Viscoelastic Relaxation in Semidilute and Concentrated Polymer Solutions

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ABSTRACT: This article deals with the viscoelastic modes experimentally observed in semidilute poor-solvent systems. Comparisons are made between experimental data and the predictions of a recent theoretical description. The latter pivots on a coupling parameter β which is proportional to the difference in partial specific volumes of the polymer and solvent and which is postulated to give rise to the amplitude of the viscoelastic component in the spectrum. It is found here that the relative amplitude of the viscoelastic modes is unrelated to the density parameter, β, and furthermore, a substantial amplitude of the viscoelastic modes is observed under conditions where $\beta = 0$. A discrepancy of 3 orders of magnitude results for the predicted longitudinal modulus and the plateau modulus. For a highly concentrated polymer/solvent mixture (0.7 g/mL) under the condition $\beta = 0$, the spectrum of the plasticized polymer does not correspond solely to the relaxation of the density fluctuations as was theoretically predicted.

Introduction

The influence of solvent quality on chain dynamics in semidilute polymer solutions (typically of concentration $c < 0.2$ g/mL) is strong, suggesting significant differences in the underlying physics in the cases of Θ solutions and good solvents. This aspect has been recently reviewed,[1] and only the salient features will be outlined here to provide a background for the discussion.

In contrast to thermodynamically good solvents, the dynamic light scattering (DLS) autocorrelation function in poor solvents close to Θ conditions is multimodal, with relaxation times spanning over 8–9 decades on the time scale. The high frequency limit reflects a fast diffusive (q^2-dependent, where q is the scattering vector) component which may be attributed to the relaxation of the collective motions of the transient network. The slower modes, which have a very broad distribution depending on the concentration and the molecular weight, are independent of q. As the solvent quality is increased in a given system, for example, by increasing the temperature, the diffusion mode becomes increasingly dominant; in so-called marginal solvents the slow modes are clearly present but of low amplitude, while in typically good solvents they can barely be detected.[2,3]

A reasonable postulate is that the slow q-independent modes are related to the viscoelastic properties of the transient network. The seat of the viscoelastic effects lies in the topological constraints which come into play above a certain minimum concentration and molecular weight necessary to produce entanglements. On a time scale shorter than the characteristic lifetime of the entanglements, the system will behave as a cross-linked network. There will thus be contributions to the longitudinal modulus from both the osmotic modulus and the elastic modulus of the transient network. In the low frequency limit, the chains can disentangle and the concentration fluctuations will relax as in a viscous solvent.

Recent experimental contributions[1,2,4] have addressed the problem. Relaxation time distributions were derived by inverse Laplace transformation (ILT) of data from DLS and dynamic mechanical measurements on high MW polystyrenes in semidilute entangled solutions in the viscous solvent dioctyl phthalate (DOP). Although the experimental range covered by the two techniques differs at the fast end of the time scale, it was established that the dynamic processes probed at long times are characterized by a similar wide range of relaxation times and that the concentration and molecular weight dependencies of the relaxation times were almost coincident. The sensitivity to the dynamic processes differs for the two techniques, as might be expected.

Subsequently, Wang[5-7] made a theoretical study of the interrelationship between the relaxation of the diffusive concentration fluctuations and viscoelastic relaxation in such systems. The novelty of this approach mainly consists in the introduction of a coupling parameter β, which is proportional to the difference in densities of polymer and solvent, and through which the concentration and viscoelastic relaxations would be coupled in semidilute solutions. In spite of certain phenomenological successes, an unclear feature of the theory in its present form is that no underlying relationship with a structural model is provided (the transient gel and the accompanying entanglement phenomenon), the effects of which are most clearly revealed by experiments made on semidilute Θ solutions. Thus, no predictions for the concentration dependence or molecular weight dependences of either the amplitude or the relaxation times of the viscoelastic modes are made, although it has been[2,4] shown that these dependencies are strong. Furthermore, there are fundamental differences between the dynamic behavior in semidilute solutions and in highly concentrated solutions (typically $c > 0.5$ g/mL) in which a molecular weight dependence of the dynamics is not observed. For these reasons it seems highly desirable to examine the possible effects of the coupling parameter and the role of the viscoelastic contribution to the dynamic light scattering spectrum. The aim of this contribution is to present experimental data on a variety of polymer/solvent systems, all having as a common feature an accessible Θ temperature, but which differ strongly in the magnitude of the β parameter, as defined below. The

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results will be discussed in the framework of the theoretical approach introduced above, and possible origins will be proposed for the observed serious qualitative discrepancies between the trends anticipated from the theory and the experimental findings.

Considering DLS experiments, the spectrum of light ($I(q,\omega)$) scattered at a particular vector q is given by[5,6]

$$I(q,\omega) = \mathrm{Re}\int_0^\infty \langle \delta\epsilon(q,t)\delta\epsilon^*(q)\rangle e^{-i\omega t}\,dt \qquad (1)$$

where ϵ is the dielectric constant, $q = (4\pi n/\lambda)\sin(\theta/2)$, and n is the refractive index, λ the wavelength and θ the scattering angle.

For a binary mixture, fluctuations in the dielectric constant, $\delta\epsilon$, may have three sources: fluctuations in composition (or concentration), δc; fluctuations in pressure (or density), δp; and fluctuations in temperature δT.[8]

$$\delta\epsilon(r,t) = (\delta\epsilon/\delta c)_{T,p}\delta c(r,t) + (\delta\epsilon/\delta p)_{T,c}\delta p(r,t) + (\delta\epsilon/\delta T)_{p,c}\delta T(r,t) \qquad (2)$$

It can be shown[5] that, for the frequencies accessible in DLS, the last term in δT is negligible.

Inserting eq 2 into eq 1 leads to a spectrum for the scattered light with the terms

$$I(q,\omega) = (\delta\epsilon/\delta c)_{T,p}{}^2 I_{cc}(q,\omega) + (\delta\epsilon/\delta p)_{T,c}{}^2 I_{pp}(q,\omega) + ((\delta\epsilon/\delta c)_{T,p}(\delta\epsilon/\delta p)_{T,c}[I_{pc}(q,\omega) + I_{cp}(q,\omega)]) \qquad (3)$$

The first and second terms of eq 3 represent the autocorrelation functions of the concentration and density (pressure) fluctuations; the third and fourth terms are the cross-correlation functions between concentration and density fluctuations. The majority of light scattering experiments have been made on polymer systems at low concentration and are referred to the first term in eq 3 containing $(\delta\epsilon/\delta c)_{T,p}$, which is much larger than $(\delta\epsilon/\delta p)_{T,c}$. Analysis of the first term leads to a definition and measurement of a diffusion coefficient, which, in dilute solutions, corresponds to translational diffusion of polymer coils in the solvent. In semidilute solutions it corresponds to the cooperative diffusion coefficient describing motions in the transient polymer network. Thus, for dilute ($c < c^*$) and semidilute ($c^* \le c < c_s$) polymer solutions, the second, third, and fourth terms in eq 3 may be neglected. The overlap concentration defined here is

$$c^* = 3M/4\pi R_g{}^3 N_A \qquad (4)$$

Here c_s is a concentration above which monomer–monomer friction has to be taken into account, in addition to the monomer–solvent friction. It is customary to consider c_s as of the magnitude 0.15 g/mL although recent experiments suggest that some dynamic properties of semidilute solutions are observed up to a concentration exceeding 0.4 g/mL.[1]

There are, however, some well-defined cases where a description of the spectrum of the light scattered by a polymer solution solely in terms of diffusion coefficients is inadequate. One example comprises semidilute solutions in which the existence of several dynamic processes is well-established, in particular, in semidilute systems at the Θ temperature.[1,2]

Comprehensive measurement of the spectrum of the scattered light in a single experiment over the whole accessible frequency range of photon correlation spectroscopy has become possible through the advent of multi-τ correlators. Development of mathematical analysis techniques has made it possible to reliably extract relaxation time distributions from these data.

Mathematical progress was devoted to treating the ill-posedness of the inverse Laplace transformation (ILT) necessary to convert the measured dynamic properties into physical information on the system. Subsequent to the pioneering work of Provencher[9] with the algorithm known as CONTIN, other successful techniques with a similar goal have been developed by Zimmerman,[10] Jakes,[11] Livesey et al.,[12] and others. Today the majority of the ILT of experimental data is performed using either CONTIN or REPES programs. A recent review of the field has been provided by Štepánek.[13]

In previous reports[1,2] we have reviewed the salient features of the light scattered by semidilute Θ-solutions where the departures from a single diffusive process are most pronounced, and we utilized these techniques to interpret the data. It was shown that the q-independent dynamic processes reflect the viscoelastic properties of the solutions. We have also demonstrated[3] that such processes can also be observed in a semidilute solution under good solvent conditions, although with a very small amplitude in this case.

A second class of problems is met in the description of the light scattered by bulk polymers in the molten state, for which the first term in eq 3 is irrelevant, i.e. for one-component systems where fluctuations with composition ($\delta\epsilon/\delta c$) cannot occur. In such cases, the spectrum of the scattered light is due to the fluctuations in density, i.e. the second term in eq 3. The third and fourth terms can be neglected. Light scattered from bulk homopolymers was studied in particular by Fischer, Wang, Patterson, and Fytas.[15-17] It has been shown that the dynamic properties in these cases can be related to the longitudinal compliance[14] and the bulk dynamic properties then depend strongly on the glass transition temperature and thus on the dynamics of the local structural relaxations of shorter parts of the polymer chains.

A third area where the simple picture of polymer dynamics with either pure concentration fluctuations or pure density fluctuations is unsatisfactory is represented by plasticized polymers which can for present purposes be described as polymer–solvent mixtures containing less than 50% solvent. The diffusive process is still observable above $\Phi = 0.5$ but is strongly slowed down with a further increase in volume fraction of polymer, Φ, as observed by Patterson et al.[15]—see also ref 24. However, far above the glass transition the diffusive process may be accelerated, as has been shown on poly(butyl acrylate) solutions.[25] At some point a second, nondiffusive relaxation with a broad range of relaxation times appears which corresponds to the α-relaxation of the polymer. Clearly, the accumulated data over the past years emphasizes the need for a more complete discussion of eq 3 which is not limited to the two reference cases where only pure concentration fluctuations or pure density fluctuations are concerned.

Using linearized generalized hydrodynamics, Wang[5,7] has recently proposed a theory which incorporates into the spectrum of scattered light the contribution from the viscoelastic properties of the solution and which combines both the fluctuations in concentration and density. The approach yields expressions for the four terms which are combined to give eq 3; the reader is referred to the original references for the derivation of these results. An important physical parameter which appears in eqs 7 and 8 below is the unitless coupling parameter $\beta = (c/\rho)(\delta\rho/\delta c)_{T,p}$ where ρ is the solution density. β can be expressed in terms of the partial specific volumes of the polymer, v_p, and solvent, v_s, as

$$\beta = (c/\rho)(v_s - v_p)/v_s \tag{5}$$

and can be either positive or negative depending essentially on whether the polymer has a larger density than the solvent ($\beta > 0$) or lower ($\beta < 0$).

The following relationship is given in ref 6 for the autocorrelation function of the light scattered in a semidilute solution:

$$g_1(q,t) = A_f e^{-D_c q^2 t} + \sum_i B_i e^{-t/\tau_i} \tag{6}$$

The amplitude of the collective diffusion term for the case where $D_c q^2 \gg \tau_2^{-1}$ (the usual experimental situation) is given by

$$A_f = 1 - [\beta M_o/(\beta M_o + M_\pi)] \tag{7}$$

where M_π is the osmotic modulus and $M_o = \sum_i M_i$ is the amplitude of the total longitudinal stress modulus.

The individual amplitudes of the q-independent relaxational terms are given by

$$B_i = \beta M_i/(\beta M_o + M_\pi) \tag{8}$$

The treatment leading to eqs 7 and 8 is qualitatively similar to that of Brochard and de Gennes[26,27] for semidilute solutions which was subsequently modified by Adam and Delsanti.[28] The results of ref 28 also describe the spectrum of decay times for a semidilute solution in terms of two components. The fast component of amplitude A_f corresponds to the transient network with diffusion coefficient D_g and decay time $\tau_g = (D_g q^2)^{-1}$, the slow one with amplitude A_s to the structural relaxation with relaxation time τ_r. The ratio of these amplitudes is given by $A_s/A_f = (M_o/M_\pi)$. Expression 7 and 8 above lead to an analogous equation, provided that $\beta = 1$ and only a single stress relaxation time is considered instead of a spectrum as in refs 5–7. The theory of Brochard and de Gennes has been applied and found useful by several authors for the analysis of dynamic light scattering experiments (e.g. see refs 2, 4, 29, 30).

Experimental Section

Solutions were prepared using narrow-distribution polystyrene fractions of $M_w = 4.9 \times 10^6$ (Toya Soda Ltd., Tokyo, Japan) and the following analytical grade solvents: diethyl malonate (DEM) (Fluka); diethyl oxalate (DEO), diethyl phthalate (DEP), dioctyl phthalate (DOP), and cyclohexane (CH), from Merck Ltd. Germany. The various solutions used here are summarized in Table I which includes the Θ temperatures of the solutions and the corresponding β parameters (see below).

The semidilute solutions ($c \approx 0.07$ g/mL) were prepared by dissolving polystyrene into Millipore-filtered solvents of analytical grade. Solutions were allowed to reach equilibrium by maintaining them at 70 °C during a period of several months, regularly revolving the sample holder. In the case of the cyclohexane solution, PS was dissolved in cyclopentane at $C = 0.5\%$, and the solution was centrifuged, followed by evaporation of the cyclopentane, and redissolution in filtered cyclohexane. The solutions were then refiltered using Millipore filters. Concentrations were determined by weight.

Thermal Polymerization. A mixture of carefully dried and vacuum distilled styrene and diethyl malonate was dosed into the stock ampule of a dust-free polymerization apparatus and degassed by several freze–thaw cycles. The apparatus was then sealed. Dust was removed from the mixture by repeated slow freezing in the ampule, followed by decantation. Finally, the cell containing the pure monomer mixture was sealed and placed in an oil bath. The thermal polymerization was carried out at 120 °C for 36 h. The conversion approached 99% and the weight average molecular weight of the polystyrene 2.3×10^5 for the sample of 0.7 g/mL.

Table I. Polystyrene ($M_w = 4.9 \times 10^6$)–Solvent Systems Investigated

Semidilute Solutions ($C \approx 0.07$ g/mL)

solvent	Θ	β at $T = \Theta$	dn/dc/(mL/g)
cyclohexane	34.8	0.36	0.171 (25 °C)
dioctyl phthalate	22.0	0.0875	0.103 (25 °C)
diethyl malonate	32.0	0.0346	0.167 (25 °C)
diethyl oxalate	65.0	0.0131	0.172 (70 °C)
diethyl phthalate/ dioctyl phthalate (0.75:0.25)		0 (25.5 °C)	

Concentrated Solutions

solvent	concn (g/mL)	β
diethyl malonate	0.7	0.0346 (32 °C) 0 (−13.4 °C)

Temperature Dependence of β for Polystyrene in Four Different Solvents ($\beta = \beta_0 + \beta_1 T$)

solvent	β_0	β_1
cyclohexane	+0.344	4.6×10^{-4}
DEM	+0.00938	7.88×10^{-4}
DOP	−0.0383	5.72×10^{-3}
DEO	−0.0161	4.5×10^{-4}

[a] Concentrations: cyclohexane, 0.064 g/mL; DEM, 0.076 g/mL; DeP, 0.0699 g/mL; DEO, 0.0714 g/mL; DEP/DOP, 0.067 g/mL.

Density Measurements were made using a Kratky digital densimeter (Model DMA02, Anton Paar AG, Graz, Austria). Densities (ρ) of solutions of a polystyrene fraction ($M_w = 1.67 \times 10^5$) in the respective solvents were measured at a series of concentrations typically over the range $c = 0.02$–0.3 g/mL. From the linear plots of ρ versus c, the values of β at each measurement concentration were calculated as $\beta = (c/\rho)(\delta\rho/\delta c)_{T,P}$. Values of β are included in Table I. It was also established using the same technique that polystyrene in a mixture of 25% DEP:75% DOP (V/V) has a value of $\beta = 0$ at $T = 25.5$ °C.

Dynamic light scattering measurements were made in an apparatus consisting of a He–Ne laser (35 mW, Spectra Physics), a goniometer with an ITT FW130 photomultiplier and ALV preamplifier, and an ALV 3000 autocorrelator operated in the multi-τ regime with 23 simultaneous sampling times. Data analysis was performed in two ways: (a) by fitting the experimental data to the sum of a Gaussian and a generalized exponential function (GEX)—see ref 13—and (b) by using the nonlinear Laplace inversion algorithm REPES as described in refs 11 and 13. This program yields the distribution of decay times in the equation

$$g_1(t) = \int_0^\infty A(\tau) \exp(-t/\tau)\,\mathrm{d}\tau \tag{9}$$

where $g_1(t)$ is the measured field correlation function.

Intensity light scattering measurements were performed with a photon-counting device supplied by Hamamatsu. The light source was a 3-mW He–Ne laser (632 nm). Benzene was used for calibration with the Rayleigh ratio for benzene $R_{90} = 8.51 \times 10^6$. Values of the refractive index increment for polystyrene in the different solvents are included in Table I. The reduced scattering intensity Kc/R_θ at angle θ was determined for the same solutions as used for the dynamic light scattering measurements. The osmotic modulus was calculated as $M_\pi = c(\delta\pi/\delta c)_{T,p} = (Kc/R_0)RTc$ where R_0 is the Rayleigh ratio extrapolated to zero angle and calibrated with benzene and K is the optical constant. Values of (Kc/R_0) were obtained by measuring the reduced total scattered intensity.

Results and Discussion

Semidilute Solutions. Figure 1 shows correlation functions for the samples listed in Table I; i.e. Θ solutions at a concentration $C \approx 0.07$ g/mL but having very different

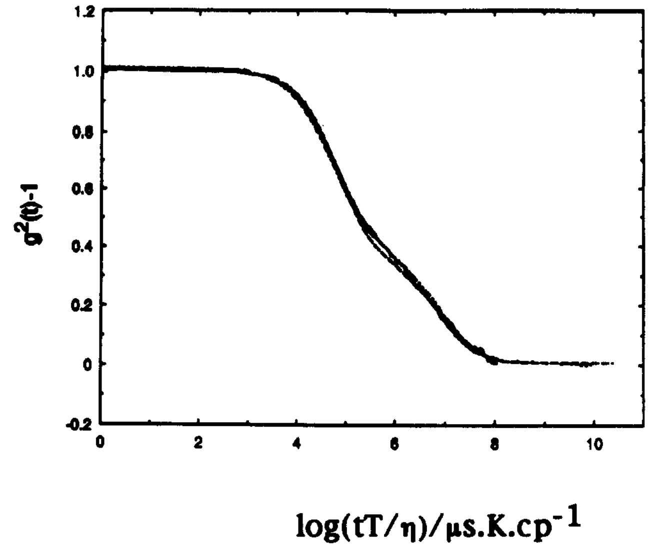

Figure 1. Normalized second order correlation functions for the polystyrene solutions listed in Table I in four different solvents at the respective Θ temperatures: dioctyl phthalate; diethyl oxalate; diethyl malonate; cyclohexane. The delay time axis has been multiplied by (T/η) to bring the correlograms into coincidence.

values of the β parameter. The data are normalized by their intercepts, and the time axis for the various curves has been multiplied by the factor (T/η) which brings the curves into coincidence, giving a single master curve. The accumulated data display the typical signature of semidilute Θ solutions: i.e. a well-defined fast component which was shown to be diffusive (q^2-dependent) and which describes the transient gel mode and a slow, much broader, part of the correlation function which is found to be q-independent.

Although the value of β varies by a factor of ≈30 between the PS/cyclohexane and the PS/diethyl oxalate (DEO) systems, the proportion of the slow and fast components is remarkably constant. The autocorrelation function and the spectrum of decay times is shown in Figure 2 for the mixed-solvent system PS/diethyl phthalate (DEP)/dioctyl phthalate (DOP) (although this a marginal rather than a Θ solvent) measured at a temperature of 25.5 °C at which $\beta = 0$. It exhibits a substantial amount of the slow component in contrast to the prediction of eq 7.

Taken together, the results lead to the conclusion that the existence and amplitude of the slow component in the correlation function for semidilute Θ solutions of polystyrene is unrelated to the value of the density parameter β.

Employing the static and dynamic light scattering results, we can quantitatively evaluate the various quantities entering eqs 7 and 8.

The osmotic modulus (M_π) of the semidilute Θ solution was determined from total intensity light scattering as a function of temperature in the different solvents. By extrapolating to $M_\pi = 0$, we can identify the temperature of spinodal decomposition of the solution. Examples are given in Figure 3 for two solvents, diethyl malonate and cyclohexane.

The fraction, A_f, corresponding to the collective diffusion component, was obtained by fitting the correlation function to Gaussian plus GEX distributions, as earlier described,[4] and also by inverse Laplace tranformation (ILT) using REPES. In both cases the value of A_f agreed to within 5%. While the Gaussian GEX fits give, by definition, a bimodal distribution of relaxation times, ILT yields a

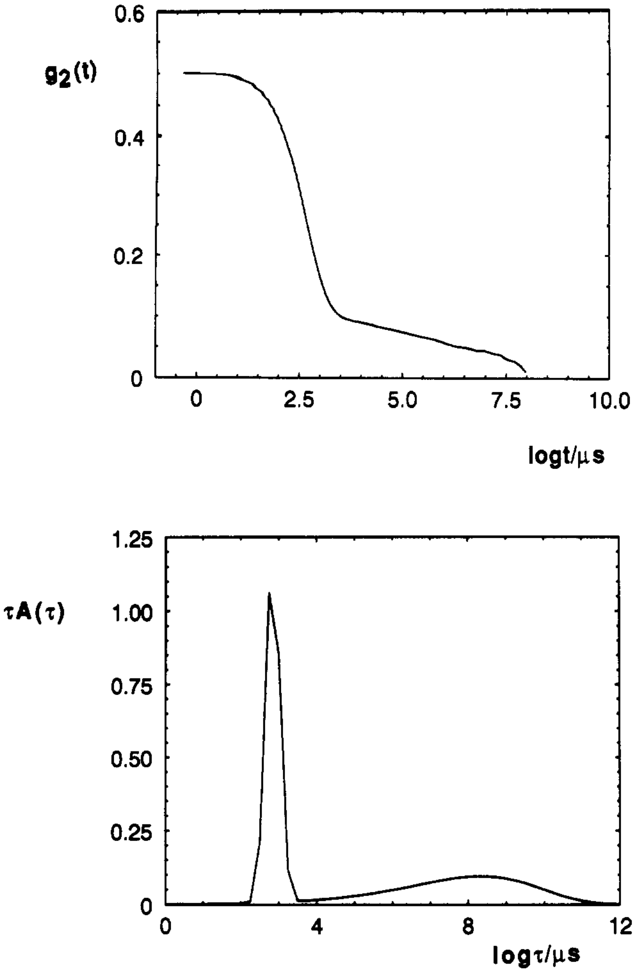

Figure 2. (a, top) Correlation function and (b, bottom) spectrum of decay times for a solution of polystyrene ($M_w = 4.9 \times 10^6$); $C = 0.067$ g/mL in the mixed solvent DEP/DOP at 25.5 °C at which $\beta = 0$. See Table I.

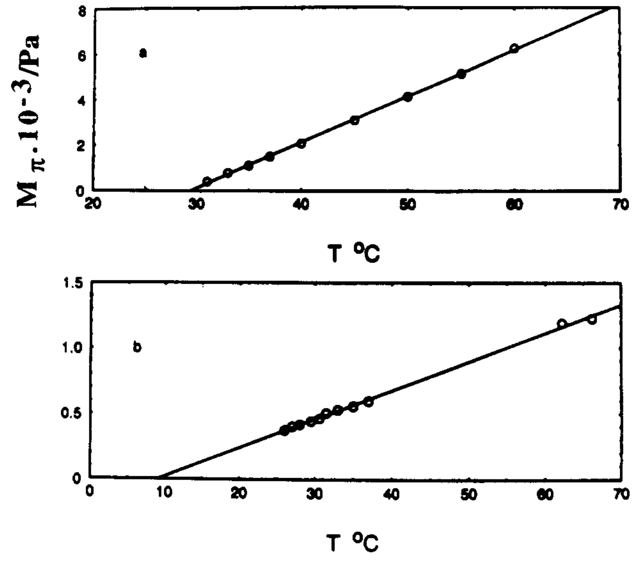

Figure 3. Osmotic modulus M_π as a function of temperature for the solutions of PS ($M = 4.9 \times 10^6$) in (a) cyclohexane and (b) diethyl malonate.

sharp D_c component plus a broad distribution of slower times, as we have described in detail in earlier communciations (see, for example, refs 13, 18, and 21).

The temperature dependence of A_f is displayed in Figure 4 for the studied systems. As anticipated, A_f increases with increasing temperature. The temperature depen-

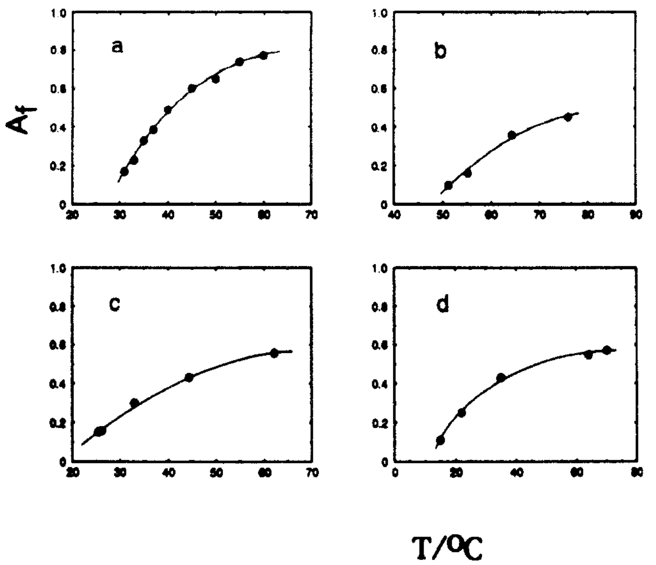

Figure 4. Temperature dependence of A_f (the fraction of the mode corresponding to the collective diffusion coefficient) for the solutions of PS in (a) cyclohexane, (b) diethyl oxalate, (c) diethyl malonate, and (d) dioctyl phthalate.

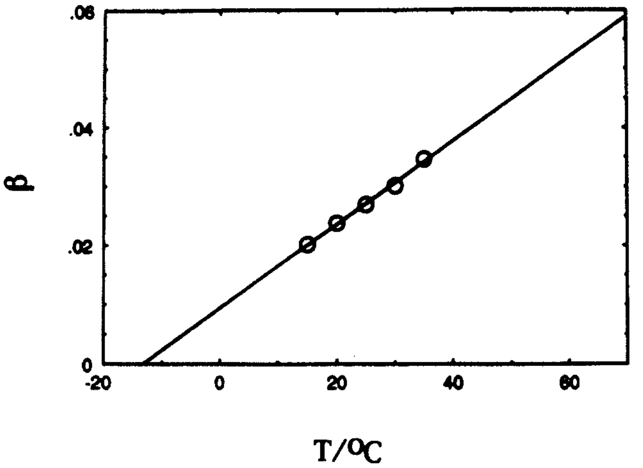

Figure 5. Temperature dependence of the density parameter β for the system PS/diethyl malonate.

dence of the β parameter was determined over the same temperature range encompassed by the DLS measurements. Figure 5 shows β as a function of temperature for the system polystyrene/diethyl malonate. β was found to be approximately a linear function of temperature: $\beta = \beta_0 + \beta_1 T$. Value of β_0 and β_1 are given in Table I for the various solvent systems used.

Using values for M_π, A_f, and β, it is possible to calculate the amplitude of the longitudinal modulus M_0 from eq 7. Values of M_0 obtained in this way are shown in Figure 6. Since M_0 has the character of a mechanical modulus, it should not vary much with temperature; however, we observe in Figure 6 a strong temperature dependence of M_0 in the different systems (note the logarithmic vertical axis), particularly in the vicinity of the Θ temperature. The high temperature value of M_0 (i.e. the part not influenced by the Θ temperature) lies in the range 0.04–1 MPa for the various systems and temperatures.

M_0 is given by the usual equation:

$$M_0 = K_0 + (4/3)G_0 \tag{10}$$

where, according to ref 5, G_0 is the shear modulus and K_0 the compressional modulus of the whole solution. Since the solvent DOP is viscous and has a very low vapor pressure, its solutions of PS are suitable for dynamic mechanical measurements; we have earlier reported measurements of G' and G'' as a function of concentration and temperature in this system.[4b] We have now extracted from these measurements the plateau modulus $G_N{}^0$, which is the quantity entering eq 10 above. Values of $G_N{}^0$ are shown in Figure 7. These results are in good agreement with the values obtained from the theoretical relationship of Ferry[19] and de Gennes:[20]

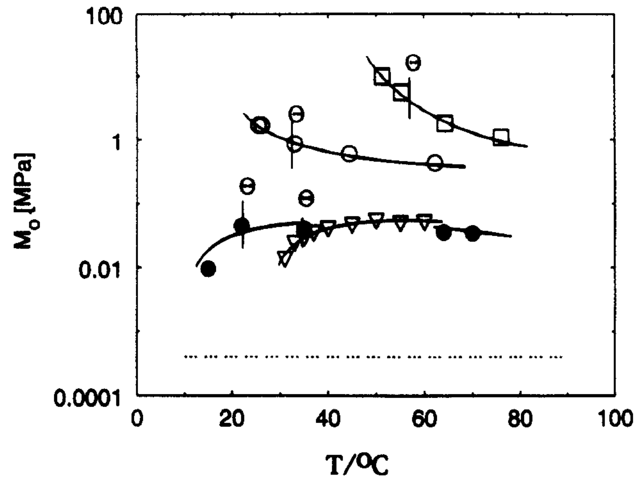

Figure 6. Temperature dependence of the longitudinal modulus M_0 calculated using eq 7 for polystyrene in diethyl oxalate (□), diethyl malonate (○), dioctyl phthalate (●), and cyclohexane (▽). The horizontal line denotes the value $G_N{}^0$ = 400 Pa for the shear modulus of a 0.07 g/mL solution of PS in DOP at 22 °C.

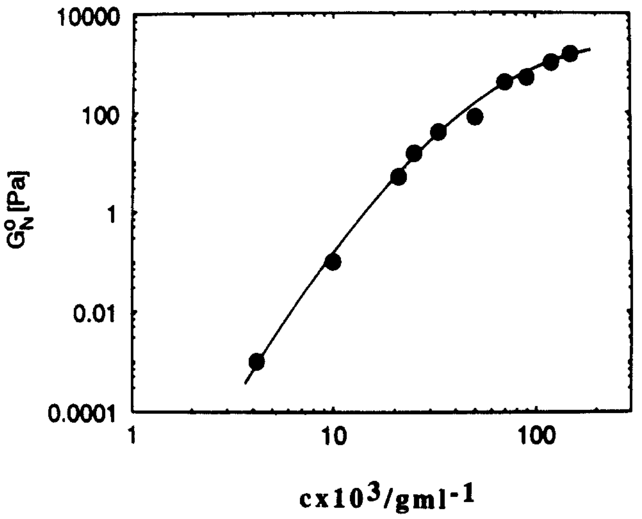

Figure 7. Dependence of the plateau shear modulus $G_N{}^0$ on concentration for the system ($M_w = 4.9 \times 10^6$) in DOP at the Θ temperature 22 °C. The line is a guide to the eye.

$$G_N{}^0 = G_N{}^{00}\Phi^x \tag{11}$$

in which Φ is the polymer volume fraction and $x = 2$ in the classical treatment of Ferry ($x = 2.25$ in de Gennes' scaling theory) together with the literature value of $G_N{}^{00}$ for polystyrene: $G_N{}^{00} = 2 \times 10^5$ Pa.[19] From Figure 7 we determine a value of $G_N{}^0 \approx 400$ Pa for the plateau modulus of a solution of the same concentration (0.07 g/mL) and molecular weight as used in this work.

Concerning the quantity K_0, in eq 10, which was introduced in ref 16 as the compressional modulus of the polymer solution, we note, firstly, that for a 0.07 g/mL solution the static compressional modulus will approximately equal that of the pure solvent, i.e., will be of the order 10^{11} Pa. The frequency range of interest in DLS is ca. 1 Hz to 1 MHz. To our knowledge, the frequency dependence of K_0 has not been measured for polymer solutions; however, in ref 16 it was shown that the compliance $B'(\omega)$ for poly(vinyl acetate) at 50 °C does not vary by more than a factor of 2 over the frequency range of interest (1 Hz to 1 MHz). Taken together, these data indicate that M_0 as defined by eq 10 is about 5 orders of magnitude larger than M_0 as measured using static and dynamic LS and employed in the theoretical work in refs 5–7. If, contrary to ref 5, the solvent contribution is not included in K_0 in eq 10, then K_0 should in fact be replaced by the osmotic modulus which is of the order 10^2–10^3 Pa. In this case we should obtain a value of M_0 of the order 10^2–10^3 Pa (since $G_N{}^\circ \approx 400$ Pa) which is then 2–3 orders of magnitude smaller than the measured M_0. The theoretical value is shown as the dotted line in Figure 6, employing the value $G_N{}^\circ = 400$ for polystyrene.

In conclusion, for the semidilute solutions, we have used four experimentally-determined quantities, A, β, M_0, and M_π, to test the validity of eq 7 above. We find a discrepancy of several orders of magnitude between the measured and calculated values of M_0 and $G_N{}^\circ$.

Taken together with the fact that our results do not correlate with the value of β, we are forced to the conclusion that the assumptions used in refs 5–7 to describe the coupling between the concentration and viscoelastic fluctuations by means of the β parameter are unrealistic.

Concentrated Solutions. In a concentrated binary solution, concentration, density, and optical anisotropy fluctuations due to segmental motions contribute to the polarized (VV) correlation function while only the reorientational fluctuations are observed in the depolarized (VH) DLS experiment. Depending on the nature of the solvent, contributions from both polymer and solvent may be observable in the DLS time window. In the bulk polymer, the isotropic scattering is due to density fluctuations and the relaxational spectrum is known to be very similar to that associated with reorientational fluctuations due to the strong coupling between the two processes.

It was argued in ref 7a, however, that when the polymer concentration is increased to a point such that a further increase does not significantly change the solution density, β becomes small. The power spectrum is then postulated to become similar to that for the bulk polymer (density fluctuations) because it was assumed that the concentration fluctuations do not contribute significantly. Since, however, β increases with concentration and will probably not be negligible at high concentration, we seek the situation where $\beta \approx 0$ in order to test the validity of the postulate that the concentration fluctuations are not coupled when $\beta = 0$.

Figure 8a shows the correlation functions in the VH and VV geometries for a solution of PS in diethyl malonate at a concentration of 0.7 g/mL and $T = -13.4$ °C at which temperature β is zero; since Figure 5. However, the VV correlation function differs considerably from that in the VH and this difference must be almost entirely due to contributions from concentration fluctuations in agreement with observed DLS results recently obtained for other concentrated systems and bulk polystyrene.[32] The characteristic average relaxation time for the VV scattering is much longer than that for the VH scattering: $(\log \tau/\mu\text{s})_{\text{VV}} = 4.3$ compared to $(\log \tau/\mu\text{s})_{\text{VH}} = 3.11$. Furthermore, as would be expected if there are contributions from concentration fluctuations, the Kohlrausch–Williams–Watts (KWW) exponents obtained by fits to the functions in Figure 8a differ: 0.6 (VV) and 0.27 (VH), respectively. This finding thus supports a significant contribution from concentration fluctuations in the VV geometry.

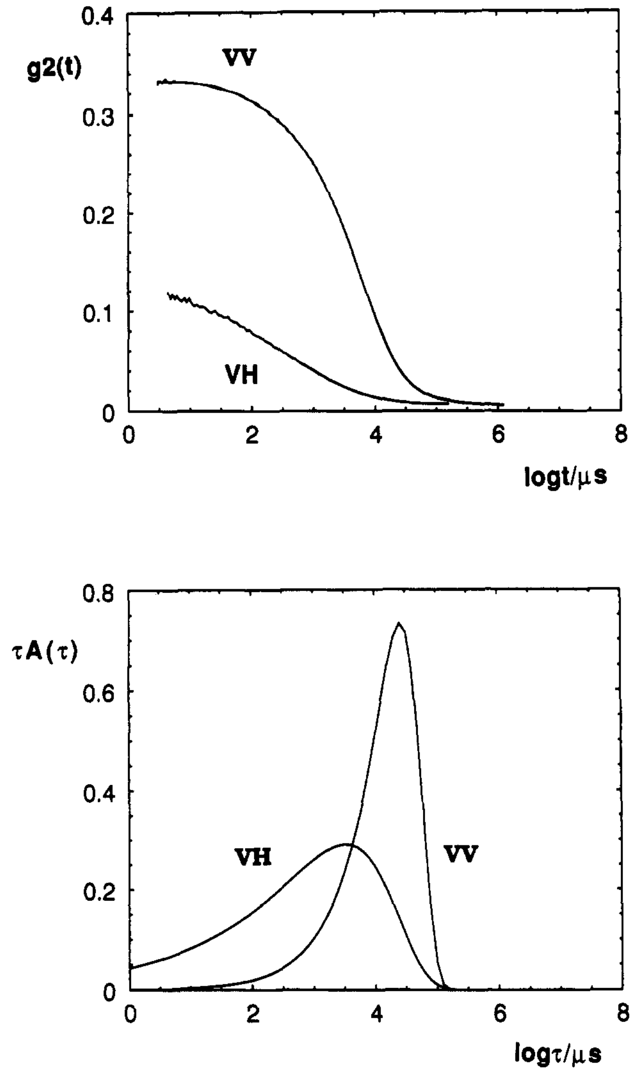

Figure 8. (a, top) Correlation function and (b, bottom) relaxation time spectra for a solution of polystyrene (average $M_w = 2.35 \times 10^5$) thermally polymerized in diethyl malonate. $C = 0.7$ g/mL and temperature $T = -13.4$ °C at which $\beta = 0$.

Relaxation time spectra obtained by inverse Laplace transformation using the inversion routine REPES (see refs 11 and 13) are shown in Figure 8b and show the substantial differences between the VV and VH modes, both as regard relaxation times and widths of distribution.

Thus, even when $\beta = 0$, the two correlograms are quite different owing to a substantial contribution from concentration fluctuations in the VV geometry, and we are led to the conclusion that, also in the case of highly concentrated solutions, the dynamic structure factor has a more complex structure in the highly concentrated range than proposed by Wang.

(We note here, however, that the q dependence of the relaxation rate exhibits complicated crossover behavior which is the subject of recent work.[31,32] In the present system, the polarized measurements at a series of angles over the range 60–140° give correlation functions which are almost superimposable and thus almost q-independent. This is the case when the relaxation rate of the concentration fluctuations approaches that of the reorientational fluctuations. This behavior has been predicted by Jäckle and Frisch[22,23] and was recently demonstrated with data in the PS/toluene system[31] and in the PS/DOP system.[32])

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