$$\sum_{j\neq i}[(\mathbf{r}_i - \mathbf{r}_j)_{\min} \times \mathbf{F}_{ij}^{B} + \boldsymbol{T}_{ij}^{B} + \boldsymbol{T}_{ji}^{B}] = 0 \qquad (A.2)$$

If centers *i* and *j* are not connected by a bond, all terms in the bracket of eq A.2 automatically vanish. In case atoms *i* and *j* are bonded to each other, the torque balance on bond *ij* (Appendix B of ref 2) gives

$$(\mathbf{r}_i - \mathbf{r}_j) \times (-\mathbf{F}_{ij}^{B}) + (-\boldsymbol{T}_{ij}^{B}) + (-\boldsymbol{T}_{ji}^{B}) = 0$$

or

$$(\mathbf{r}_i - \mathbf{r}_j)_{\min} \times \mathbf{F}_{ij}^{B} + \boldsymbol{T}_{ij}^{B} + \boldsymbol{T}_{ji}^{B} = 0$$

and the contribution from bonded pair *ij* is again zero. Thus eq A.2 is true, which proves the symmetry of tensors $\mathbf{w}_i$ and σ_i.

Registry No. Polypropylene (homopolymer), 9003-07-0.

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Dynamical Properties of High Molecular Weight Polystyrene in the Dilute–Semidilute Transition Region in Cyclopentane at the Θ Temperature

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ABSTRACT: Data for the polystyrene ($M = 8 \times 10^6$ and $M = 15 \times 10^6$)/cyclopentane Θ system (Θ = 21 °C) are presented. Quasi-elastic light scattering measurements were made on semidilute solutions in the high-*q* region to characterize the gel mode. The time correlation function was found to be consistent with a bimodal expression including a small base-line term, as predicted by Brochard: exponent 1, a gel mode of low-intensity amplitude and concentration independent over the interval up to about 10C^*; exponent 2, a slower hydrodynamic mode of the same magnitude as that evaluated with the cumulants method at low *q* values. This mode is of dominant amplitude and has a small negative dependence on concentration. Both relaxations were found to be q^2-dependent and also independent of molecular weight. The presence of two cooperative modes illustrates the fundamentally heterogeneous character of Θ semidilute solutions. The results are in agreement with the predictions of Brochard for the gel mode. The hydrodynamic mode, however, does not exhibit the anticipated linear dependence on concentration in the interval studied. The present data also indicate the presence of a very slow relaxation that has been assigned to a base-line term in the bimodal analysis of the faster decays. Its amplitude increases with concentration and also more weakly with decreasing angle at a given concentration. The estimated relaxation rate when approximated as a third exponential changes with the sampling time used.

Introduction

Brochard and de Gennes[1] and Brochard[2] treated the dynamics of semidilute polymer solutions in Θ solvents. Their model assumes two elastic moduli (the osmotic and gel moduli), and thus two modes are potentially observable in dynamic light scattering experiments. Entanglements will lead to a transient network[3] of lifetime T_R. If $\Gamma T_R < 1$ (where Γ is the relaxation rate associated with the concentration fluctuations), then the chains are able to disentangle during a diffusion time $(D_s q^2)^{-1}$. Here q^2 is the scattering vector and D_s is a "slow" cooperative diffusion coefficient (an osmotic diffusion coefficient, related to the osmotic modulus), which is predicted to be directly proportional to concentration. By observations at sufficiently small *q*, in the hydrodynamic limit, one should be able to determine D_s. On the other hand, at high frequencies when $\Gamma T_R > 1$, a fast gel-like mode (D_g) should be detectable above the threshold value of *q* defined by the relationship

$$q_g^{\,2} = (T_R D_g)^{-1} \qquad (1)$$

D_g is predicted to be independent of concentration. The model of Brochard[2] thus leads to a bimodal character for the dynamic structure factor, $S(q,t)$, in the gel region with the participation of D_s and D_g. However, a very slow *q*-independent relaxation is also suggested as existing together with D_g and D_s.

Solely from an experimental viewpoint, there is abundant evidence that the semidilute solution structure in Θ media is more complicated than that in good solvents. Few studies exist of such systems using quasi-elastic light scattering (QELS). This is partly a consequence of the relatively high monomer concentrations required to attain C^* in Θ solvents and also the emphasized problems of working with highly self-entangled polymers and particu-

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larly those of very high molecular weight. The time correlation function is invariably observed to deviate strongly from a single exponential, a feature that gives qualitative support for the model of Brochard. In order to isolate the gel mode, it is necessary to resort to analysis of the correlation function. This is the approach here. From theory it is anticipated that a small number of modes will be met. The present paper is mainly directed to characterization of the gel mode, although even the hydrodynamic regime (low q) has received scant attention in the literature and must be regarded as relatively uncharacterized. It was originally suggested by Brochard and de Gennes[1] that the relative weighting of the fast mode is so small that only the complementary slow one will be accessible. Brochard[2] was subsequently more optimistic regarding its resolution from $S(q,t)$. We employ here the method of discrete multiexponentials using an equally-weighted nonlinear regression procedure with nonnegativity constraint and apply it to $S(q,t)$ data for two high molecular weight polystyrenes in the cyclopentane Θ system. With such samples sufficiently small q values are not accessible for isolating the slow component alone. The measurements here refer to the angular region corresponding to $q > q_g$ and refer to the range $1 < qR_g < 2.5$. This implies that above a reduced concentration C/C^* of about 1–3 the gel mode will be accessible; i.e., the internal modes of very large coils detected in this q range in dilute solution should have become indistinguishable from the collective motions of the transient gel formed above C^*.

This has recently been demonstrated by Kubota et al.[15] for PS in methyl acetate and earlier by Chu and Nose[5] in a series of papers on the PS/*trans*-decalin system. As will be shown (Figures 3 and 6) the present measurements extend to about $8C^*$ for $M = 8 \times 10^6$ and to $10C^*$ for $M = 15 \times 10^6$, where $C^* = 3M/4\pi R_g^3 N_A$ is used as the definition.

The QELS data are complemented by macroscopic gradient diffusion measurements. A previous paper[12] dealt with bimodal analysis of the time correlation function in the same system but for samples of lower molecular weight.

Experimental Section

Polystyrene ($M = 8 \times 10^6$, $M_w/M_n = 1.08$; $M = 15 \times 10^6$, $M_w/M_n = 1.30$) was obtained from Toya Soda Ltd., Japan. The cyclopentane was spectroscopic grade from Merck, Darmstadt, FRG and was used without additional purification.

Solutions. To avoid possible mechanical degradation, the sample and solvent were sealed in glass vials and these slowly rotated for a period of 4 months at 25 °C (Θ = 20.8 °C). The solutions were filtered in a closed-circuit filtration unit using 3.0-μm Fluoropore filters. Completely dust-free solutions could be prepared in this way, and they were bled off into NMR tubes. Dilutions were performed by filtering various amounts of solvent into the weighed tubes. The solutions were allowed to stand for at least 1 week after filtration prior to light scattering measurements. Higher concentrations could be prepared by evaporation of the solvent from a known amount of the stock solutions in the light scattering cells in a dust-free atmosphere.

Dynamic Light Scattering. All data were obtained in the homodyne mode with full photon-counting detection and a 128-channel Langley–Ford autocorrelator. Incident radiation at 488 nm was from a Coherent Super-Graphite 4-W argon ion laser containing a quartz etalon frequency stabilizer in the cavity to ensure single-mode operation and to enhance the signal/noise ratio.

The scattering cells were 10-mm-diameter precision NMR tubes, and these were immersed in a large-diameter bath of index-matching liquid (decalin).

The correlation function was treated interactively with the same microcomputer as employed for data collection and reduction. Fits were made with one-, two-, and three-exponential functions with and without a base-line term. The programs were written in Forth for rapidity and compactness, and the microcomputer was fitted with an arithmetic processor for increased speed and accuracy. All of the data were first analyzed with a cumulants program.

Classical gradient diffusion measurements were made with a shearing-type cell for free diffusion and a schlieren optical system. The half-width at the inflection point (ΔX) was measured in a microcomparator and $(\Delta X)^2$ plotted vs. time. The mutual diffusion coefficient was evaluated from the slope according to

$$(\Delta X)^2 = 2D_m t \tag{2}$$

The starting time correction was always zero within experimental error; otherwise the experiment was rejected. D values were also calculated by the height–area method. The two procedures gave values that were identical within experimental uncertainty.

The boundary was always made between two solutions differing in concentration by about 1%. The diffusion coefficients then correspond to the average concentration, $\bar{C}$, across the boundary. It was established that in dilute solution the D vs. C relationship closely matched the value obtained with dynamic light scattering.

Results

The present data have been obtained on semidilute solutions of polystyrene in cyclopentane at the Θ temperature (21 °C). It is well established[5,7,10,12,15] that the time correlation function of the light scattered in such Θ systems is strongly nonexponential. Thus, for example, Nose and Chu[5] showed that two components could be resolved with a histogram method and/or bimodal analysis in the system PS/*trans*-decalin under Θ conditions. Subsequently others have used a similar approach or resolved[8] the fast and slow components having well-separated relaxation rates by using appropriate sampling times. We have performed experiments over the angular range $20° < \theta < 80°$. Care was taken at each concentration to exclude measurement angles at which interference from internal motions could be suspected. Thus measurements were restricted to the angular region where the cumulant value, $\bar{D}_{\text{cum}}$, was strictly independent of angle. The correlation functions for the present data were also found to be strongly nonexponential at all but the lowest measurement angles (i.e., $\theta < 20°$). The threshold parameter, q_g^2, defined in eq 1, was found to correspond to $\theta \simeq 20°$, where T_R was estimated for PS ($M = 8 \times 10^6$) from[3]

$$T_R = \left(\frac{6\pi\eta_0}{k_B T}\right) R_g^3 (C/C^*)^3 \tag{3}$$

where η_0 is the solvent viscosity and k_B Boltzmanns' constant.

The value of the radius of gyration, R_g, in cyclopentane at the Θ temperature is assumed to approximate that in cyclohexane for which data are tabulated in ref 6. Present attention is focused on the angular range $20° \leq \theta \leq 80°$. All data were initially processed by a cumulant fit program using a third-order cumulant fit. Runs exhibiting a deviation of delayed channels from the calculated base line or unusual intensity were rejected. A comparison of fits was next made with three parameters (single exponential plus floating base line), four parameters (bimodal), five parameters (bimodal plus floating base line), and six parameters (three exponentials). The basis for this approach is the expectation from current theory[1-3] that two modes are present, rather than a wider spectrum of relaxations. However, a bimodal fit is only the most simple of numerous alternatives that may have similar statistical significance. The best fit was consistently obtained with the five-parameter function when the concentration exceeded 0.5% ($\simeq C^*$) according to the equation

$$g^{(2)}(\tau) - 1 = \beta[A_s \exp(-\Gamma_s\tau) + A_g \exp(-\Gamma_g\tau) + B]^2 \tag{4}$$

expressing the normalized second-order correlation func-

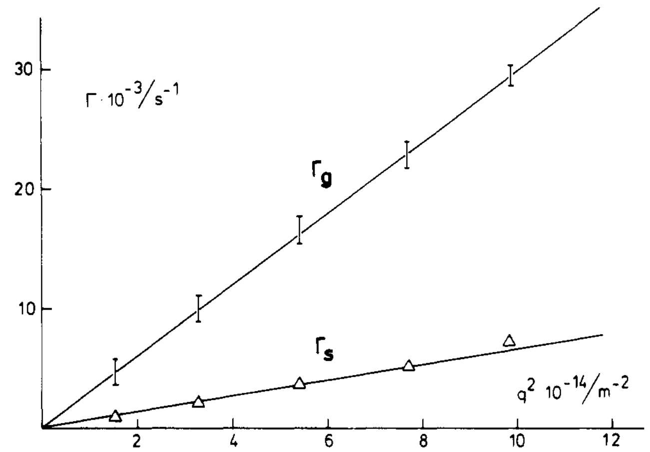

Figure 1. Bimodal analysis (eq 4) results for a semidilute solution of PS ($M = 8 \times 10^6$) in cyclopentane at 21 °C (Θ conditions). $C = 0.77\%$ (w/w). Γ_g corresponds to the gel mode and Γ_s to the slow mode.

tion in terms of two relaxation rates. β is an instrumental parameter, here approximately 0.65. The presence of a small base-line term B, suggests that the model of Brochard[2] may be inadequate to describe the complexity of the system.

The choice of the most appropriate fit was made partly on the basis of the Q function

$$Q = 1 - \frac{\sum_{i=1}^{n-1} \epsilon_i \epsilon_{i+1}/(n-1)}{\sum_{i=1}^{n} \epsilon_i \epsilon_i / n} \qquad (5)$$

If there is no grouping of residuals, ϵ, Q will approximate unity; otherwise Q will be significantly less than 1. Q values exceeding 0.9 were consistently found. Furthermore, the five-parameter fit gave the lowest minimum of the reduced sum of squares of residuals to the fit, χ^2. A five-parameter fit, with the base-line term corresponding to an infinite number of channels, gave a slightly lower χ^2 value than the four-parameter model. The base-line term was always small ($\simeq$1–2%). The general level of the data precision corresponded to a variance of 2×10^{-7} (standard deviation of the error, 4×10^{-4}).

An extensive series of simulations had previously been made[12,13] to establish both the reliability and limitations of the present fitting procedures. Normally distributed pseudorandom numbers of a size typical of the residuals in a real run were added to "experiments" constructed with parameter values corresponding to the range of the actual runs. It was found that when the relaxation rates differ by at least a factor of 2, the minor component in, for example, a bimodal fit, is well-defined when contributing down to about 5% of the total intensity. Resolution of the two exponents, however, requires that they differ in relaxation rate by at least 30%. For the present data the relaxation rates of the two components differ from each other by more than a factor of 3 (see, for example, Figure 1), which provides a favorable condition for their separation. Furthermore, the relative intensity contributions are well apportioned (see below). We thus have confidence in the results when using eq 4 with the present data. It may be noted that Zimmermann and Štěpánek[11,22] find three-exponential fits to be most appropriate for the PS/cyclohexane Θ system—see the discussion below on the base-line term.

Data for the relaxation rate (Γ) as a function of q^2 are shown in Figure 1 for the fast and slow modes evaluated

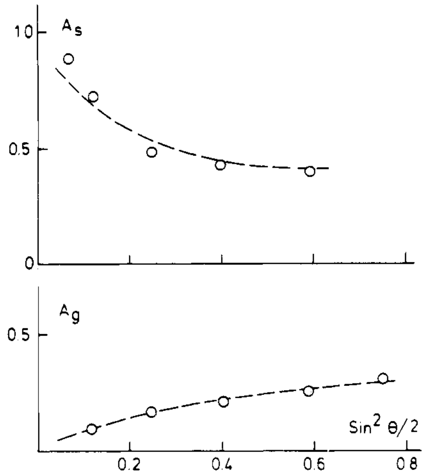

Figure 2. Contributions to the total intensity from the gel mode (A_g) and the slow mode (A_s) as a function of $\sin^2(\theta/2)$. These data correspond to the relaxation rates shown in Figure 1. ($C = 0.77\%$ (w/w); $C^* = 0.58\%$).

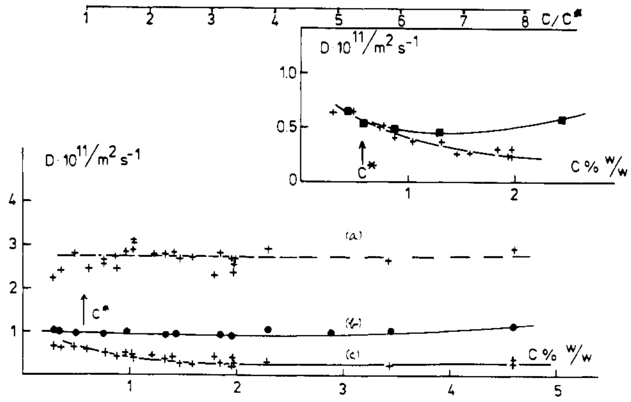

Figure 3. Concentration dependence of diffusion coefficients for semidilute solutions of PS ($M = 8 \times 10^6$) in cyclopentane at 21 °C: (a) gel mode, D_g; (b) cumulant evaluation (filled points); (c) slow mode, D_s. D_g and D_s have been obtained as the best slope from plots of the kind illustrated in Figure 1. Insert: comparison of D_s from bimodal analysis with gradient diffusion data, $\bar{D}_{CGD}$ (filled points) ($C^* = 3M/4\pi R_g^3 N_A$).

with eq 4. These are typical for those collected at each concentration in the range above 0.5% (w/w). Below this value, the base-line term in eq 4 could be disregarded. Both modes can thus be attributed to diffusional motions. As described below, both modes are shown to be molecular weight independent and are of cooperative character.

The question arises whether the bimodal nature of the correlation function is influenced by the finite polydispersity of the sample. When the semidilute solutions were diluted to high dilution, the correlation functions were found to be monomodal at low angle ($\theta \leq 20°$), showing that polydispersity should not be a significant influence on the overall pattern of the results. At low angle, essentially unimodal behavior was observed up to the overlap concentration, C^*.

Figure 2 shows the relative intensity contributions from the two modes as a function of $\sin^2(\theta/2)$. The fractional intensity from the gel mode, A_g, increases with angle since shorter range motions will be emphasized as q^{-1} decreases. A_s increases strongly with decreasing angle and at low angles the slower mode can be isolated relatively free of the gel mode. The magnitude of the base-line term, however, also increases with decreasing angle.

Figure 3 illustrates the concentration dependence of the diffusion coefficients, D_g and D_s. While the statistical fit using eq 4 was excellent for the individual runs, the points

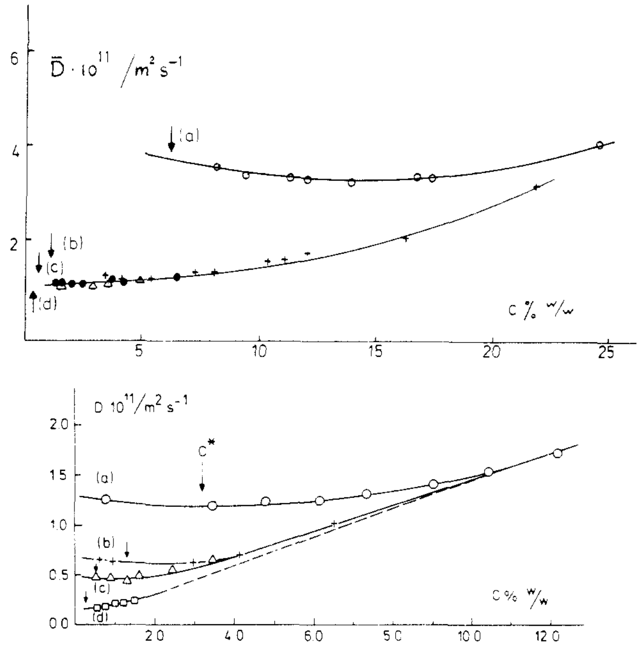

Figure 4. (A) Concentration dependence of diffusion coefficients evaluated by the cumulant method for various fractions of polystyrene in cyclopentane at 21 °C (Θ conditions): (a) $M = 9.3 \times 10^4$ (○); (b) 9.5×10^5 (+); (c) 8×10^6 (△); (d) 15×10^6 (●). The vertical arrows indicate the value of C^* for each fraction. (B) Classical gradient diffusion data for polystyrenes of various molecular weight in cyclopentane at 21 °C: (a) 950 000, (b) 3×10^6, (c) 8×10^6, (d) 15×10^6. The broken line has been given a slope of unity for comparison.

show considerable scatter as a function of concentration. Somewhat greater uncertainty is associated with the fast mode owing to its representation in relatively few channels when an optimum sampling time is used to include both relaxations. D_g is concentration-independent in the studied interval up to about $C/C^* \cong 8$, and this is in agreement with the prediction of Brochard[2] for the gel mode. A similar overall pattern is observed for the fraction with $M = 15 \times 10^6$—see Figure 6. D_g has previously been shown[5,12] to have a zero or weakly positive dependence on concentration, but the slope tends to increase with C. This finding is apparently in disagreement with the results of Adam and Delsanti[7,21]—see below. The slower mode, D_s, obtained by bimodal analysis at semidilute concentrations at $q > q_g$, may be isolated almost free of the faster mode by making measurements at sufficiently low angle (in the present case $\Theta \leq 25°$ for $M = 8 \times 10^6$). This provides support for the validity of using eq 4 for isolating two modes in the higher angular range. The D_s values obtained in this way also fall on a smooth curve together with the translational diffusion coefficient obtained by low-angle measurements at dilute concentrations (see Figure 3). It is concluded that D_s corresponds to a correlation length of the magnitude of the radius of the coil. The accumulated experimental data[5,15] together with those for samples of lower molecular weight[12] and the present data provide evidence for the presence of a substantially slower mode than D_g with a weak negative dependence on concentration in the range above C^*. As was noted above, the hydrodynamic mode, D_s, is predicted to be directly proportional to concentration, and the present results stand in conflict with this. Inspection of the cumulants data in Figure 4A shows that there is only a very gradual increase in $\bar{D}$ over a substantial range of concentration with these molecular weights. The modest concentrations attainable with such samples thus effectively prohibit characterization of the limiting slope using QELS measurements. Examination of even higher concentrations is prevented by the simultaneous development of a very slow relaxation that has been assigned here to the base-line term—see below. The latter cannot be meaningfully characterized with our present equipment. Values of $\bar{D}_{\mathrm{cum}}$ (cumulants analysis) are included in Figures 3 and 6. These are approximately independent of concentration. These data are shown together with data for two lower molecular weight fractions in Figure 4A over a wider range of C. Two points are noteworthy: (1) the shallow dependence of $\bar{D}_{\mathrm{cum}}$ on C over extended ranges and the eventual increase in $\bar{D}_{\mathrm{cum}}$ in the case of the lower molecular weights, as anticipated with a decrease in correlation length at high C; (2) the molecular weight dependence of $\bar{D}_{\mathrm{cum}}$ for all except the lowest fraction, $M = 9.3 \times 10^4$.

The insert to Figure 3 compares values of $\bar{D}_{\mathrm{CGD}}$ (gradient technique) with the slower mode D_s, while Figure 4B shows $\bar{D}_{\mathrm{CGD}}$ for four samples of different M. Each curve displays the characteristic upswing that is well documented (e.g., ref 17) and is a consequence of the composite nature of the diffusion coefficient evaluated by this technique, with contributions from both the hydrodynamic and the gel modes to the decay of a macroscopic gradient. Comparison of Figure 4, parts A and B shows that while the gradient data are highly molecular weight dependent, the cumulants-evaluated data from QELS are strictly molecular weight independent over the same concentration interval. Moreover, the $\bar{D}_{\mathrm{CGD}}$ values are significantly lower at a given concentration. While the cumulants value represents the weighted average of the two cooperative modes sampled in the QELS experiment, the gradient values will also reflect processes occurring over a much longer time scale. The self-diffusion of single and multiple chains in the semidilute network, for example, is highly molecular weight dependent. We find the base-line term to have significant weighting, and it tends to increase with increasing concentration. This term appears to comprise the slow mode, which has received attention in the literature, but the origin of which is still unclear. It may correspond to the q-independent slow relaxation described by Brochard.[2] An attempt was made to see whether this is a slow diffusional mode by using a three-exponent fit. The value of χ^2 was, however, found to be significantly lower with the five-parameter fit (with the third exponential set at an infinite number of channels) than for the six-parameter fit. Measurements were also made with longer sampling times and evaluation with a six-parameter fit, but it was found that the apparent relaxation rate corresponding to the third exponential decreases with increasing sampling time (see also ref 7). That the magnitude of the base-line term increases with concentration is suggestive of the formation of a microgel phase where the size of the particles increases with C. Recently, Eisele and Burchard[9] described a slow component in dynamic light scattering on poly(vinylpyrrolidone) in aqueous solution with an analogous character. *Significantly, they reported a parallel increase in the apparent radius of gyration with increasing concentration*, again indicating cluster formation.

Figure 5 shows the contribution of the gel mode (A_g) to the total intensity, and it increases slowly with increasing C in the range examined, while the amplitude of A_s decreases. These data resemble those for the PS–methyl acetate system described by Kubota et al.[15] and is the behavior qualitatively anticipated in the dilute–semidilute region: the number density of the segments and also their effective length remain approximately constant owing to the limited ability of large coils to interpenetrate. The corresponding quantity (A_f) in a good solvent shows[14] a

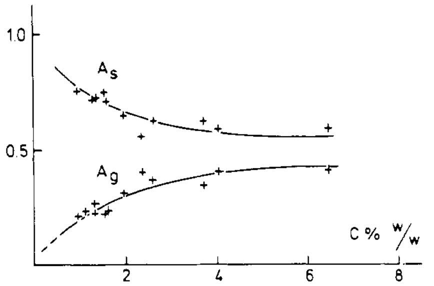

Figure 5. Relative intensity contributions of the gel mode (A_g) and the slow mode (A_s) as a function of concentration for PS ($M = 15 \times 10^6$) in cyclopentane at 21 °C: $\Theta = 40°$; $qR_G = 1.45$.

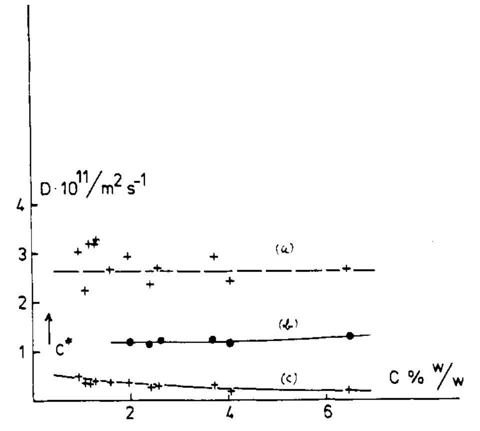

Figure 6. Concentration dependence of diffusion coefficients for semidilute solutions of PS ($M = 15 \times 10^6$) in cyclopentane at 21 °C. Symbols as in Figure 3. D_g and D_s are evaluated from plots of the type shown in Figure 1 ($C^* = 0.35\% = 3M/4\pi R_g{}^3N_A$).

more rapid rate of increase. This may be expected since the coil dimensions are correspondingly greater.

As the temperature is increased above the Θ point and the quality of the solvent improves, changes in the solution structure are anticipated. Data for the present system are shown in Figure 7, where ξ_D has been evaluated from D_g, D_s, and $\bar{D}_{\mathrm{cum}}$ at different temperatures in the vicinity of the Θ temperature using the relationship

$$\xi_D = k_B T/6\pi\eta_0 D \tag{6}$$

where $D = (\Gamma/q^2)_{q\to 0}$, k_B is Boltzmann's constant, and η_0 is the solvent viscosity. The predicted relationship between ξ_D and temperature is $\xi_D \sim \mathcal{T}^{-0.25}$, where $\mathcal{T} = (T - \Theta)/\Theta$ is the reduced temperature. This exponent has found support in neutron scattering measurements,[25] although a range of values has been reported. The exponents derived from the log–log plots of the data in Figure 7 are −0.37, −0.27, and −0.09 respectively for the slow mode, cumulants data, and fast mode. The more pronounced dependence of the slow cooperative mode on temperature is noteworthy and indicates a greater sensitivity to a polymer–solvent interaction parameter. We note that Munch et al.[10] find that the exponent in $\xi_D \sim \mathcal{T}^{-b_D}$ is sensitive to specific polymer–solvent interactions. This is not unexpected if the slow mode is related to the extent of interpenetration of the polymer coils.

Munch et al.[10] also observed the nonexponential nature of the correlation function and described the considerable change in the variance in the vicinity of the Θ point. The insert to Figure 7 shows such a trend for the present system. In the insert to Figure 7 we also depict the temperature dependence of the amplitude of the gel mode, A_g. These results contrast with those of Adam and Delsanti,[21] who suggest that the nonexponential character of the correlation function disappears at temperatures above the

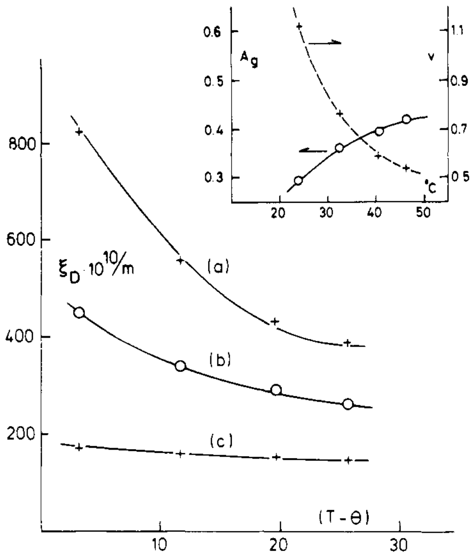

Figure 7. Dependence of the dynamic correlation length, ξ_D (eq 6), on the reduced temperature in the vicinity of the Θ point. (a) and (c) are respectively the slow and fast cooperative modes evaluated with eq 4; (b) uses cumulants data, $\bar{D}_{\mathrm{cum}}$. The exponent in $\xi_D \sim (T - \Theta)^{-b_D}$ has the values (a) −0.37, (b) −0.27, and (c) −0.09. The insert illustrates the temperature dependence of the gel mode intensity amplitude and the variance in the vicinity of the Θ point. All data are for PS $M = 15 \times 10^6$ in cyclopentane at $C = 1.7\%$ (w/w) ($C/C^* = 5.1$) at 21 °C.

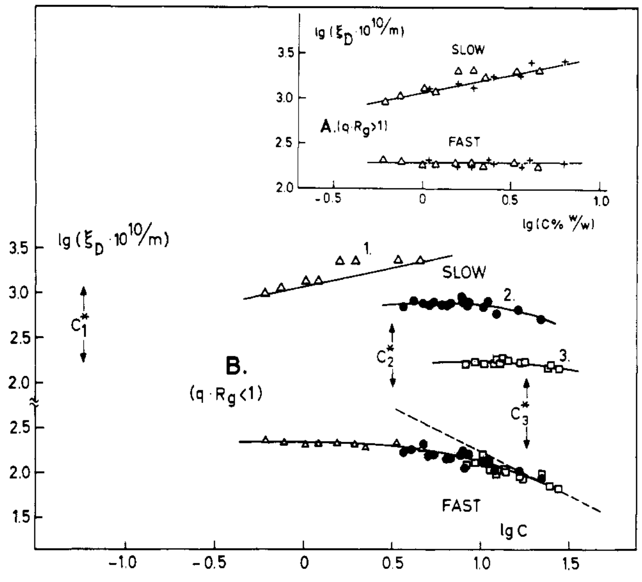

Figure 8. (A) log–log plot of ξ_D vs. C for data obtained with $qR_g > 1$. Data are for $M = 8 \times 10^6$ (△) and 15×10^6 (+). The fast and slow modes (eq 4) were used to calculate ξ_D with eq 6 ($\xi_D \sim C^{0.45}$ (slow); $\xi_D \sim C^0$ (fast)). (B) log–log plot of data at $qR_g < 1$. (1) $M = 8 \times 10^6$ (△); (2) $M = 9.3 \times 10^5$ (●); (3) $M = 9.3 \times 10^4$ (□). The appropriate values of C^* are indicated. The broken line has a slope of unity for comparison. Fast and slow diffusional modes (eq 4) have been used to calculate ξ_D (eq 6).

Θ point. Due to the anticipated slow approach to solution-structure equilibrium, it was of interest to remeasure the solutions after a period. They were then reexamined after 6 months from the first series and found to give essentially the same amplitude/relaxation rate behavior.

The data on PS, $M = 8 \times 10^6$, described above, have been complemented on a fraction with $M = 15 \times 10^6$ over a somewhat greater concentration range (up to $C/C^* \cong 10$). The results are summarized in Figures 6 and 8A. The latter shows that at $qR_g > 1$ both modes are molecular weight independent and are probed as cooperative motions. This conclusion also applies to the data in the good solvent

THF and the marginal solvent ethyl acetate. These modes thus will correspond to the gel and osmotic diffusion coefficients referred to in the Introduction. A small contribution from an even faster component could be detected at the highest concentrations when measurements were made with sampling times shorter (1×10^{-7} or 2×10^{-7} s) than the optimum value needed to simultaneously monitor the two main decay processes. It presumably arises from local modes of relaxation. Figure 8B illustrates data at $qR_g < 1$ for three molecular weights. Bimodal behavior is also observed. The fast mode is molecular weight independent. The broken line has been given a slope of unity for comparison with theory and is not unreasonable for an asymptotic value. The slow mode at $qR_g < 1$ is, however, molecular weight dependent and $\xi_D \sim M^{0.6}$ is a fair approximation. These data thus emphasize the previous conclusion[12] that at $qR_g < 1$ a gel mode and a translational component are represented in the time correlation function over extended ranges of concentration (up to 25% for $M = 9.3 \times 10^5$).

Discussion

The present data form a self-consistent picture and, moreover, one that is in substantial agreement with current theory[2] for the dynamical behavior of Θ solutions. It has not been possible on these very high molecular weight fractions to attain the extremely low angles required to make measurements in the $q < q_g$ region over a sufficiently wide span of concentration for direct examination of the concentration dependence of D_s ($\theta < 18°$ for PS 8×10^6). It is well documented that with intermediate molecular weights the composite $\bar{D}$ value such as that evaluated from QELS data at $qR_g < 1$ using the method of cumulants[10,15] initially decreases in dilute solution (in Θ solvents) and reflects the concentration dependence of the inverse friction coefficient of the isolated coil. It then remains approximately constant over a broad range of C before finally increasing as the gel character receives dominant weighting at increasing degrees of overlap (see Figure 4A). The same picture is seen with gradient diffusion measurements[17] (a time-averaged quantity). As was shown by Chu et al.[5,15] and Brown and Johnsen,[12] the correlation function is consistent with a bimodal expression, although more complicated alternatives cannot be excluded. It also cannot be contended that the components separated with current techniques are uncontaminated by other modes—either faster local modes or slower motions due, for example, to translational motions close to C^* and entanglement relaxations. The main feature, however, is adequate recognition of the composite character of the time correlation function for samples of both high and intermediate[12] molecular weight. Hecht et al.[4] made measurements at low angles on PS, $M = 26 \times 10^6$, in cyclohexane (Θ). The data were evaluated by the cumulants method, and $\bar{D}$ was found to be directly proportional to C. It is however doubtful whether $q < q_g$ is accessible to QELS measurement with such a high molecular weight and must then inevitably result in a mixture of the gel mode and slower motions. Nevertheless a definite tendency for ξ_D for the slow mode to decrease at the highest concentrations is shown in Figure 8B (i.e., an increase in D_s). A much greater concentration interval for the highest molecular weight will be necessary to establish the exponent.

Adam and Delsanti[7,21] recently reported a QELS study of the PS/cyclohexane system in which they force fit their $S(q,t)$data to a single exponential. In the $q > q_g$ region, as here, they evaluate a single diffusive mode using short sampling times together with a slow, q-independent, "structural" relaxation at long sampling times. The coefficient, D_g, derived in this manner was proportional to C, a conclusion in apparent conflict with these results. Although their procedure to obtain D_g may lead to a composite D value (since it is not possible to eliminate contributions from slower modes by reducing the sampling time) a slope of unity is not incompatible with the present data, as shown in Figure 8B by the broken line. If the contributing modes are inadequately separated, the concentration dependence will, however, be influenced by the progressive change in weighting of the fast and slow components as concentration increases.

It is relevant to note that Koberstein et al.[24] conclude that a unique value of the correlation length cannot be used as an adequate description of PS in cyclohexane (or in a good solvent) and that the semidilute solutions of higher molecular weight polymers are fundamentally heterogeneous regardless of solvent quality. These conclusions were based on results from elastic light and neutron scattering experiments. Such behavior thus qualitatively harmonizes with that here regarding two cooperative modes.

Amis et al.[8] dealt with bimodal characteristics of the PS/cyclohexane system (Θ). A fast (D_c) and a very slow mode—both q^2 dependent—were obtained from thee correlation function, using respectively short and long sampling times. The fast mode was, as here, found to be almost independent of C. On the other hand, the concentration and molecular weight dependences of the slow mode were in line with reptation models. Their slow mode is some several powers of 10 slower than the fast mode. It is possible that Amis et al. in fact characterize transient knots of chains or possibly microcrystallites resulting from the manner of solution preparation. With the present system, we were unable to separate D_g and D_s by varying the sampling time.

Štěpánek et al.[11,22] have used the Simplex approach and a procedure in which only the range of the possible relaxation times is given, with no assumptions regarding the number of components. In the PS/cyclohexane system they conclude that there are at least three modes present, of which the fastest (the gel mode) is again found to be practically independent of concentration.

Conclusions

As recognized by Brochard and de Gennes,[1,2] Θ solutions are considerably more complicated than their semidilute counterparts in good solvents, and they predict a slow hydrodynamic mode together with a fast gel mode in the $q > q_g$ region. It is shown here that the time correlation functions are consistent with a bimodal model and that the components are resolvable with the method of discrete multiexponentials. While the intensity amplitude of the fast mode is small (at least in the accessible concentration range), the gel mode coefficient is found to be concentration-independent in accordance with predictions. The complementary hydrodynamic mode decreases weakly with increasing C ($D_s \sim C^{-0.45}$). Both D_g and D_s are molecular weight independent, i.e., are cooperative in nature. (Surprisingly, this conclusion extends also to good solvents.[14]) The concentration dependence of D_s is then the point of departure from the predicted directly proportionality with C.

As shown in Figure 8B, the molecular weight independence reflects the limited concentration range used for these very high molecular weight samples. Clearly $10C^*$ is inadequate. Further work is needed to fully establish the concentration dependence of D_s by measurements in the low-q region on samples of high molecular weight over wider spans of concentration.

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The significant weighting of the base-line term in the present analysis, which includes a very slow relaxation, further complicates data interpretation for Θ systems. Estimation of an apparent relaxation rate shows that this slowest component(s) is of the magnitude of the disentanglement time T_R. Some aspects suggest that it may reflect the separation and rearrangement of entanglement zones.

A salient difference is noted here in comparison with the behavior in good solvent systems[14] where there is a smooth increase in the number density of segments of progressively shorter length as interpenetration proceeds. In a Θ solution of large molecules the coils may entangle in a more complex manner and lead to very slow structural rearrangements. Measurements are needed at higher concentrations, but the asymptotic semidilute region is experimentally difficult to gain access to for high molecular weight samples. The structural relaxation referred to above seems to be the limiting factor in applying the QELS technique to such systems. Developments in multi-τ correlators provide optimism for future studies of this feature.

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Effect of Tube Renewal on the Viscoelastic Properties of Concentrated Solutions of Polymers

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ABSTRACT: The viscoelastic properties of binary blends of polystyrene fractions have been studied in the terminal region of relaxation. Since one of the components is entangled ($M > M_c$), these blends are in fact concentrated polystyrene solutions, the low molecular weight component acting as a solvent. The effect of molecular weight on the so-called "monomeric" friction factor ζ_0 has been quantified. An improvement of the reptation model is proposed, taking into account the "tube renewal" mechanism. Reasonable agreement was found with experimental data relative to the viscoelastic parameters of the entangled component (i.e., steady-state recoverable compliance $J_e°$, terminal relaxation time τ_0, and zero-shear viscosity η_0). The main results are that $J_e°$ varies with the high molecular weight polymer volume fraction ϕ as ϕ^{-2} and that τ_0 and η_0 exhibit values far from a pure reptation behavior for $\phi M/M_e < 30$–50; the reptation regime is however achieved at higher entanglement density.

Introduction

Many studies[1-6] have been performed on the viscoelastic properties of concentrated polymer solutions. The diluents used are good solvents, Θ solvents, or even commercial oils. Some data were presented for solutions in which the solvent was a low molecular weight polymer of the same species as the entangled polymer.[4,5] The concentration dependences of the plateau modulus $G_N°$ and steady-state recoverable compliance $J_e°$ generally follow power laws: $G_N° \propto \phi^a$ and $J_e° \propto \phi^{-a}$, with $2.0 < a < 2.3$ (ϕ is the volume fraction of polymer). But the viscosity data vary strongly according to the authors, from ϕ^3 to ϕ^6 and even higher exponent values. The main reason for these discrepancies in exponent values for the concentration dependence of viscosity is the "correction" or "noncorrection" of the viscosity through the friction factor ζ_0. Empirical[7] and theoretical[8,9] models indeed provide

$$\eta_0 \propto \phi \zeta_0 M_e (M/M_e)^b \qquad (1)$$

where the average spacing between entanglements, M_e, depends on polymer concentration as ϕ^{-1}. So, the exponent b can be calculated from the variation of η_0/ζ_0 vs. ϕM.

The friction factor ζ_0 depends on temperature, concentration, and diluent nature. Its temperature dependence is the same as that of the viscosity η_0 and is represented by the WLF equation. The parameters of the WLF

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