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Dynamic Behavior in Concentrated Polystyrene/Cyclohexane Solutions Close to the Θ-Point. Relaxation Time Distributions as a Function of Concentration and Temperature

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ABSTRACT: Dynamic light scattering measurements are reported on concentrated solutions ($C < 0.8$ g/mL) of polystyrene ($M_w = 9.3 \times 10^5$) in cyclohexane over a range of temperature 30–70 °C. At the Θ-temperature, between concentrations of 0.65 and 0.7 g/mL, the relaxation time distribution changes from one typical of semidilute solutions (diffusive mode plus structural relaxation) to one typical of density fluctuations (single, q-independent mode). At 0.7 g/mL, the relaxation rate is q^2-dependent above 58 °C and q-independent below 41 °C. The strong temperature dependence of the density fluctuations is non-Arrhenius close to the T_g at $C = 0.7$ g/mL (281K) and has some characteristics of an α-process. The shape of the relaxational component is narrower than usually observed in polymer melts and glass-forming liquids. Between 41 and 58 °C the behavior is that of a mixed mode; there appears to be a strong coupling of the density to the concentration flucuations as predicted by Jäckle, Pieroth, and Wang. At 0.8 g/mL the relaxation rate is q-independent over the temperature range 35–70 °C.

Introduction

Recent reports from this laboratory have described dynamic light scattering results and Rayleigh–Brillouin experiments on concentrated polymer solutions.[1-4] Of these, the first dealt with preliminary measurements on polystyrene (PS) in cyclohexane at and above the Θ-temperature of 34.5 °C.[1] It was observed that up to a concentration of ~0.65 g/mL the spectrum of relaxation times resembles that seen in semidilute Θ-systems: i.e., it is made up of a sharp q^2-dependent (diffusive) peak (q is the scattering vector) and a broad range of slower q-independent decay times (structural relaxations). The latter have been shown[5] to derive from viscoelastic relaxation characterized by a broad distribution of relaxation times. Wang[6] has recently demonstrated using linear viscoelastic theory how the viscoelastic modes contribute to the dynamic light scattering spectrum.

The cooperative diffusion coefficient describing the relaxation of the transient network of strongly overlapped coils[7] is found to pass through a pronounced maximum in the vicinity of 0.5 g/mL. At 0.70 g/mL there is a dramatic change in the relaxational spectrum: the main mode is now slower by approximately two decades and has become q-independent. It was concluded that this behavior reflects density fluctuations in the vicinity of the glass transition ($T_g \approx 281$ K at this concentration[1]). Several features are worthy of comment: (a) the transitional behavior occurs over narrow ranges of concentration and temperature; (b) the q-independent structural relaxation maintains a relatively narrow and well-defined profile over the whole range of temperature. This is remarkable since density fluctuations characterizing relaxations in amorphous polymers are typically very broad, extending over several decades on the time scale (see, for example, refs 8 and 9), which suggests significant differences in dynamical behavior for polymers in the presence of a solvent as opposed to melts. The presence of both concentration and density fluctuations in the DLS time window that was noted for the PS/toluene system[2] was not noted in the present system. These observations prompt a more complete study focused on the upper concentration range. This paper is directed to elucidation of this behavior.

Experimental Section

Polystyrene (PS, Pressure Chemicals, Philadelphia) solutions were prepared by very slow evaporation of a 2% stock solution in cyclohexane (analytical grade; Fluka), the cells sealed and left to equilibrate at 60 °C for several months.

Dynamic light scattering measurements were made, mostly in the V–V geometry, using the apparatus and technique described earlier.[5] The laser was a 35-mW He–Ne (633 nm) Spectra Physics model. An ALV-Langen, multibit, multi-τ autocorrelator was operated with 23 simultaneous sampling times covering approximately nine decades in delay time. Two different methods were used to obtain the distribution of relaxation times from the measured autocorrelation functions:

(i) Inverse Laplace transformation (ILT) (where $g_1(t) = \int_0^\infty A(\tau) \exp(-t/\tau)\, d\tau$ and $A(\tau)$ is the distribution function of decay times τ) was performed using a constrained regularization algorithm denoted REPES,[10] which is similar in many respects to the inversion routine CONTIN.[11] However, REPES directly minimizes the sum of the squared differences between the experimental and calculated $g_2(t)$ functions and uses an equidistant logarithmic grid of fixed components (here a grid of 12 per decade) and determines their amplitudes.

(ii) The correlation functions were also fitted to the sum of two distributions; see, for example, Figure 1A. One is Gaussian in log τ and represents the fast peak:

$$\omega_1(\tau) = \pi^{-1/2}(\tau\sigma)^{-1} \exp[-(\log(\tau/\tau_f)/\sigma)^2] \qquad (1)$$

The other is the so-called generalized exponential (GEX) distribution representing the total of all slow components:

$$\omega_2(\tau) = |s|\tau^{p-1}\tau_0^{-p} \exp[-(\tau/\tau_0)^s]/\Gamma(p/s) \qquad (2)$$

With s and p negative, the distribution is of the Pearson type, τ_f and τ_0 are relaxation times which position $\omega_1(\tau)$ and $\omega_2(\tau)$ on the log (time) axis, σ characterizes the width of the Gaussian, and the parameters s and p determine the shape of the GEX distribution. With regard to the relaxation time distributions in Figures 1–3 it is pointed out that closely similar peak shapes and positions are obtained using REPES with high smoothing (probability to reject 0.99) and the GEX distribution.

Results and Discussion

Polarized dynamic light scattering measurements (I_{VV}) have been made in the homodyne mode to characterize the dynamical behavior in concentrated polystyrene

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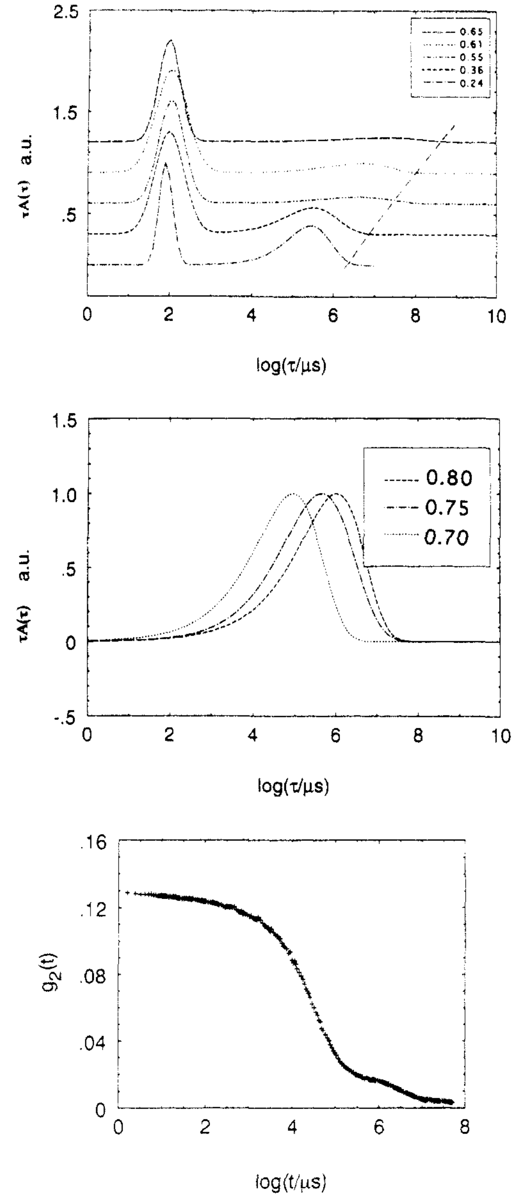

Figure 1. (A, top) Relaxation time distributions (Gaussian + generalized exponential distribution; see Experimental Section) in the polystyrene/cyclohexane system at the concentrations shown (g/mL) at 35 °C. $\tau A(\tau)$ is plotted versus log τ in an equal-area representation. The q^2-dependent peak at short times characterizes the gel mode and the broader peak (q-independent) the viscoelastic modes.[10] The dashed line is a guide to the eye denoting the slowest relaxational time. (B, middle) Data for the high concentrations under same conditions as (A). The peak positions are angle-independent. (C, bottom) Correlation curve for C = 0.70 g/mL (Θ = 140°); 35 °C.

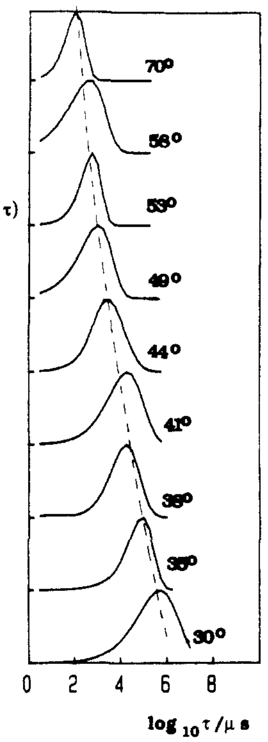

Figure 2. Relaxation time distributions for C = 0.7 g/mL at different temperatures, determined at angle 140°. The dotted line is a guide to the eye.

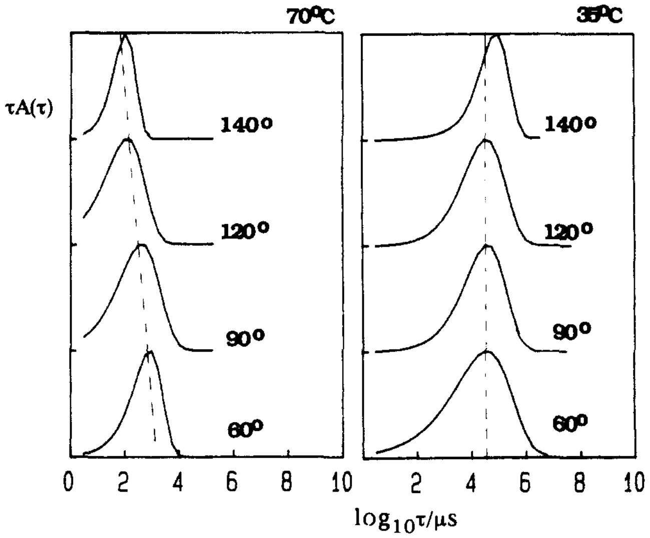

Figure 3. Angular dependence of distributions at (a) 70 and (b) 35 °C for PS in cyclohexane at 0.7 g/mL. At 70 °C the relaxation rate is q^2-dependent and at 35 °C q-independent.

solutions in cyclohexane as a function of temperature. The data in Figure 1A show the concentration dependence of $A(\tau)$ extending up to C = 0.65 g/mL. Surprisingly, these distributions obtained by fitting to the sum of Gaussian + GEX distributions, as described in the Experimental Section and ref 5, show the same features up to a concentration as high as 0.65 g/mL as previously seen for semidilute Θ-solutions.[12] Thus, at short times there is a narrow, q^2-dependent mode, with a relaxation time independent of molecular weight and a slow, broad peak which is q-independent and strongly dependent on the molecular weight. The former derives from the relaxation of the transient network and is well-described by theory.[7] As was demonstrated in the earlier report,[1] the relaxation rate of this gel mode passes through a maximum in the vicinity of 0.5 g/mL. By contrast, the broad peak characterizing viscoelastic modes[5] becomes much slower as the concentration is increased (the approximate position of the slowest relaxation time has been indicated by the diagonal dashed line) and broadens considerably. It also decreases in its relative amplitude.

In a narrow concentration interval between 0.65 and 0.70 g/mL, an abrupt change occurs in the dynamics of the solutions. Figure 1B illustrates the distributions found for concentrations of 0.7–0.8 g/mL. These are single-peaked, somewhat asymmetric, and q-independent: they differ substantially from the distributions at C = 0.65 g/mL and lower. Although a Gaussian component was submitted together with the GEX in the analysis of the data leading to Figure 1B, the amplitude of the Gaussian component became essentially equal to zero in the fitting. The peaks in Figure 1B depend more strongly on concentration than those for the gel mode in Figure 1A. Figure 2 shows relaxation time distributions for the sample of 0.7 g/mL at an angle of 140° as a function of temperature (a

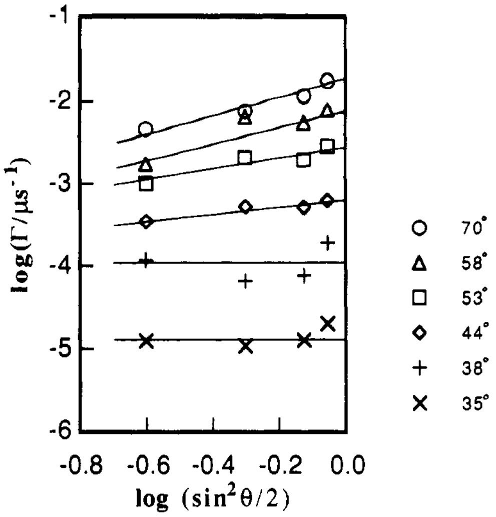

Figure 4. Logarithmic plot of relaxation rate (Γ) versus q^2 (inverse Laplace transformation) for C = 0.7 g/mL at different temperatures: (a) 58 and 70 °C, q^2-dependent; (b) 35 and 38 °C, q-independent; (c) 44 and 53 °C, intermediate q-dependence.

similar pattern is noted at the other angles). The distributions are single-peaked and comparatively narrow; the position on the time axis is strongly dependent on temperature. As pointed out in the previous report,[1] the relaxation time of the main component is q^2-dependent at the higher temperatures and q-independent at the lower temperatures. This is demonstrated in Figure 3, which compares data at this concentration at 70 and 35 °C. Similar behavior was observed in the PS/toluene system.[2]

Figure 4 shows a log–log plot of relaxation rate versus q^2 for the sample at C = 0.7 g/mL, where these data are taken from the ILT analyses using REPES. The data display some scatter, which results from the low total scattering intensity (amounting to a few thousand photons per second); the correlation functions are noisy even after several hours of data accumulation. A pronounced slowing of the characteristic decay time of the major component is observed as the temperature is lowered.

Prior to an analysis of the temperature dependence, the angular dependence of the decay rate will be considered. Within experimental uncertainty, it is found that the data at 58 and 70 °C are q^2-dependent (i.e., diffusive) while at 30–41 °C the relaxation rate is q-independent (structural relaxation). Data at 44 and 53 °C exhibit an intermediate q-dependence; i.e., they display the characteristics of a mixed mode. The change in the angular dependence of the decay rate thus occurs over a narrow temperature range. Moreover, the total scattering intensity is approximately independent of temperature over the studied range. Correlation functions were also measured on the 0.7 g/mL solution in the V–H geometry at 35, 50, and 70 °C. These curves followed a pattern similar to those determined in the V–V geometry at 35 and 50 °C, in accord with earlier observations of Wang et al.[13] that there is a strong coupling in viscous systems between the correlation functions measured in V–V and V–H modes (i.e., there is a strong coupling between translational and rotational degrees of freedom) and that they exhibit a similar time dependence. At 70 °C the diffusive relaxation is not detected in the V–H geometry. The relaxation time distributions corresponding to the V–V and V–H functions at 35 °C are shown in Figure 5 and emphasize the close similarity of the data sets in respect to both position and peak width.

It is difficult to imagine a situation where a given dynamic process changes in character from diffusional to relaxational and vice versa with change in temperature. Two possible explanations are as follows:

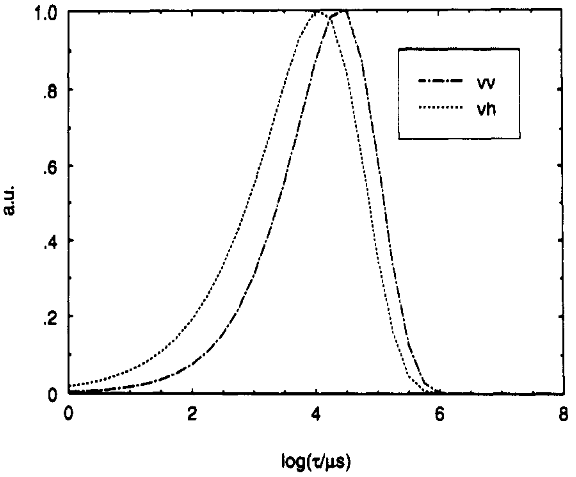

Figure 5. Relaxation time distributions for the 0.70 g/mL solution obtained from correlation functions measured in V–V and V–H geometries at 35 °C.

(a) There is an overlap of two dynamical processes, as was earlier observed in the PS/toluene system:[2] one fast and diffusive the other slow and relaxational. The ratio of their amplitudes varies in such a way that only the diffusive component is seen at high temperature and only the relaxational component at low temperature. In this case, a range of temperatures might be anticipated (here in the vicinity of 50 °C) where both modes have comparable amplitudes and thus should be visible simultaneously. It appears, however, that the relaxational times are so close that they cannot be resolved. Several data analysis techniques were used but we were unable to resolve a meaningful doublet in the region of interest.

(b) In the temperature interval 40–55 °C the characteristic relaxation times of the processes are so close to each other that there may be a strong coupling of the concentration fluctuations to the density fluctuations. This situation is unusual, however, since it is usually assumed that density and concentration fluctuations will not be correlated because concentration fluctuations are considered to have a time scale which is much slower than the decay times of the density fluctuations. However, behavior strikingly similar to that of PS in cyclohexane was found for the polystyrene/toluene[2] system at high polymer concentrations close to T_g. Coupling phenomena in concentrated systems have been predicted theoretically. Thus, Jäckle and Pieroth[14] have derived the spectrum of thermal fluctuations of density and concentration in binary liquid mixtures and shown that the spectrum is made up of contributions of density, concentration, and density–concentration fluctuations. For a system close to its glass transition temperature, T_g, they considered the underlying coupling between the slow structural relaxation of the polymer matrix and the fast diffusion of small molecules (e.g., a low molecular weight solvent). That such a coupling does occur was recently shown by Gapinski et al.[15] in measurements on a PMMA/toluene glass (some 50 °C below T_g), where the diffusive motions of the toluene can be observed owing to coupling with the slow structural relaxation of the polymeric matrix.

Recently, Wang[6], using hydrodynamic theory, gave a discussion of the conditions under which coupling of concentration to density fluctuations may occur in polymer solutions, although he did not specifically discuss the "resonance" situation. The degree of coupling is shown to depend on a parameter β, which is proportional to the difference between the partial specific volumes of polymer and the low molecular weight solvent. Since β is very

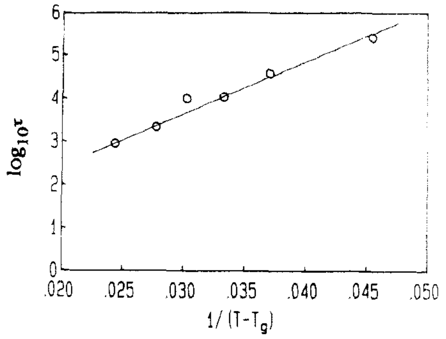

Figure 6. Plot according to eq 3 with $T_o = T_g$ (the glass transition temperature).

dependent on concentration, strong coupling is anticipated at high polymer concentrations in most polymer/solvent mixtures.

Of the different relaxation processes which may occur in concentrated polymer solutions, the α-relaxation is a localized main-chain motion involving short segments composed of several monomer units and is thus independent of the total chain length. For an α-relaxation it is well-established that the average relaxation time $\langle\tau\rangle$, which changes strongly with temperature near T_g, is well-described by the Vogel-Fulcher-Tammann equation:

$$\langle\tau\rangle = \tau_0 \exp[B/(T - T_o)] \tag{3}$$

where B is an effective activation parameter. T_0 may be close to or equal to T_g and is the ideal glass transition temperature at which the relaxation time diverges to infinity. It can be used to describe $\langle\tau\rangle$ over a broad range of relaxation times: 10^{-10}–10^2 s. According to eq 3, the dynamics of the α-relaxation depend on the distance to the reference temperature T_0. Figure 6 shows the dependence of the logarithm of the experimentally determined average relaxation time (the moment of the dominant peak in Figure 3) for temperatures below 50 °C as a function of $(T - T_g)^{-1}$. Here T_0 has been approximated by T_g since the value of T_0 is not known and the scatter of the data over this very limited range of relaxation time does not allow us to use T_0 as a freely adjustable parameter in the fitting procedure. With this approximation, it is seen in Figure 6 that the data are compatible with a linear relationship. $B = 217$ K and $\log \tau_0 = -3.4$. These values are of an order similar to those for the poly(cyclohexyl methacrylate)/dioctyl phthalate (DOP) system studied in ref 16 when extrapolated to a solvent content of 30%. Replacing T_0 by $T_g \pm 15$ °C leads to a curved diagram. The observation that T_0 is relatively close to T_g suggests that the main relaxation time becomes infinite at T_g. This should be compared with the generally reported value of T_0 of some tens of degrees below T_g, indicating the existence of a supercooled state (at the lower end of which the relaxation time becomes infinite). We thus conclude that the relaxational process observed in this system corresponds to the primary glass–rubber transition or α-process.

Another structural relaxation which may be observed in some dense polymer systems using DLS is the secondary or β-relaxation. From dielectric relaxation and dynamic-mechanical measurements, it is known that the β-relaxation correspond to local rearrangements involving side groups to the main chain. However, the characteristic time of such processes now follows an Arrhenius temperature dependence:

$$\langle\tau\rangle = \tau_0 \exp(E/RT) \tag{4}$$

and is thus independent of the value of T_g. When the present data are replotted according to eq 4, the result is a totally curved diagram showing that the data are incompatible with a β-relaxation.

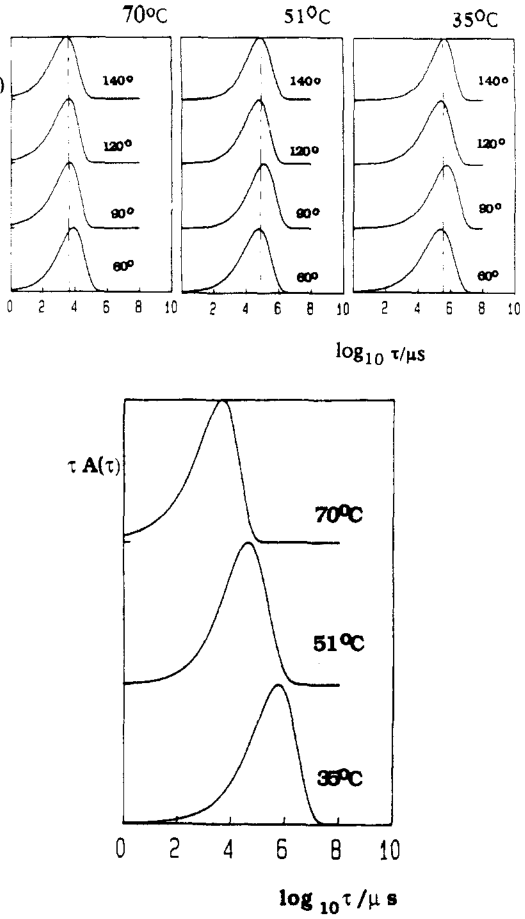

Figure 7. (A, top) Relaxation time distributions for $C = 0.8$ g/mL at different angles and the three temperatures shown. The peak positions are approximately q-independent over the temperature range studied. (B, bottom) Relaxation time distributions ($\Theta = 90°$) at three temperatures for $C = 0.8$ g/mL.

The shape of the relaxational component is narrower (Figure 2) than that usually observed in melts of polymers and glass-forming liquids,[8,9] where a breadth of at least three decades is reported for the main peak. Behavior similar to the present was also noted for the PS/toluene system. It results appear to show that the solvent may localize the dissipation and enhance a particular dynamic mode in the system. Data at concentrations of 0.75 and 0.8 g/mL show qualitatively different behavior compared with those at 0.7 g/mL. At the two former concentrations the observed relaxation is q-independent over the temperature range 35–70 °C; examples are given in Figure 7.

It is recalled that, in the PS/toluene system[2] at a concentration of $\Phi_p = 0.89$ and 25 °C, two modes could be separated: these are respectively q^2-dependent (concentration fluctuations) and q-independent (density fluctuations) relaxations and both may be simultaneously observed in the DLS time window at this concentration. This may also apply in the present system, but these modes are not resolved. Diffusive and relaxational decays were also observed in the poly(cyclohexyl methacrylate)/DOP system studied by Fytas et al.,[16] although in their case, the diffusive process was much slower than the α-relaxation.

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Registry No. Polystyrene, 9003-53-6; cyclohexane, 110-82-7.