.

(25) de Gennes, P.-G. *Scaling Concept in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(26) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P.-G. *Macromolecules* **1975**, *8*, 804.

(27) Kirkwood, J.; Riseman, J. *J. Chem. Phys.* **1948**, *16*, 565.

(28) Floudas, G.; Fytas, G.; Alig, I. *Polymer* **1991**, *32*, 2307.

(29) Wang, C. H.; Fytas, G.; Zhang, J. *J. Chem. Phys.* **1985**, *82*, 3405.

(30) Horkay, F.; Burchard, W.; Geissler, E.; Hecht, A.-M. *Macromolecules* **1993**, *26*, 1296.

(31) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 594.

(32) Van Krevelen, D. W. *Properties of Polymers*; Elsevier: New York, 1976; Chapter 15.