*Macromolecules* **1994**, *27*, 5667-5673

# Light Scattering and Viscoelasticity of Polymer Solutions

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*Received November 1, 1993; Revised Manuscript Received July 2, 1994*⊛

ABSTRACT: A detailed light scattering study of polystyrene (PS) in benzene solution at various scattering angles and PS concentrations has been carried out. The study includes static and dynamic light scattering measurements covering a dynamic range of $10^{-6}$ to $10^2$ s. The osmotic modulus of the polymer solution is measured as a function of polymer concentration by using the static light scattering technique. In the semidilute concentration regime, the homodyne intensity–intensity time correlation function deviates from a single exponential decay. The deviation was found to depend strongly on the polymer concentration. Angular-dependent measurements have facilitated the resolution of the time correlation function into a narrow cooperative diffusion mode and a broader slow component. At a large scattering vector, the slow component is found to be independent of the scattering angle. We have interpreted the experimental result in terms of the theory previously developed in this laboratory. We have attributed the slow component to the effect of viscoelasticity of the polymer solution. In addition, quasielastic light scattering studies of semidilute solutions of PS in mixed solvents consisting of benzene and diethyl phthalate with different values of the coupling parameter $\beta$ (defined in the text) have also been investigated. For the solutions with $\beta = 0$, no viscoelastic component is observed in the QEL scattering spectrum, consistent with the theoretical prediction.

## Introduction

Laser light scattering is an important technique for the study of the static and dynamic behavior of polymers in solution, as evidenced by many experimental and theoretical studies.[1] In the dilute solution with a monodisperse molecular weight polymer, the data from dynamic light scattering are characterized by an essentially single-exponential decaying autocorrelation function if the condition $qR_g < 1$ is met, where $q$ is the magnitude of the scattering vector, equal to $(4\pi n/\lambda)\sin(\theta/2)$. Here $n$ is the refractive index of the solution, $\theta$ is the scattering angle, and $\lambda$ is the wavelength of the incident light in vacuo. $R_g$ is the mean radius of gyration of the macromolecule in solution. The exponential decay is due to translational diffusion of the polymer in the solution.

When the polymer concentration goes beyond the overlap concentration $C^*$ $(=M_w/[(4/3)\pi R_g^3 N_a])$, the autocorrelation function of the scattered light deviates from the single-exponential decay. Here $M_w$ is the molecular weight of polymer and $N_a$ is the Avogadro constant. The deviation is interpreted as due to scattering from more than one relaxation mode, with one of the modes attributed to mutual diffusion and the others to slow modes which have been the subject of much discussion.[1]

Assuming that the semidilute polymer solution is a transient gel, Brochard and de Gennes were first to discuss the dynamic structure factor of light scattering associated with concentration fluctuations in terms of osmotic and longitudinal modula of the transient gel.[2] Adam and Delsanti have studied the light scattering spectrum in the semidilute solution using a linear correlator and found two distinct modes at long and short times.[3] To interpret the experimental results, they have modified Brochard–de Gennes' transient gel theory and have found that in the gel regime the time autocorrelation function consists of the sum of two exponential functions:[4]

$$g(q,t) = A_s \exp(-(t/\tau_{sg})) + A_L \exp(-(t/\tau_{1g})) \qquad (1)$$

where the amplitude factors and relaxation times are related and are given by $A_L/A_S = M_g/M_\Pi$ and $A_L/A_S = \tau_{1g}/\tau_R - 1$. Here $M_g$ and $\tau_R$ are respectively the magnitude and relaxation time of the dynamic longitudinal relaxation modulus of the transient gel, $M(\omega)$. The relation among $M_g$, $M(\omega)$, and $\tau_R$ is given by $M(\omega) = M_g - M_g/(1 + i\omega\tau_R)$. $\tau_{sg}^{-1}$ is proportional to $(M_\Pi + M_g)\,q^2$, and $M_\Pi$ is the osmotic modulus of the solution.

The advent of multi-$\tau$ digital electronic correlators has facilitated a comprehensive photon correlation spectroscopic (PCS) study of the scattered light from a polymer solution over a wide dynamic range from $10^{-6}$ to $10^2$ s in a single experiment.[5] For a polymer solution in the concentration range extending from the overlap concentration $C^*$ to several times $C^*$, the shape of the time autocorrelation function $g(q,t)$ as detected by the multi-$\tau$ correlator is complex. The shape depends on the concentration, molecular weight of the polymer, and the solvent quality.[1,6]

Using a multi-$\tau$ correlator, Brown and co-workers[6-8] have in recent years studied semidilute polymer solutions consisting of polystyrene (PS) in $\Theta$ solvents, such as cyclohexane (CH) and dioctyl phthalate (DOP). They have found in the semidilute polymer solution that, in addition to a sharp $q^2$-dependent diffusive mode, a group of continuously distributed $q$-independent modes spanning a wide dynamic range is also present in the PCS spectra. These $q$-independent modes are prominent in PS/CH and PS/DOP systems but are barely detectable in the PS/toluene system. (Toluene is a good solvent for PS.) Following Adam and Delsanti, they interpreted the $q$-independent modes as viscoelastic modes associated with polymer entanglements.

Recent experiments carried out in our laboratory using PS in diethyl phthalate (DEP)[9] in $CCl_4$[10] and benzene[11] (all good solvents for PS) have also revealed very pronounced viscoelastic modes in the PCS spectrum for solutions in the semidilute regime. We have also found that viscoelastic modes are found also present in polymers with molecular weights less than the entangled molecular weight, as to be shown later in this paper. Therefore, it appears that polymer entanglement is not a prerequisite for the appearance of the viscoelastic modes, although the entanglement of polymer chains is expected to enhance the slow modes in the QEL scattering spectrum.

In an effort to help understand the effect of viscoelastic modes on the quasielastic light scattering (QEL) spectrum

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⊛ Abstract published in *Advance ACS Abstracts*, August 15, 1994.

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in semidilute and concentrated solutions, Wang has recently carried out a theoretical study of the QEL spectrum in the polymer solution using nonequilibrium thermodynamics in which the effect of solution viscoelasticity is incorporated.[12,13] Wang's theory does not assume the polymer chain entanglement, which, as mentioned above, is the essential ingredient of Brochard–de Gennes' theory. Wang's theoretical result shows that a difference between the partial specific volume of the polymer $U_P$ and that of the solvent component $U_s$ is required in order to observe the viscoelasticity effect from the polymer solution. In the semidilute concentration regime, the contrast factor associated with the refractive index fluctuation detected in the QEL experiment arises mainly from concentration fluctuations. In other words, in order to detect the viscoelastic modes through the concentration fluctuation mechanism, a coupling parameter $\beta$, proportional to $U_{ps} = U_p - U_s$, must be nonzero to have the viscoelastic modes encoded on the concentration fluctuation spectrum.

In this paper, we have investigated the static and quasielastic light scattering of PS in benzene with the concentration varying from the dilute to concentrated range. We have found that in the semidilute and concentrated regimes, the behavior of the viscoelastic component of PS in benzene is quite different from that found in PS in Θ and marginal solvents. In addition, as mentioned above, in Wang's theory, the amplitude of the viscoelastic component depends not only on the osmotic and longitudinal modula of the solution but also on the $\beta$ value. To test the theory, we prepare solutions of PS in the mixed solvent of benzene and diethyl phthalate (DEP). By varying the ratio of two solvents, yet keeping the polymer concentration fixed, we can change the $\beta$ value. We show in the PS/(benzene + DEP) system that the magnitude of viscoelastic modes varies with $\beta$ and disappears from the PCS spectrum for solutions with $\beta = 0$.

## Experimental Section

The main polystyrene (PS) sample used in this study was purchased from Polyscience Inc. and has an average molecular weight $M_w$ of $1.83 \times 10^5$ with the polydispersity index $M_w/M_n$ of 1.05. Another PS sample purchased from Toyo Soda Manufacturing Co. with $M_w = 1.67 \times 10^4$ ($M_w/M_n = 1.02$) was also used. Polymer solutions were prepared by dissolving PS in benzene (Fisher Scientific). Dust in solutions with less than 15% (wt/wt) concentration was removed by filtering through a 0.1 μm millipore filter into light scattering cells. Solutions with higher concentrations were difficult to filter and dust in these solutions was forced to the bottom of the cell by centrifugation at 4000g for over 80 h at elevated temperatures. For the PS (using $M_w = 1.83 \times 10^5$ and $M_w/M_n = 1.05$) solution in mixed solvents, $C_6H_6$ and DEP (purchased from Aldrich) were used. To prepare the solution, a predetermined amount of PS was put in the $C_6H_6$/DEP mixed solvent in a flask with a tight stopper and placed in an oven at 50 °C for over 1 week to allow PS to completely dissolve. The solution was then filtered by a 0.1 μm Millipore filter into the light scattering cell. The dust free solution in the light scattering cell was frozen in dry ice for over 10 h; the light scattering cell containing the solution was then flame sealed to certify that the relative concentration of various components remained unchanged during the course of the light scattering experiment.

Static light scattering measurements were performed at 20 °C by using an apparatus consisting of a Brookhaven 200SM goniometer and a Spectra Physics 125 He–Ne laser at a wavelength of 632.8 nm with a power of about 40 mW. The scattering intensity was measured at the scattering angle varying from 30 to 150°. The overlap concentration, $C^*$, calculated by using the expression given above is 0.0282 g/mL.

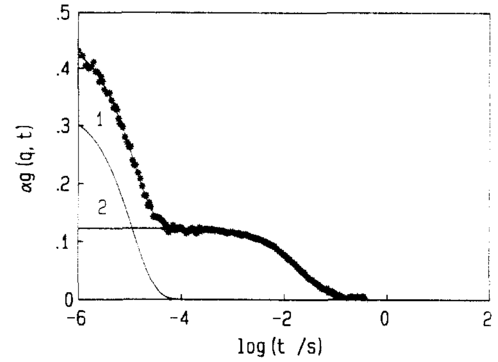

**Figure 1.** Field–field time correlation function $g(q,t)$ obtained for the PS/$C_6H_6$ solution with PS equal to 0.126 g/mL at 90° scattering angle. The correlation function is decomposed into two components in accordance with eq 3. Curve 1 is the mode associated with cooperative diffusion, and curve 2 is the viscoelastic component.

Dynamic light scattering measurements were carried out by using an ALV-5000 correlator and a Spectra-Physics argon ion laser with a wavelength of 488 nm. Normalized homodyne intensity–intensity correlation functions ($G(q,t)$ of polymer solutions with different concentrations were measured at 20 °C. The dynamic structure factor which is proportional to the normalized field–field correlation function $g(q,t)$ is obtained via the Sigert relation

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

where the baseline is taken to be 1. $\alpha$ is the contrast factor less than 1, due to the fact that only a fraction of the dynamic scattering intensity falls within the correlator window and also to the fact that a finite sized pinhole is used in the experiment.

## Results and Discussion

In Figure 1 we show a representative field–field correlation function $g(q,t)$ obtained for the PS/$C_6H_6$ solution with PS equal to 14.0 wt % ($\rho_2 = 0.126$ g/mL) at a 90° scattering angle. The correlation function covers 8 decades in delay time; one notes that a characteristic stepwise decay is clearly evident in the $10^{-4}$–$10^{-3}$ s dynamic range. Analysis using the CONTIN program[14] 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 whose position is independent of $q$ for larger $q$ (to be defined later). We have found, however, that the Kohlrausch–Williams–Watts (KWW) function given by

$$g(q,t) = x_1 \exp[-(t/\tau_1)^{\gamma_1}] + x_2 \exp[-(t/\tau_2)^{\gamma_2}] \qquad (3)$$

fits the observed $g(q,t)$ with good statistical accuracy. From an operational perspective, the CONTIN and KWW approaches are equivalent. In eq 3, the amplitude factors satisfy $x_1 + x_2 = 1$; $\gamma_1$ and $\gamma_2$ are shape parameters, which are either less than or equal to one. In Figure 1 we also show the resolution of the experimentally obtained $g(q,t)$ into two curves in accordance with eq 3. The best fit gives $\gamma_1 = 0.99$, $\gamma_2 = 0.87$, $\tau_1 = 1.1 \times 10^{-5}$ s, and $\tau_2 = 2.5 \times 10^{-2}$ s.

For $D_c q^2 \gg \tau_s^{-1}$ with $\tau_s$ being the shortest stress relaxation time that is detected by the correlator (~1 μs), it has been shown that $g(q,t)$ is given by[13]

$$g(q,t) = A e^{-D_c q^2 t} + B \int_0^\infty f(\tau) e^{-t/\tau} \, d\tau \qquad (4)$$

where $D_c$ is the cooperative diffusion coefficient given by

$$D_c = (\beta M_0 + M_\Pi)/\zeta\rho_2 \tag{5}$$

$\zeta$ is the friction coefficient, and $\rho_2$ is the polymer concentation (in grams per milliliters). $f(\tau)$ is the distribution function of relaxation times. The amplitudes $A$ and $B$ are given by

$$A = 1 - \frac{\beta M_0}{\beta M_0 + M_\Pi} \tag{6a}$$

$$B = \frac{\beta M_0}{\beta M_0 + M_\Pi} \tag{6b}$$

where $M_\Pi = \Phi_1\rho_2\,(\partial\Pi/\partial\rho_2)_{T,P}$ is the osmotic modulus,[15] $\Pi$ is the osmotic pressure, and $\Phi_1$ is volume fraction of the solvent. $M_0$ is the amplitude of the longitudinal stress modulus due to the polymer component in solution.

Equation 4 shows that the time correlation function $g(q,t)$ is divided into two groups: one consists of a single exponential decay with the decay rate given by $D_c q^2$, and the other, of a group of viscoelastic modes associated with relaxation time constants $\tau$. Note that the time constant of the single exponential decay term depends on $q^2$ and the relaxation times of the viscoelastic modes are $q$-independent in the large wave vector regime. Equation 6b predicts that the viscoelastic component vanishes for systems with $\beta = 0$. On the other hand, for a concentrated solution or polymer melt, we have $\beta M_0 \gg M_\Pi$ and viscoelastic modes dominate the dynamic light scattering spectrum.

To confirm the assignment, we have carried out the angular-dependent measurement of the autocorrelation function. We have used a multiparameter program to fit the correlation function according to eq 3. The quality of the fit of the correlation functions at various scattering angles is similar to that of Figure 1, which is rather satisfactory. The average relaxation rates obtained from the fit are shown as a function of $q^2$ in Figure 2. The relaxation rate associated with curve 1 shows a distinctive $q^2$ dependence, thus indicating a diffusive character, whereas the relaxation rate associated with curve 2 has a complex $q$ dependence at small $q$ and becomes $q$-independent as $q$ becomes greater than $q^2 = 9 \times 10^{-10}$ cm$^{-2}$. In accordance with ref 13 the $q$-independent result at large $q$ for curve 2 is associated with viscoelastic modes. The fact that $\langle\tau_s\rangle^{-1}$ decreases rapidly with decreasing $q$ at small $q$ is due to mixing of diffusion and viscoelastic modes.

Having identified the diffusion mode, we have proceeded to calculate the mutual diffusion coefficient $D_c$ by using the formula $D_c = \langle q^2\tau_f\rangle^{-1}$. The results of $D_c$ as a function of PS concentration at 20 °C are shown in Figure 3. The mutual diffusion coefficient of PS in benzene in the semidilute region is on the order of $10^{-10}$ m$^2$/s, which is in agreement with the result given in ref 3. This value appears to be much faster than the cooperative diffusion coefficient of PS in DEP[9] and $CCl_4$.[10] At low concentrations, $D_c$ increases rapidly with increasing PS concentration; however, at high concentrations, $D_c$ increases slowly with increasing concentration.

As given in eq 5, the cooperative diffusion coefficient $D_c$ is determined by the osmotic modulus, the longitudinal modulus of the solution, the coupling coefficient $\beta$, the polymer concentration $\rho_2$, and the friction coefficient $\zeta$. In order to investigate effects of these quantities, we have tried to determine them experimentally to the extent possible.

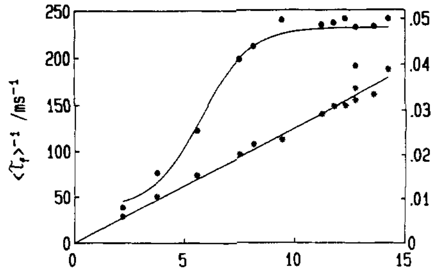

**Figure 2.** Plots of mean relaxation rates $\langle\tau_f\rangle^{-1}$ and $\langle\tau_s\rangle^{-1}$ for the PS/benzene solution ($M_w = 1.83 \times 10^5$, $\rho_2 = 0.126$ g/mL) as a function of $q^2$. Here $\langle\tau_f\rangle^{-1}$ shows a $q^2$ dependence, whereas $\langle\tau_s\rangle^{-1}$ shows no $q$ dependence at large $q$. $\tau_f$ is equivalent to $\tau_1$, and $\tau_s$, equivalent to $\tau_2$ in accordance with eq 4.

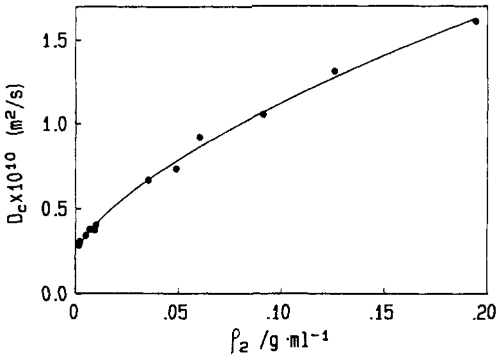

**Figure 3.** Concentration dependence of the cooperative diffusion $D_c$ for the PS/benzene system.

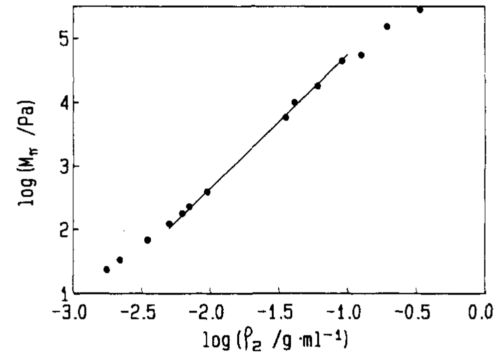

**Figure 4.** Concentration dependence of osmotic modulus $M_\Pi$ for the PS/benzene system. The line is drawn according to $\rho_2^{2.25}$ in the semidilute region.

The osmotic modulus $M_\pi$ is determined by static light scattering. The absolute intensity of light scattered at an angle $\theta$ from a polymer solution with a concentration $\rho_2$ is expressed in terms of the Rayleigh ratio $R(q)$ as[16]

$$R(q) = KM\rho_2 S(q) \tag{7}$$

where $K$ is an optical constant equal to $(4\pi^2 n^2/N_A\lambda^4)(dn/d\rho_2)^2$, $n$ is the refractive index, $\lambda$ is the wavelength of the incident light and $dn/d\rho_2$ is the refractive index increment. $S(q)$ is the static structure factor at the scattering vector $q$. The quantity $(\partial\pi/\partial\rho_2)/\rho_2$, known as "the inverse osmotic compressibility", is equal to $RTK/R(\theta{=}0)$, where $R(\theta{=}0)$ is the Rayleigh ratio at zero scattering angle. We have measured the quantity of $K\rho_2 RT/R(q)$ as a function of scattering angle and extrapolated the result to $\theta = 0°$ to obtain $\partial\pi/\partial\rho_2$. By multiplying the result of $\partial\pi/\partial\rho_2$, we obtain the osmotic modulus of the solution, which is shown in Figure 4 as a function of PS concentration. Over the entire concentration range studied, we have found that $M_\Pi$ increases with the polymer concentration, and the increase can be described by a power law. In the semidilute

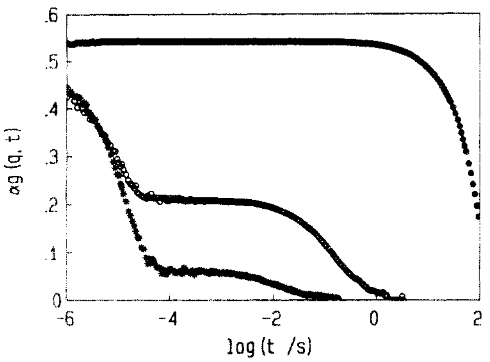

**Figure 5.** Homodyne intensity–intensity correlation functions of PS/benzene at three different concentrations ($M_w = 1.83 \times 10^5$): (*) $\rho_2 = 0.091$ g/mL, $B/(A + B) = 15\%$; (○) $\rho_2 = 0.194$ g/mL, $B/(A + B) = 43\%$; (●) $\rho_2 = 0.511$ g/mL, $B/(A + B) = 100\%$.

region, $M_\Pi$ is scaled as $\rho_2^{2.10}$, as indicated by the line in Figure 4, which is not far from the power law $\rho_2^{2.25}$ dependence, predicted by scaling theory.[17]

We next determine the coupling parameter $\beta$. The $\beta$ parameter, defined by $\beta = \rho_2(\partial\rho/\partial\rho_2)/\rho$, can be determined by measuring the density of the solution $\rho$ as a function of the polymer concentration $\rho_2$. For systems without a strong interaction between polymer and solvent, it is found experimentally that $\beta$ increases linearly with the concentration, i.e. $\beta = k\rho_2$, where $k$ is a constant at a given temperature. From this result, a simple calculation leads to $k = (1/\rho_2^0)\ln(\rho_2^0/\rho^0)$, where $\rho^0$ is the density of the solvent and $\rho_2^0$ is the density of the polymer. For the PS/DEP system at 23 °C, we have found experimentally $k$ to be 0.055 ± 0.005, in comparison with the theoretical result of 0.060. For the PS/cyclohexane system at 34.5 °C, the experimental result of $k$ is 0.353, in comparison with $k = 0.318$, predicted theoretically. Thus, the relative error in $\beta$ between the experimental and predicted results is less than 10%. This indicates that one can use the theoretical expression to predict the $\beta$ values of polymer solutions with certain confidence. For the PS/benzene system at 20 °C, we have found that $\beta = 0.1697\rho_2$.

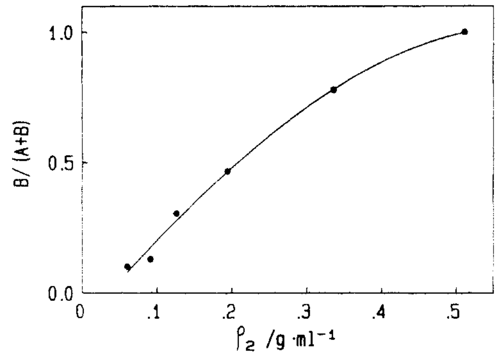

**Figure 6.** Concentration dependence of the relative amplitude factor $B/(A + B)$ of the slow component for the PS/benzene system ($M_w = 1.83 \times 10^5$).

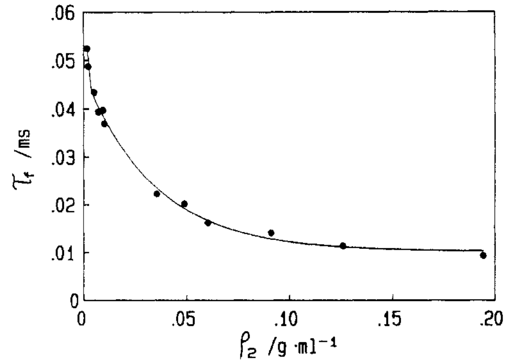

**Figure 7.** Concentration dependence of the relaxation time of the fast mode of the PS/benzene system ($M_w = 1.83 \times 10^5$).

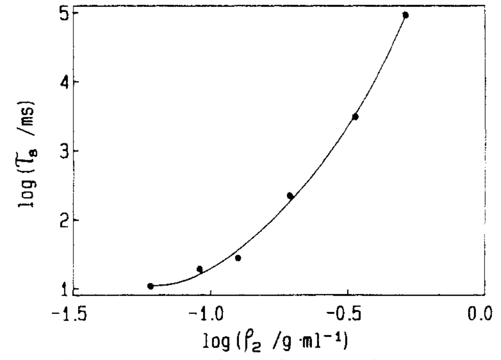

**Figure 8.** Concentration dependence of the average relaxation time of the slow component for the PS/benzene system ($M_w = 1.83 \times 10^5$).

We next consider the longitudinal modulus $M_0$. Our laboratory is not equipped to measure $M_0$. However, according to eqs 6a and 6b, it is possible to obtain $M_0$ from the amplitude factor associated with either the fast or the slow component of the correlation function. To accomplish this, we have accumulated the dynamic light scattering data of the PS/benzene solution for a sufficiently long time so as to obtain the correlation function with good statistical accuracy for facilitating data analysis. Representative time correlation functions for three polymer concentrations are shown in Figure 5. The relative amplitude factor of the slow component as a function of PS concentration is shown in Figure 6. It can be seen that the relative amplitude of the slow component increases rapidly with increasing PS concentration. When the PS concentration is 0.091 g/mL, the amplitude of the slow component is 15%. At the concentration greater than 0.511 g/mL, it is 100%; no fast mode can be observed at this concentration. To ascertain that the absence of the fast component is not due to its displacement to the shorter time region at high concentrations and goes beyond the shortest time limit of the correlator window and, hence, cannot be observed, we have investigated the concentration dependence of the relaxation time of the fast component $\tau_f$ with concentration. As shown in Figure 7, $\tau_f$ decreases rapidly at low PS concentration, but the decrease becomes rather slow at high concentrations. Therefore, the absence of the fast mode is not due to its diplacement outside the limit of the correlator, but rather due to the amplitude decrease. The amplitude decrease is associated with the fact that $M_\Pi/\beta M_0 \rightarrow 0$ owing to the rapid increase of $\beta M_0$ in relation to $M_\Pi$ at high PS concentrations. It should also be noted that with the increase of the PS concentration, not only the amplitude of the slow component becomes larger but also the average relaxation time of the slow component increases rapidly with increasing PS concentration. Shown in Figure 8 is the change of the average relaxation time of the slow component $\langle\tau_s\rangle$ with PS concentration. The results indicate that $\langle\tau_s\rangle$ exponentially increases with PS concentration. From the above discussion, it is safe to use the amplitude factor of the slow component in conjunction with the $\beta$ and osmotic modulus data to obtain the longitudinal modulus $M_0$. Figure 9 shows the concentration dependence of $M_0$, which can be expressed by $M_0 = 1.82 \times 10^8\rho_2^{2.48}$ Pa.

The longitudinal modulus $M_0$ determined in this work corresponds to the value at the frequency of $10^6$ Hz, due to the fact that the shortest delay time of the present

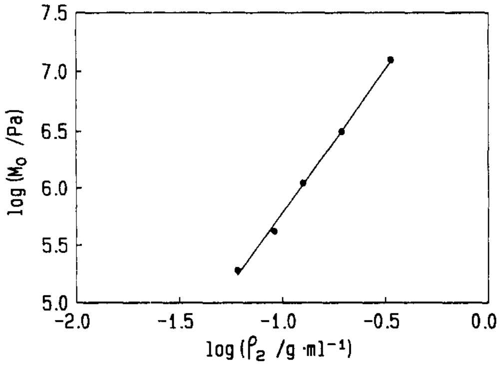

**Figure 9.** Plot of the longitudinal modulus of the PS/benzene system determined from the slow component in the QEL scattering spectrum as a function of concentration (PS $M_w$ = 1.83 × $10^5$).

correlator is 1 μs. One recalls that $M_0 = \Delta K + 4/3G$, where $K$ and $G$ are the compressional and shear moduli, respectively. In general the compressional modulus is larger than the shear modulus in the polymer solution or melt. However, due to the fact that QEL scattering is due to 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.[18] In the polymer liquid, the equilibrium compressional modulus is about $10^9$ Pa,[19] in comparison with $10^{11}$ Pa that one determines from Brillouin scattering.[20] Thus, it appears that the shear modulus $G$ makes the dominant contribution to $M_0$. By assuming that the relaxation shear modulus $G(t)$ is given by $G_N{}^0 \exp(-t/\tau_R)$, where $\tau_R$ is the terminal (or longest) relaxation time and $G_N{}^0$ is the plateau modulus of the entangled solution, Adam and Delsanti,[4] using the equation $G_N{}^0 = \eta_s/\tau_R$, have determined $G_N{}^0$ for the PS/benzene solution by measuring the zero shear viscosity $\eta_s$ of the solution. Their result yields $G_N{}^0 = 8.32 \times 10^5 c^{2.36}$ dyne/cm$^2$, where $c$ is the weight fraction. At $c$ = 1, one has $G_N{}^0 = 8.32 \times 10^5$ dyne/cm$^2$. This result should be contrasted with the plateau modulus of PS in the undiluted state[22] at 190 °C, which is 2.0 × $10^6$ dyne/cm$^2$. The plateau modulus of the undiluted PS at 190 °C is greater than $G_N{}^0$ ($c$ = 1) in the semidilute solution at room temperature obtained by Adam and Delsanti[4] by a factor 2. On the other hand, while the exponent (2.48) associated with the concentration factor obtained for $M_0$ from our experiment is rather close to the concentration exponent (2.36) reported in ref 4, the amplitude factor for $M_0$ is about 3 orders of magnitude greater than that given in ref 4. At $\rho_2$ = 0.126 g/mL, we obtain $M_0 = 1.8 \times 10^7$ dyne/cm$^2$. Though this value is greater than $G_N{}^0$ of PS at 190 °C by about 1 order of magnitude and in light of the fact that the present $M_0$ value corresponds to the value at $10^{-6}$ s (or 1 MHz) at room temperature, we can conclude that our result is not in contradiction with the temperature–time superposition associated with the viscoelastic polymer solution.

For a polymer with a high molecular weight, scaling theory[21] has shown that the plateau shear modulus $G_N{}^0$ of the polymer solution depends on the concentration as $\rho_2{}^{9/4}$. Since the PS molecular weight used in this study exceeds the entanglement molecular weight $M_e$, which equals 3.5 × $10^4$,[22] one is tempted to relate the $M_0$ value shown in Figure 9 to the plateau shear modulus $G_N{}^0$. The exponent 2.48 that we have found in the concentration dependence of $M_0$ is close to, albeit slightly larger than, the value of 9/4 predicted by the scaling argument. However, it should be pointed out that without removing the density dependence in the $\beta$ factor associated with $M_0$ in eqs 6a and 6b, the concentration dependence of $M_0$ would be $\rho_2{}^{3.48}$, which would deviate greatly from the scaling theoretic result.

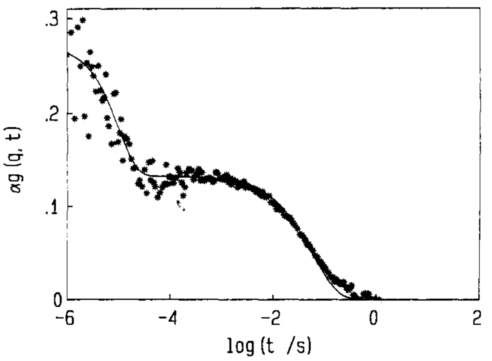

**Figure 10.** Homodyne intensity–intensity correlation function of low molecular weight PS in benzene ($M_w$ = 1.83 × $10^4$, $\rho_2$ = 0.276 g/g).

It is interesting to investigate the dynamic properties of PS with a low molecular weight in a good solvent, especially at the molecular weight less than the entanglement molecular weight $M_e$. Broachard and de Gennes' theory[2] for light scattering in the semidilute solution is built upon the chain entanglement concept, but with the molecular weight smaller than $M_e$, there is no entanglement among different chains and no knots are tied along each chain in a good solvent. As a result, according to their theory, there would be no viscoelastic modes predicted. Figure 10 shows the autocorrelation function of PS/benzene with the concentration of 0.276 g/g, where PS has the molecular weight of 1.67 × $10^4$, more than a factor of 2 smaller than $M_e$. Clearly, as shown in Figure 10, the slow component is present. This result thus indicates that the polymer chain entanglement is not required for the appearance of the slow viscoelastic component, despite the fact that the chain entanglement definitely enhances the viscoelastic modes. According to Wang's theory, if the solution has a nonvanishing $\beta$ (the concentration–density coupling parameter), the solution viscoelasticity effect will couple to the concentration fluctuation and appear in the QEL scattering spectrum. Our experimental study shows that the criterion to observe the viscoelastic modes is $\beta M_0 > M_{\Pi}/20$. When the ratio $\beta M_0/M_{\Pi}$ exceeds 0.05, one can detect the viscoelastic modes with relative ease, regardless of the presence of the chain entanglement effect.

We now examine the effect of changing the amplitude of the viscoelastic component by changing $\beta$, while keeping the polymer concentration fixed. This is accomplished by using mixed solvents. However, after adding DEP to the PS/benzene solution to vary the coupling parameter, we have found that the viscoelastic component of $g(q,t)$ changes with time, in contrast to the binary PS/$C_6H_6$ solution in which the time dependence is not observed. In the case of PS/$C_6H_6$ solutions, time correlation functions $g(q,t)$ obtained for various PS concentrations are readily reproducible at different times. Checking the reproducibility is very important because as the concentration becomes higher than $C^*$, there is a possibility that the solution exists in the nonequilibrium state after preparation. A nonequilibrium system indicates that $g(q,t)$ will evolve with time. At the 14.0 wt % concentration, we have found that the PS/$C_6H_6$ solution reaches equilibrium very quickly, but this is not the case when DEP is added to the solution. We have followed the time evolution of the PCS correlation function by intermittently measuring $G(q,t)$ for the PS solution in various ($C_6H_6$ + DEP) mixed

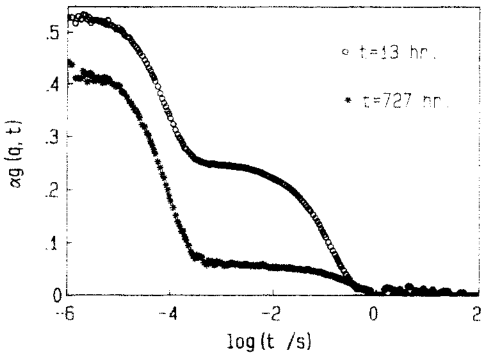

**Figure 11.** Correlation functions for PS (14.0 wt %) in $C_6H_6$/($C_6H_6$ + DEP) with $C_6H_6$ equal to 28.2% (w/w) obtained at two different times.

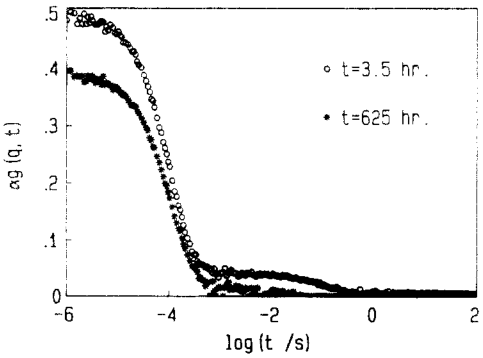

**Figure 12.** Time correlation functions of PS in the $C_6H_6$ plus DEP mixed solvent at two different times. The total PS concentration is 14 wt % and $C_6H_6$/($C_6H_6$ + DEP) equals 34.0 wt %.

solvents with different relative solvent concentrations, the total PS concentration being kept fixed.

We show in Figure 11 the time correlation functions obtained at two different times of the PS (14 wt %) in the $C_6H_6$ plus DEP mixed solvent, with $C_6H_6$/($C_6H_6$ + DEP) equal to 34.0 wt %. At $C_6H_6$/($C_6H_6$ + DEP) equal to 34.0 wt % and the total PS concentration equal to 14.0 wt %, the coupling parameter $\beta$ is found to be equal to $1.7 \times 10^{-3}$, and according to theory we expect to observe the viscoelastic modes. The results in Figure 11 clearly support the prediction. However, the shape of the time correlation function characterizing the solution viscoelasticity is more pronounced in the fresh solution than in the aged one, as is clearly demonstrated by the correlation functions for the solution 13 h after it is prepared in contrast with that after equilibration for over 4 weeks (727 h). The results clearly show that different time scales with respect to achieving internal equilibrium are involved in the PS solution with the mixed solvent. The time evolution in the solution with the mixed solvent is probably associated with the differential solvation process of PS chains by benzene and DEP. Differential solvation leads to selective absorption; it also takes time to reach the mutual equilibrium.

We have analyzed the PCS autocorrelation functions $g(q,t)$ of mixed solvents obtained at various times by fitting them to eq 3. We have found that in the course of time when the viscoelastic component undergoes evolution, the cooperative diffusion component remains unchanged, with the width parameter $\gamma_1$ equal approximately to 1 and the relaxation time $\tau_1$ equal to 86.5 $\mu$s. On the other hand, the width parameter $\gamma_2$ associated with the viscoelastic component, somewhat broader in the mixed solvent than in pure solvent, decreases slowly as the sample is aged. The characteristic relaxation time $\tau_2$ increases significantly with increasing time of equilibration and approaches equilibrium after more than 1 month. The amplitude factor of the slow component factor $x_2$ is about 47% of the total contrast for the solution which is equilibrated for 13 h, and it approaches 14% after it is equilibrated for about 1 month. the decrease in $x_2$ is rapid during the first 100 h and, henceforth, slows down considerably.

Since PCS is based upon the principle of fluctuations in the equilibrium state, the results in the solution involving mixed solvents show that the osmotic equilibrium in the solution is achieved in a much shorter time than the mechanical equilibrium associated with viscoelasticity. Fluctuations from the osmotic equilibrium are due to concentration fluctuations, and fluctuations from the mechanical equilibrium are due to density fluctuations. Localized segmental motion and viscoelasticity both affect density fluctuations. While the dynamics of localized segmental motion are fast in comparison with that associated with the concentration fluctuation, as shown here, viscoelastic effects are slow compared with the concentration fluctuation. The gradual change of the viscoelastic component in the PS solution with mixed solvents simply indicates that the approach to mechanical equilibrium, which involves long time Rouse-like Brownian dynamics of the polymer chains in solution, takes a considerably longer time than the approach to compositional equilibrium. Thus, in the QEL spectrum, the cooperative diffusion component is associated with the fast mode and the viscoelastic component is associated with slow modes.

The solution with $C_6H_6$/($C_6H_6$ + DEP) equal to 28.2% (w/w), but with PS still kept equal to 14 wt %, gives a very interesting result, as shown in Figure 12. At this relative polymer/solvent concentration, this solution gives a negligible $\beta$ value. Thus, according to eqs 6a and 6b, no viscoelastic component is expected. As shown in Figure 12, the sample with only 3.5 h of equilibration gives a noticeable viscoelastic component. However, as the equilibration under isothermal conditions continues, the amplitude of the viscoelastic component decreases, becoming nearly 0 after 26 days (625 h) of equilibration; the slow component completely disappears after 1 month of equilibration. Thus, after the equilibrium state is reached, the experimental result is in agreement with the theoretical prediction.

In summary, we have carried out a detailed light scattering study of the PS/benzene system at various concentrations at 20 °C. The study includes both static and dynamic light scattering measurements covering a dynamic range of $10^{-6}$ to $10^{2}$ s. From the angular-dependent static light scattering measurements, we have determined the osmotic modulus as a function of PS concentration. In the semidilute concentration regime, we have observed viscoelastic modes in polymer solutions with the polymer weight both above and below the entanglement molecular weight. The experimental results were explained by Wang's theory. We have observed the viscoelastic component in PS solution with the PS molecular weight less than the entanglement molecular weight. The result indicates that viscoelasticity rather than entanglement is required for the observation of the slow component. For the entangled system, the concentration dependence of the longitudinal stress modulus obtained in the semidilute region is consistent with the scaling theoretical prediction. From the quasielastic light scattering studies of semidilute solutions of PS in the mixed solvents of benzene plus DEP, we have shown that the relative amplitude of the viscoelastic component depends on the coupling parameter $\beta$, in addition to the osmotic modulus and longitudinal stress modulus of the polymer solution. We have found that the amplitude and a relaxation time distribution of the viscoelastic component of the QEL scattering spectrum of PS in the mixed solvent depend on time. For the solution with $\beta = 0$, we have observed no viscoelastic component in the quasielastic light scattering spectrum, in agreement with the theoretical prediction of our theory.

Finally, we should remark that Brown and Štepánek have reported observing viscoelastic modes in the QEL scattering time correlation function of PS in several Θ solvents in the semidilute concentration regime.[23] Their results are not consistent with the present work. The validity of Brown and Štepánek's experiments has been questioned by Sun and Wang.[24] Akcasu, Kleine, and Wang (AKW) have employed the projection operator technique using a set of dynamic variables including a nonconserved diffusion current to describe the coupling of concentration fluctuations to the viscoelastic modes.[25] AKW have found an extra term in the viscosity kernel and suggest that the solution viscoelastic effect might still be present when $\beta = 0$. However, the extra term has recently been shown to be zero by Wang.[26] Doi and Onuki[27] as well as Milner[28] also discussed the effect of the coupling of concentration fluctuations to solution viscoelasticity. Their works are similar to that of Brochard and de Gennes[2] assuming $\beta = 1$ and do not describe how the concentration and viscoelasticity are coupled.

**Acknowledgment.** We thank the Material Research Division at the NSF (Grant DMR 912933) for support of this research. We also thank X. Q. Zhang for technical assistance.

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