(5) Patt, S. L.; Shoolery, J. N. *J. Magn. Reson.* **1982**, *46*, 535.

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Dynamical Properties of High Molecular Weight Polystyrene in Cyclopentane at the Θ Temperature

This communication is prompted by an apparent inconsistency between recently reported results[1-3] for the dynamical behavior of polystyrene (PS) in semidilute Θ solutions. Such systems have been treated theoretically by Brochard and de Gennes.[4,5] Hecht et al.[1] reported the relationship

$$D \sim C^{0.94\pm0.08}$$

where the quasi-elastic light scattering (QELS) measurements were made on a PS of $\bar{M}_w = 2.6 \times 10^7$ ($\bar{M}_w/\bar{M}_n = 1.30$) dissolved in cyclohexane at 34 °C. D was evaluated by using a two-parameter cumulant fit. It was inferred that the time scale of the measurements corresponded to that at which the semidilute solution behaves as a viscous fluid (i.e., $\Gamma T_R < 1$, where Γ is the relaxation rate and T_R is the lifetime of the interchain entanglements characterizing the transient network.[4,5] Adam and Delsanti[2] have also described measurements on the same system on a similar time scale but for samples of much lower molecular weight ($M < 10^6$). They found that D (evaluated by using a single-exponential fit to the QELS data) increased linearly with increasing concentration:

$$D_c\ (\mathrm{cm^2\ s^{-1}}) = 1.25 \times 10^{-6} C^1$$

In addition, Adam and Delsanti analyzed the structure factor for higher molecular weight samples in terms of a bimodal model, on a time scale at which the solution behaves as a gel. At the shortest times, a q^2-dependent relaxation (termed the gel diffusion coefficient) was separated, and this quantity was also found to be linearly dependent on concentration. At the longest times, a q-independent structural relaxation was obtained.

Subsequently, Brown[3] analyzed the dynamic structure factor obtained in semidilute Θ solutions of high molecular weight PS ($\bar{M}_w = 8 \times 10^6$ and 15×10^6) in cyclopentane at 21 °C. On short time scales (gel regime), a bimodal model with a floating base line was used to describe the data, and two q^2-dependent modes were resolved. The fast component was observed to be concentration independent at modest semidilute concentrations up to 15C^* (using $C^* = 3M/4\pi R_g^3 N_A$, a finding that agrees with the theoretical prediction of Brochard.[5] However, the slow component was noted to *decrease* with increasing concentration, in conflict with the results described in ref 1 and 2. This unsatisfactory situation stimulated us to further examine the PS/cyclopentane system using the same sample ($\bar{M}_w = 15 \times 10^6$) but extending the measurements over a much wider range of concentration and a broad span of angles.

The experimental details and the data analysis are as described previously.[3] Great care was taken to ensure solution homogeneity. These were prepared by concentrating optically clear solutions in a dust-free atmosphere by very slow evaporation. The 10-mm NMR tubes were then flame-sealed at −15 °C and placed in an oven at 50 °C for 6 months to achieve homogeneity; the data shown in Figure 1A were obtained by using a three-cumulants fit.

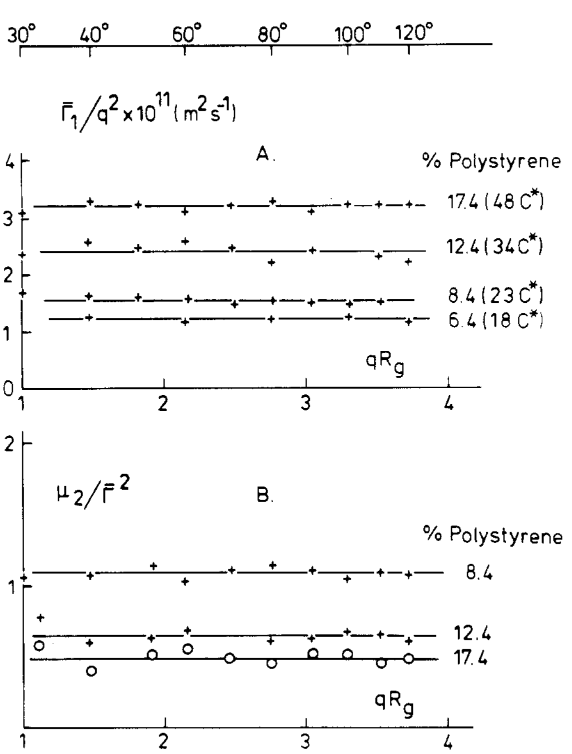

Figure 1. (A) Initial decay rate (Γ_1/q^2) as a function of qR_g for polystyrene ($\bar{M}_w = 15 \times 10^6$) in cyclopentane at the Θ temperature (21 °C) at a series of concentrations in the semidilute regime. C^* is defined as $C^* = 3M/4\pi R_g^3 N_A$. (B) Values of the normalized second cumulant, $\mu_2/\bar{\Gamma}^2$, corresponding to the data in (A).

Over the angular range 30–120° the first cumulant (Γ_1/q^2) is independent of q. This is the behavior anticipated in the semidilute region with parameters corresponding to the hydrodynamic regime (i.e., macroscopic displacements in the range $q\xi < 1$, where ξ is the dynamic correlation length). In poor solvents, where the radius of gyration, R_g, is small, the crossover to q^3 behavior will be accessible only at very much lower concentrations at high angles.

Figure 1B shows the normalized second cumulant as a function of qR_g at a series of concentrations. This parameter is large but decreases with increasing concentration at a given angle. The probable root of this behavior is the increasing dominance of the gel mode at the expense of translational motions at the higher concentrations.

Figure 2 presents the results of a discrete multiexponential analysis in terms of two frequency components. The slopes yield the following: curve A, $D_g = (\Gamma_g/q^2)$; curve B, $D_s = (\Gamma_s/q^2)$; curve C, $\bar{D}_{cum} = (\Gamma_1/q^2)$. These data suggest that both fast and slow components may be diffusive in character, although the slower mode has a proportionally greater uncertainty, the error bars denoting the 95% confidence interval. We note that this interpretation differs from that of Adam and Delsanti,[2] who resolved their data into q^2-dependent and q-independent quantities, depending on the sampling time.

Figure 3 shows the concentration dependence of the two diffusion coefficients. Each point of this diagram was obtained as the slope of a plot over the angular range 30–120° as shown in Figure 2. The curve for the gel mode (curve A) at the higher concentrations corresponds to $D_g \sim C^1$. A similar result is found for the cumulant-evaluated data (curve B). However, $\Gamma T_R < 1$ will, in general, only be realized with modest molecular weights ($M < 10^6$), as emphasized in ref 2. With higher M and usual measurement parameters, the quantity $\bar{D}_{cum}$ will inevitably be a mixture of contributions from different relaxational modes and will be difficult to interpret. The exponent of unity

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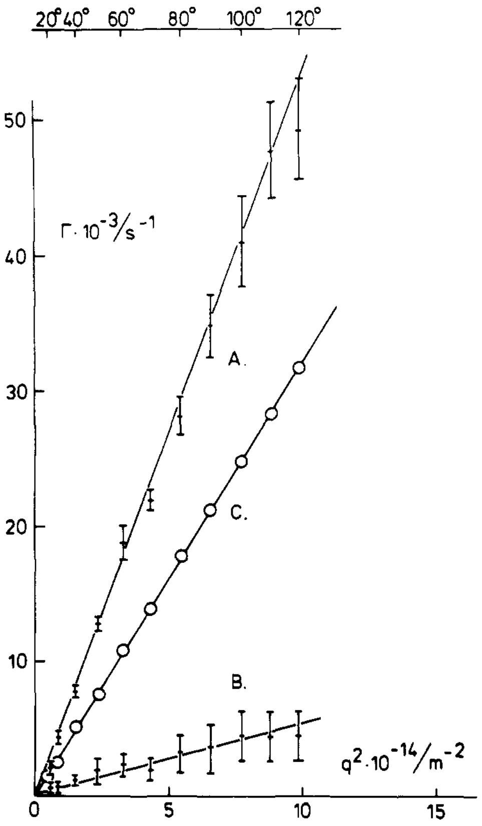

Figure 2. Relaxation rate, Γ, plotted as a function of the square of the scattering vector (q^2). Curves A and B are data for the gel and slow modes obtained with a bimodal fit as described in ref 3. Curve C is data obtained with a cumulant fit and corresponds to a weighted average of the modes (curves A and B). (The diffusion coefficients shown in Figure 3 have been obtained from such plots by taking the best average slope.) Data are for a molecular weight of $\bar{M}_w = 15 \times 10^6$ at $C = 17.4\%$ (w/w). Error bars are the 95% confidence intervals.

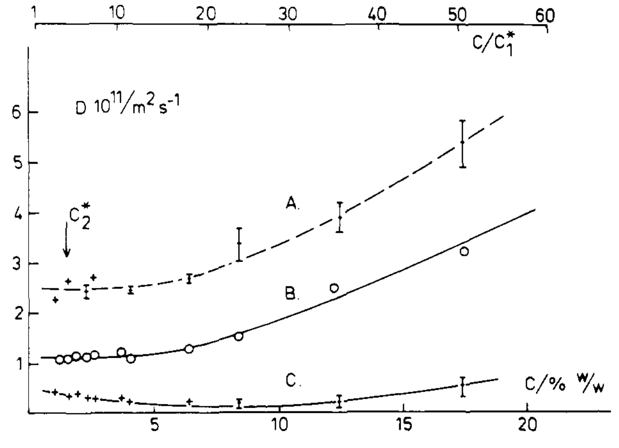

Figure 3. Diffusion coefficients for polystyrene ($\bar{M}_w = 15 \times 10^6$) in cyclopentane at 21 °C (Θ conditions). The gel mode (curve A) and the slow mode (curve C) have been obtained by using multiexponential analysis; curve B was obtained by using a cumulant fit. The limiting expressions using log–log plots for data in curves A and B correspond to an exponent of about unity ($C_1^* = 3M/4\pi R_g^3 N_A$; $C_2^* = M/R_g^3 N_A$).

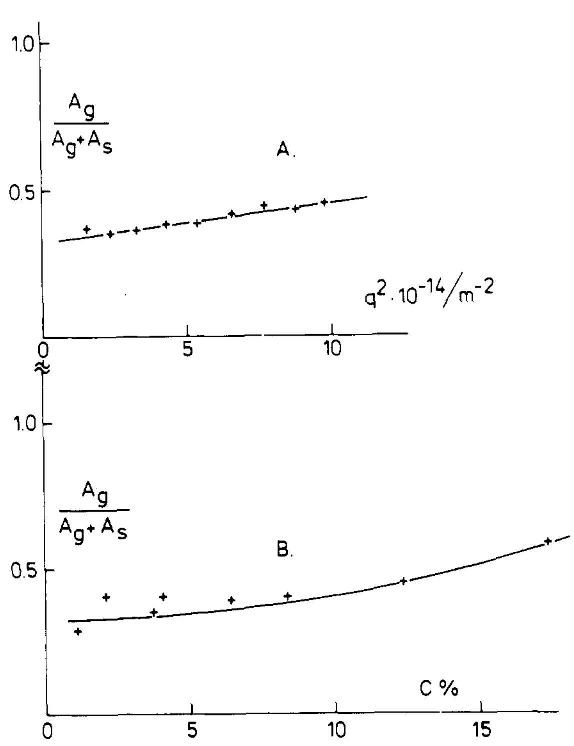

Figure 4. Contributions to the total intensity from the gel mode as (A) a function of q^2 for $\bar{M}_w = 15 \times 10^6$ at a concentration of 8.4% and (B) as a function of concentration for the same fraction at a measuring angle of $\theta = 40°$. The relative intensity has been obtained by using a bimodal fit according to $g^{(2)}(\tau) - 1 = \beta[A_s \exp(-\Gamma_s\tau) + A_g \exp(-\Gamma_g\tau)]^2$. Γ_s and Γ_g are the relaxation rates, and A_s and A_g are the corresponding relative intensities for the slow (s) and gel (g) modes, respectively.

for the gel mode at high C thus agrees with the findings of the earlier investigators.[1,2] The concentration independence of D_g observed up to a value of $C = 15C^*$ as previously reported[3] represents divergent behavior for very high molecular weight samples (at least in cyclopentane). We note that the D_g values are approximately superimposable on values for a fraction of $\bar{M}_w = 9.3 \times 10^5$, previously obtained[8] in the same system, whereas those for the slower mode D_s are molecular weight dependent ($D_s \sim M^{-0.5}$).

Figure 4 shows the variation of the relative intensity of the gel mode as a function of q^2 as well as the concentration dependence of this quantity. The latter change is significantly less pronounced than for the same fraction in the good solvent THF.[10]

The data for the slower mode shown in Figure 3C depict the initial decrease in D anticipated for translational motions at lower concentrations. However, a significant increase in D is noted at higher values of C. To obtain a clearer picture of the nature of the slower mode (and also the overall nonexponential character of the correlation function) the latter was analyzed for data obtained at a number of concentrations using a number of analytical methods. Some of these results are shown in Figure 5. The various approaches show that three distinct modes are present. The two fastest (which agree with the results of the bimodal analysis as shown) are q^2 dependent. The third and slowest appears to be q independent and is thus most likely a structural relaxation. A recent report of a similar analysis of data in Θ systems[12] suggests that the spectra increase in complexity as C increases. However, the spectrum for the highest concentration presently used (17.4%) indicates a single gel mode accompanied by a more or less smoothed-out continuous distribution of slow components. These data were obtained with a new multi-τ correlator[11] enabling 23 different τ ranges to be covered and accumulated simultaneously. These data will be described in more detail in a future report. The overall pattern is thus in more close agreement with the earlier findings of Adam and Delsanti,[2] although these workers only described the limiting components at the ends of the spectrum.

Θ solutions have been relatively little studied as regards

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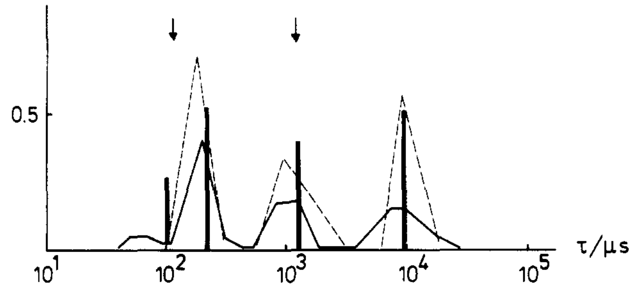

Figure 5. Distribution of decay times using various methods[12] for data obtained on solutions of PS ($\bar{M}_w = 15 \times 10^6$) in cyclopentane (21 °C) at a concentration of 4.7% (w/w) (measurements at $\theta = 60°$): (a) CONTIN[13] (continuous line); (b) linear-programming method,[14] which uses fixed components equidistant on a logarithmic scale and minimizes the sum of absolute values of residuals (result shown as the broken line); (c) positive-coefficient exponential sum (PES) method,[15] which fits the experimental curve to the expression $(\sum_{i=1}^{N} c_i e^{-t/\tau_i})^2 + b$, with all c_i, τ_i, and b adjusted by least squares with $c_i > 0$ and $\tau_i > 0$. Components N are increased until no new τ_i with positive c_i can be added. These values are illustrated as the vertical bars. The two vertical arrows shown are the results of bimodal analysis as described in ref 3.

dynamics, not the least because it is difficult to obtain asymptotic conditions even with very high molecular weight fractions. We have endeavored to meet this need, as shown by the data in Figure 3. It is apparently necessary to exceed $C \simeq 10\%$ (the often-used limit for semidilute solutions owing to monomer-friction complications) if a limiting exponent for the gel mode is to be established. However, the experimental difficulties are formidable in obtaining a precise description of the various components involved in the relaxation behavior. The degree of nonexponentiality is considerable, and substantial ambiguity attaches to the components regardless of the data-analysis technique employed. It is also possible that the slower modes couple to some extent with the faster motions of the transient gel at the highest concentrations.[7]

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References and Notes

(1) Hecht, A.-M.; Bohidar, H. B.; Geissler, E. *J. Phys. Lett.* **1984**, *45*, L-121.
(2) Adam, M.; Delsanti, M. *Macromolecules* **1985**, *18*, 1760.
(3) Brown, W. *Macromolecules* **1986**, *19*, 387.
(4) Brochard, F.; de Gennes, P.-G. *Macromolecules* **1977**, *10*, 1157.
(5) Brochard, F. *J. Phys.* (*Les Ulis, Fr.*) **1983**, *44*, 39.
(6) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: London, 1979.
(7) Chu, B., personal communication.
(8) Brown, W.; Johnsen, R. M. *Macromolecules* **1985**, *18*, 379.
(9) Noda, I.; Higo, Y.; Ueno, N.; Fujimoto, T. *Macromolecules* **1984**, *17*, 1055. These authors show, using osmotic pressure measurements, that the crossover to the concentrated region occurs at between 15 and 20%, irrespective of molecular weight.
(10) Brown, W. *Macromolecules* **1985**, *18*, 1713.
(11) ALV-Langen Co., F.R.G.
(12) Štěpánek, P.; Koňák, Č.; Jakeš, J. *Polym. Bull.* (*Berlin*) **1986**, *16*, 67.
(13) Provencher, S. W. *Makromol. Chem.* **1979**, *180*, 201.
(14) Zimmerman, K.; Delaye, M.; Licinio, P. *J. Chem. Phys.* **1985**, *82*, 2228.
(15) Jakeš, J.; Štěpánek, P., to be published.

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Spinodal Decomposition of Polymer Mixtures with a Thermotropic Liquid Crystalline Polymer as One Component

The mechanism and kinetics of phase separation of polymer mixtures have been the subject of extensive studies in recent years.[1-13,35-39] The studies involve time-resolved analyses of structural evolution from the mixtures in the molten, isotropic liquid state[1-8,11,13,35-39] or in a neutrally good solvent[9,10,12] (i.e., phase separation into polymer A solution and polymer B solution), induced by quenching the systems to a thermodynamically metastable or unstable state.

In this paper we present novel experimental evidence on phase separation into a liquid crystalline phase and a molten, isotropic, liquid phase via spinodal decomposition.[2,7,14] During the course of the isothermal phase separation we observed the following: (i) We found an evolution of periodic concentration fluctuations with correlation length Λ_m which increases with time spent for phase separation. (ii) The time evolution of the concentration fluctuations results in a bicontinuous, periodic network-type structure: one type of phase is rich in liquid crystal forming polymer and forms the liquid crystalline phase, and the other type of phase is rich in molten, isotropic polymers and forms the optically isotropic phase. (iii) At a sufficiently late stage, a "self-similarity"[16,17] was found between the structures obtained at different times.

Observations i–iii are essentially the same as those reported for unmixing processes of critical mixtures of metallic alloys,[18-20] small-molecule liquids,[21,22] inorganic glasses,[23] and binary liquid polymers.[24,40] It is our objective in this paper to report that this common phenomenon can also be found in the unmixing process of binary mixtures between thermotropic, liquid crystalline polymers and isotropic liquid polymers.

The system used in this study was a 50:50 mixture (by weight) of a commercial poly(ethylene terephthalate) (PET) and a copolyester of 60 mol % *p*-oxybenzoate (OBA) units and 40 mol % ethylene–terephthalate units (X-7G; Tennessee Eastman Co.). The number-average molecular weights of these polymers are both ca. 2×10^4. X-7G is among the first thermotropic liquid crystalline polymers, and its synthesis and properties have been reported by Jackson and Kuhfuss.[25] These two polymers were dissolved in *o*-chlorophenol at 60 °C, and the insoluble part, which probably consists of crystalline poly(*p*-oxybenzoate), was removed by filtration. The test specimens were prepared by casting one or two droplets of 1–5 wt % solutions on microscope cover glasses. The solvent was quickly evaporated by placing the cover glasses onto a hot plate preheated at 60 °C in a vacuum chamber. The film-casting seemed to be completed within a few minutes but the test specimens were kept under vacuum for an additional 3 h. The films thus prepared had average thicknesses of 1–10 μm at the centers of the droplets and thicker peripheries. The as-cast films were clear and exhibited no optical anisotropy under a cross-polarized optical microscope. Time evolution of the structure was observed by a Nikon Optiphot-Pol XTP-11 polarizing microscope equipped with a TH-600 heating stage (LINKAM Scientific Co.). The temperature of the heating stage was calibrated for the melting points of various standards of small molecules. The observations were started as soon as the test specimens on the cover glasses were placed on the heating stage controlled at the preset temperature. The time required for a temperature jump (T jump), i.e., the time necessary for the test specimens to reach the preset temperature, was less than a few seconds. The

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