Dynamic Behavior in Concentrated Polymer Solutions

Dynamic light scattering (DLS) has been widely applied, on the one hand, to investigations of dilute and semidilute polymer solutions up to $C \approx 0.15$ g/mL and, on the other hand, to bulk polymers. Our present objective is to extend such measurements to the intervening concentration interval in order to ultimately understand the dynamics over the entire range of concentration. The salient features of the dynamics of semidilute solutions and bulk polymers are initially summarized to provide a background.

Semidilute solutions have recently been reviewed.[1] In thermodynamically good solvents, the time correlation function corresponds closely to a single-exponential decay describing the relaxation of the transient network of entangled chains. The influence of topological constraints (entanglements) can be neglected. The concentration dependence of the dynamic correlation length (ξ_h) is well-described by scaling theory,[2] which predicts an exponent of −0.75. An exponent of −0.70 is typically found for a large number of experimental data, and the power law is valid for concentrations up to about 0.30 g/mL, at which value $\xi_h < 10$ Å. (In the bulk limit a value of 2.7 Å is anticipated for the polystyrene chain.)

The influence of solvent quality on chain dynamics is pronounced. In contrast to good solvents, the correlation function in Θ solvents is multimodal with decay times spanning over up to 8 decades on the time scale.[3,4] In addition to the fast diffusive mode characterizing the collective motions of the network, there is a broad spectrum of q-independent slower relaxations. The slower modes extend over a greater range with increasing molecular weight and concentration. For Θ solutions, the theory of Brochard and de Gennes[6] allows for two limiting regimes: in the low-frequency limit, the chains can disentangle and the concentration fluctuations then relax as in a viscous solvent. The diffusion coefficient in this hydrodynamic regime is $D_h = kT/(6\pi\eta\xi_h)$ corresponding to a relaxation rate $\Gamma_q = D_h q^2(1 - \Phi)$ and ξ_h is proportional to concentration; Φ is the polymer volume fraction, and η is the solvent viscosity. The concentration dependence of ξ_h has hitherto been examined over a comparatively restricted range up to about 0.15 g/mL. In the high-frequency limit, the topological entanglements are "frozen" and concentration fluctuations relax as in a permanent gel, $D_g = (kT/6\pi\eta)(1/\xi_h + f/a)$, and the relaxation rate, $\Gamma_g = D_g q^2(1 - \Phi)$. Here a is the monomer size and f is the number of effective entanglements per binary contact. While this theory provides an adequate description of the fast diffusive component, this is not the case for the slower modes. The latter are plausibly related to the viscoelastic properties of the transient network. In a recent comparison of DLS and mechanical measurements on polystyrene in a viscous solvent,[4] it was found that the shear modulus for semidilute polymer solutions relaxes over a broad range of relaxation times and that the range is very similar when the system is probed by these two techniques.

It is anticipated that increasing the polymer concentration above the semidilute range will lead to a decrease in the amplitude of the diffusive component and eventually result in a DLS spectrum for the bulk polymer that is due to density fluctuations and may be characterized by a very broad spectrum of q-independent mode(s). DLS results have been reported on poly(cyclohexyl methacrylate) in the presence of low concentrations of the viscous solvent dioctyl phthalate (up to 15%).[7] Both density and concentration fluctuations (respectively, the fast and slow modes) were observed in the DLS time window over a range of temperature.

DLS has earlier been used in the study of bulk polymer dynamics near to and above the glass transition temperature, T_g. Above T_g the relaxation arises from segmental motion associated with the primary glass–rubber transition of the polymer. In contrast to the solution-state properties, bulk properties are scarcely affected by molecular weight (if sufficiently high) or entanglements. The local segmental motion involves conformational transitions (the α-process). Other modes of motion of the chain backbone correspond to the overall rotation and large-scale deformation of the chain. Both the α-mode and the chain modes will contribute to the shear viscoelastic properties in the transition from rubberlike to glasslike states. These aspects have recently been reviewed.[8]

With regard to the comparison of DLS and dynamic mechanical data on semidilute solutions referred to above, it is relevant that Wang and Fischer have shown[9] that the density time correlation function is equivalent to the relaxation of the longitudinal compliance of the bulk polymer. Retardation spectra were obtained from DLS data on a poly(vinyl acetate) melt and compared to the dynamic mechanical relaxation data.

Wang has recently made[10a] a theoretical analysis of the DLS spectrum for a polymer solution. In concentrated solutions both density and concentration fluctuations need to be considered. At frequencies in the plateau stress modulus region, the theory predicts a cooperative diffusion coefficient that is dependent on both the osmotic modulus and the longitudinal elastic modulus of the solution. The analysis also describes the interplay between concentration and density fluctuations in determining the overall light scattering spectral density. As the concentration is increased toward the bulk, the concentration fluctuations lose their importance and density fluctuations dominate the spectrum. We note that Lempert and Wang[10b] have described in qualitative terms this transition for the PS/cyclohexane system.

The present experiments (on which this paper is a preliminary report) were initiated in order to characterize the transition region between semidilute solutions and the bulk state. At a subsequent stage, it may be possible to make an appraisal of the predictions put forward by Wang. Solutions with concentrations in the range 0.1–0.75 g/mL were prepared by very slow evaporation of a 2% stock solution of polystyrene (PS; Pressure Chemicals, $M_w = 9 \times 10^5$) in cyclohexane (Fluka PA). The cells were sealed and left to equilibrate at 60 °C for several months. DLS measurements were made at the Θ temperature at 34.5 °C in a previously described setup[11] using an ALV 5000 autocorrelator. The correlation functions were analyzed in two ways: (1) by Laplace inversion using the algorithm REPES[12] to give the corresponding distributions of decay time τ; (2) by employment of the sum of Gaussian + generalized exponential distributions (GEX) as described in ref 4. Figure 1 shows the evolution of the spectrum of decay times according to method 2. Up to a concentration of 0.65 g/mL the spectra consist of a dominant fast and relatively sharp component together with a structure extending over a broad range of slower decay times. This qualitatively resembles the spectrum of decay times observed previously[3] in semidilute Θ solutions of PS. In the latter case a high-MW sample (3.8×10^6) was used. Up to 0.65 g/mL, the fast component is diffusive, as is shown by the q^2 dependence of the decay rate (Γ) in Figure 2a,b for two solutions, and corresponds to the gel diffusion coefficient discussed in previous

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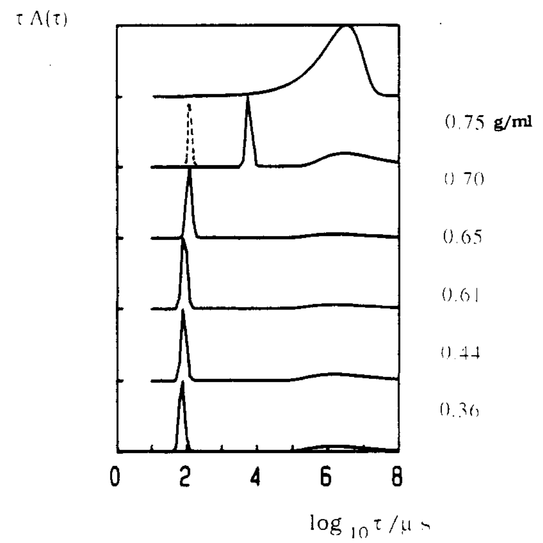

Figure 1. Relaxation time distributions obtained by fitting dynamic light scattering data to the sum of Gaussian and GEX distributions[4] for concentrated solutions of polystyrene (indicated) ($M_w = 9.5 \times 10^6$) in cyclohexane at 34.5 °C; measurement angle 90°. An equal area representation: $\tau A(\tau)$ versus log τ is used. The dotted peak (q^2-dependent) corresponds to the distribution measured at 52 °C.

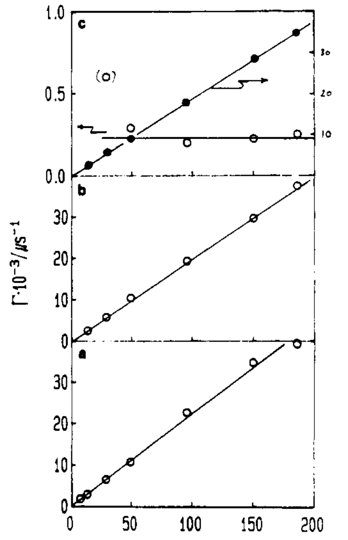

Figure 2. Relaxation rate versus the square of the scattering vector (q^2) for the main component in Figure 1 at (a) $C = 0.44$ g/mL, (b) 0.65 g/mL, and (c) 0.70 g/mL at 34.5 °C (open points). Measurements at 52 °C on the $C = 0.70$ g/mL solution are included (filled points).

papers.[3,4] This picture changes completely when the concentration is increased from 0.65 to 0.70 g/mL: Figure 1 shows that the main component at this concentration is slower by about 2 orders of magnitude. Also, the decay rate of the main component is q-independent; see Figure 2c. This is characteristic of a nonpropagating process and a signature of the transition to a spectrum of decay times dominated by density fluctuations as described above. The switchover of the decay spectrum from one characteristic of gel diffusion to one representing density fluctuations may be understood if we consider both the closeness to T_g and the predictions of the Wang theory. The glass transition temperatures of the solutions having $C = 0.70$ and 0.65 g/mL are, respectively, 281.4 and 265 K as measured using DSC (heating rate 20 °C/min); see also ref 13. However, T_g is frequency dependent, and the value is probably even higher at frequencies corresponding to the DLS measurements.

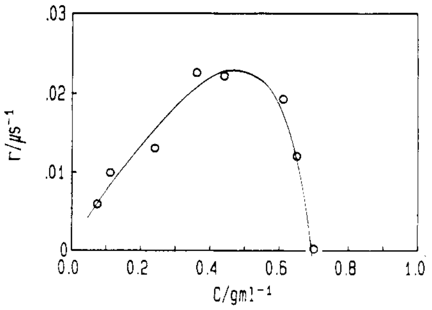

Figure 3. Relaxation rate for the main peak of the distributions in Figure 1 shown as a function of polystyrene concentration.

The solution of $C = 0.70$ g/mL lies within the range where density fluctuations should dominate the spectrum.[14,15] The dotted curve shown for this concentration gives the position of the main peak observed in measurements made at 52 °C as a function of angle. This peak is again q^2-dependent, and the gel mode has thus been recovered at this higher temperature. On the other hand, measurements at 45 °C on the $C = 0.70$ g/mL sample only show the q-independent mode having a relaxation time intermediate between those found at 34.5 and 52 °C. The changeover from a situation where concentration fluctuations dominate to one where density fluctuations dominate thus occurs over a surprisingly narrow interval, both regarding temperature and concentration. The very narrow temperature interval of the transition must reflect a close proximity to T_g. The approach to the glass–rubber transition with increase in C should have as a consequence a slowing down of all dynamic processes including gel diffusion. The distribution measured at $C = 0.75$ g/mL (q-independent) shows a substantial slowing of the average relaxation rate and an increase in line width, which occurs with a further increase in concentration. We note that Lempert and Wang[10b] found the transition to occur above $C = 0.68$ g/mL in this system.

The change in the decay rate of the dominant component is shown as a function of concentration in Figure 3. It is seen that, up to $C = 0.40$ g/mL, Γ increases with C as in semidilute solutions, then passes through a broad maximum, and finally, above $C = 0.60$ g/mL, decreases sharply as the glass transition is approached. At the same time, between $C = 0.50$ g/mL and $C = 0.70$ g/mL, the character of the main relaxation changes from diffusive to density fluctuations. The relaxation rate assigned here to density fluctuations in the $C = 0.70$ g/mL solution corresponds approximately to the frequency of the density fluctuations observed by Fytas et al.[7] when the difference in the respective solvent viscosities is taken into account. A more detailed investigation of this transition is in progress and will be reported subsequently.

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