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Distribution of Relaxation Times from Dynamic Light Scattering on Semidilute Solutions: Polystyrene in Ethyl Acetate as a Function of Temperature from Good to Θ Conditions

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ABSTRACT: Intensity correlation functions have been measured over widely spaced delay times, covering 6–8 decades, for polystyrene in semidilute solutions of ethyl acetate. The solvent quality was changed systematically by varying the temperature from +70 (moderately good) to −44 °C (Θ conditions). Measurements were performed as a function of both angle and concentration. Distributions of relaxation times were extracted from the correlation functions by inverse Laplace transformation (CONTIN and PES methods). Three relaxational modes are established in the decay time spectrum. The fast mode corresponds to network dynamics ($\mathbf{K}^2$ dependent), while the following tentative assignments of the slower modes are made: (a) middle mode, insufficiently resolved for characterization, possibly contaminated by another dynamical process; (b) slow mode ($\mathbf{K}^2$ dependent), characterizes the concentration fluctuations associated with the motions of clusters of chains.

Introduction

Semidilute solutions of macromolecules have in recent years attracted considerable attention. In one of the most fruitful approaches to such systems, the application of scaling theory to polymer solutions, summarized in book form by de Gennes,[1] has greatly stimulated experimental work in endeavors to confirm these ideas. As a result, the overall concepts of the static and dynamic properties of the so-called "transient gel" have been substantiated, although inevitably with such a sweeping approach there are areas where considerable and disturbing ambiguities remain. One of the reasons for this is that scaling theory predicts limiting exponents which are consequently difficult to verify under the curtailments of real experimental situations. In experimental investigations of the dynamic behavior of semidilute solutions, dynamic light scattering (QELS) represents the single most powerful tool that has been applied to their study, although significant contributions have also been made through application of quasielastic neutron scattering[2,3] and forced Rayleigh scattering[4–6] (FRS) techniques.

Single-coil translational motion may be measured in dilute solution at low values of the scattering vector ($\mathbf{K}$) such that $R_g/\mathbf{K}^{-1} \ll 1$, where R_g is the radius of gyration, while a cooperative diffusion coefficient related to the dynamic correlation length and defining the transient gel is obtained in semidilute solution. It is clear, however, that the proposed transition in solution structure at $C \cong C^*$ to the transient gel will in reality be gradual, and this is exemplified by the different numerical and empirical values for C^* in the literature.

With finite molecular weights, a homogeneous gel (as postulated in theoretical models and which would correspond at a particular concentration to a unique value of the correlation length) may not even be reached over the accessible range of polymer concentration.

Numerous QELS experiments on semidilute systems have shown that the intensity autocorrelation function clearly deviates from the anticipated single-exponential function even in a good solvent.[8–10] This behavior becomes increasingly accentuated with a decrease in solvent quality,[11] and ultimately the line shape is strongly nonexponential in Θ systems.[11,34,39] Since light scattering is usually bedevilled by problems with dust and/or aggregates, there has inevitably been a continuing debate as to their possible role in causing at least a part of this phenomenon. However, the systematic trends in the data[11,12] have led to the conclusion that the decay time spectra,[13–15] which may be obtained by applying analytical techniques to the correlation function, do in fact reflect multiple length scales; their origin is still in debate at this point. One possible interpretation would be that there are differences in the extent of coil interpenetration in the precursor stage of transient network formation, which apparently extend over a hitherto unexpectedly broad concentration range. This view has received significant support from results of small-angle neutron scattering experiments[16] and recently from a novel study[17] using a fluorescence method. These data tend to confirm earlier conclusions of Dautzenberg[18] in this regard.

Since dilution of the semidilute solutions to dilute solutions yields correlation functions that are close to single exponentials,[10] the observed nonexponentiality cannot be in the main a polydispersity effect. Recent experiments[13–15] in which the QELS data have been analyzed by using the CONTIN method[22] have shown that the origin of the broad line width probably lies in contributions from several *discrete* modes of relaxation. In light of the above-mentioned increase in line width with decreasing solvent quality, it is the purpose of the present article to describe a more systematic approach to the problem that is greatly aided by the use of a so-called multi-τ autocorrelator making possible an interpretation in terms of the decay time spectrum from data accumulated in a single experiment. The system polystyrene (PS)/ethyl acetate was selected. As was described in a previous report,[11] a variation in solvent quality may be achieved by the progressive addition of the isorefractive nonsolvent ethanol, and Θ conditions are ultimately reached at about 10% ethanol at 25 °C. However, the ternary system is potentially complicated by the preferential sorption of the better solvent, and it was deemed better to vary solvent quality by means of temperature change. The accessible range is from about +70 °C (moderately good solvent) to Θ conditions at about −44 °C.[19] Preliminary reports[14,15] have described certain aspects of these experiments. This paper reports the results of analysis of the correlation functions obtained in QELS experiments as a function of PS concentration in the range C^* to $42C^{*7}$ and of the scattering vector.

Even with the use of a broad-band multi-τ correlator, the simultaneous registration of all portions of the decay

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time spectrum with sufficient resolution for adequate characterization will lie at the limit of what is currently feasible. In this first contribution we give an overall view where the primary goal has been to clearly establish the presence of multiple modes in semidilute solutions, which had been strongly indicated in prior studies. A precise description of the slower modes and hence their origin, which is the ultimate objective, is still the subject of ongoing investigations.

Experimental Section

Solutions were prepared in the range 0.2×10^{-2} to 7.2×10^{-2} g mL^{-1} from a nearly monodisperse PS standard (Toya Soda Ltd., Tokyo) $\bar{M}_w = 2.95 \times 10^6$ and $\bar{M}_w/\bar{M}_n = 1.05$. The ethyl acetate was of spectroscopic grade. Initial experiments showed that trace amounts of water, probably mainly occluded in the PS (since careful drying of the solvent over molecular sieves failed to remove the effect) caused phase separation (clouding) at temperatures below −30 °C. Water-free and essentially dust-free semidilute solutions were prepared as follows: A stock solution of PS in spectroscopic grade cyclopentane was prepared at a concentration of 0.5%, and this was centrifuged at 10 000 rpm for 1 h. The measurement cell linkable to the vacuum line was flushed with acetone vapor to remove dust, dried, and then filled with a known amount of the PS/cyclopentane solution taken from the upper half of the centrifuged cell. The cyclopentane was evaporated. The measurement cells were then coupled to the vacuum line, as well as to a container containing previously dried ethyl acetate (over CaH_2 for 48 h). The ethyl acetate was then degassed by repeated freezing and thawing in liquid nitrogen under high vacuum. Still under vacuum, a predetermined amount of ethyl acetate was allowed to condense into the sample cell by cooling it in an ethanol/solid CO_2 mixture and heating the solvent container with a water bath. The sample cell was finally flame sealed at −70 °C without freezing the solvent (freezing point −82 °C). The final concentration was determined by weighing. The solutions were allowed to homogenize for 3 months with occasional shaking.

Apparatus. Complementary measurements were made on photon correlation spectrometers in Prague and in Uppsala and have been described before.[20,21] The light source in each case was an Ar ion laser. With the first apparatus (Prague) a real-time, single-bit 96-channel digital correlator was employed for sampling times shorter than 1 ms, and a 100-channel analogue correlator (Hewlett-Packard 3721-A) for longer sampling times.

With the Uppsala apparatus an ALV-Langen Co. multibit, multi-τ correlator was operated with 23 simultaneous sampling times which cover, for example, delay times over the range 1 μs to 1 min. The sample was thermostated in an index-matching liquid. The temperature could be regulated within the range −140 to +120 °C (Prague) and −20 to +70 °C (Uppsala).

Data Treatment. The correlation curves obtained with the Prague apparatus were computer-spliced to produce the composite curve having 800–1100 points as described in ref 13.

The ALV autocorrelator yields directly a correlation curve covering 6–8 decades in delay time. The multi-τ and composite correlation curves, measured under identical conditions on the same solutions, were found to be precisely superimposable. This is illustrated for the curves at an angle of 60° in Figure 5. This gives confidence in both the use of different apparatus and also the method used to obtain the composite correlation curves.

Two different methods have been used to analyze the autocorrelation functions:

(a) CONTIN.[22] This method uses a grid of fixed components (here we have used typically 90–120 components) and finds their amplitude. Stock and Ray[23] have recently found that CONTIN tends to oversmooth the spectrum of decay times. However, their testing was confined to only a narrow region (about 2 decades). Jakeš[24] has performed a further test that showed that for a wide spectrum of decay times CONTIN seriously undersmooths in the region of short decay times, whereas it oversmooths on the long-time side. This behavior could be eliminated by setting IQUAD = 1 instead of the standard IQUAD = 3, although there is still a tendency to replace asymmetric peaks by more symmetric ones. These aspects have been discussed by Jakeš[24] with reference to simulated autocorrelation functions of a very wide time span. It was occasionally found that small systematic errors (of a fraction of root mean square noise) in the correlation curves can lead to false peaks in the "chosen" solution. We have thus preferred to use solutions with a regularization parameter greater than that of the chosen solution.

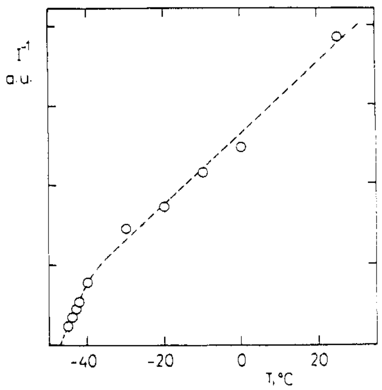

Figure 1. Temperature dependence of the reciprocal intensity of light scattered at $\theta = 60°$ with a PS sample of concentration $C = 0.0227$ g mL^{-1} in ethyl acetate.

(b) The Positive Coefficients Exponential Sum (PES) Method.[25] This uses floating components and in successive steps finds the absolute minimum of the sum of squares of residuals. While CONTIN is pseudocontinuous with fixed components and yields an estimate of the distribution of decay times, the PES method is discrete with floating components. Both methods use the sum of squares of residuals.

Results and Discussion

Determination of the Θ Temperature (PS/Ethyl Acetate System). Saeki et al.[19] estimated the Θ temperature for the PS/ethyl acetate system by extrapolation and obtained the value −44 °C. We have checked this by total intensity measurements on a solution with a concentration ($C = 2.27 \times 10^{-2}$ g mL^{-1}) which is close to the crossover concentration C^*_Θ. Assuming that the empirical relationship $C^*_\Theta = 40/M^{1/2}$ as used in ref 27 for the PS/cyclohexane system is also valid here, we obtain $C^*_\Theta = 2.3 \times 10^{-2}$ g mL^{-1} for the present molecular weight. In the same reference, the expression $\Delta T = 3000/M^{1/2}$ is given for the temperature interval between the Θ temperature and the demixing temperature for a solution of concentration C^*_Θ. For the present molecular weight, we obtain $\Delta T = 1.7$ °C. Figure 1 shows a plot of the reciprocal intensity of light scattering at $\theta = 60°$ by this solution as a function of temperature. The demixing temperature (i.e., the intercept with the T axis corresponding to infinite scattered intensity) is found to be $T_D = -46 \pm 1$ °C. The Θ temperature is estimated as $\Theta = -44.3 \pm 1$ °C. Thus the accessible temperature range in solutions of PS in ethyl acetate extend from about −44 to +77 °C, the boiling point of ethyl acetate.

Dynamic Light Scattering. Autocorrelation curves were taken up as described under the section Data Treatment, either by using the composite curve formed by computer-splicing a suitable number of consecutively made runs of progressively increased sampling time so as to cover the whole range of decay processes (Prague) or else by using a multi-τ autocorrelator (Uppsala). Measurements were made at a series of temperatures in the range −44 to +70 °C for a series of concentrations covering the range 0.2×10^{-2} (approximately C^* at 25 °C) to 7.2×10^{-2} g mL^{-1} ($\simeq 42C^*$) at a fixed angle of $\theta = 60°$. At 26 °C the measurements were extended over the angular range 30–120° at each concentration.

The values of the measurement parameters at the latter temperature are shown with reference to the $\mathbf{K}R_g$ versus

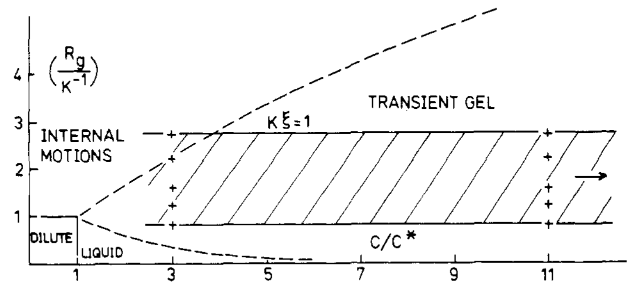

Figure 2. $\mathbf{K}R_g$ versus C/C^* diagram[28] showing the localization of the measurements as a function of angle and concentration (C). ξ is the correlation length characterizing the network, $\mathbf{K}$ the scattering vector, and R_g the radius of gyration. The C^* values[7] used here refer to a temperature of 25 °C.

C/C^* diagram[28] in Figure 2. The experiments thus refer, in general, to the transient gel regime.

Figure 3A shows a typical series of correlation curves for a PS concentration of 5.3×10^{-2} g mL^{-1} ($31C^*$ at 26 °C). A shift to longer decay time is discernible with decreasing temperature. This is, in part, due to the increase in the solvent viscosity. There is also a distinct trend in the shape of the correlation function with temperature change. This change becomes more clear in the CONTIN inversion of the curves in Figure 3A, which are shown in Figure 3B. Three different decay processes are distinguishable, and these subsequently will be referred to as the fast, middle, and slow modes. The changes in the relative amplitudes of the peaks are pronounced: the fast mode shows a monotonic decrease and the middle mode a progressive increase as the temperature is decreased. The slow mode initially increases in relative amplitude but diminishes again as the Θ temperature is approached.

Three components are present in the decay time spectra obtained with CONTIN even with a regularization parameter that is larger by 2 orders of magnitude than that of the "chosen" solution. We thus consider that these modes, which are very widely spaced on the time scale and consequently easily separated, correspond to real physical processes. The CONTIN fits should be seen as the simplest that are consistent with the data, and more complicated alternatives cannot be excluded. The present resolution into three modes is reinforced by application of an intrinsically different analytical procedure (the PES method;[24] see Data Treatment), the results of which are shown by the vertical lines in Figure 3B. These generally conform well with the CONTIN distribution. It will be recalled, however, that the PES method finds the absolute minimum of the sum of squares of deviations, disregarding all other aspects of the problem. In particular it cannot decide whether the components found describe a single broad peak or a set of more narrow peaks. Thus the method should not be used as the sole approach to understanding the content of a correlation function. As a consequence of the above, some differences may be found between the CONTIN and PES results and in particular with the slowest mode(s). This is due to the greater sensitivity of the PES method to noise in the long delay time part of the correlation function, close to the base line. This complicates the exact localization of the slow peak. Both methods agree nonetheless that the slow modes exist. One may observe that the trends in the relative amplitudes are not consistent with the behavior expected if dust were the source of the slower modes: the latter would be expected to contribute an approximately constant proportion to the spectrum for a given solution with change in temperature.

We note that an evaluation using the cumulants method gives a weighted average of D that agrees with the quantity estimated from decay times and amplitudes of the modes resulting from the CONTIN inversion.

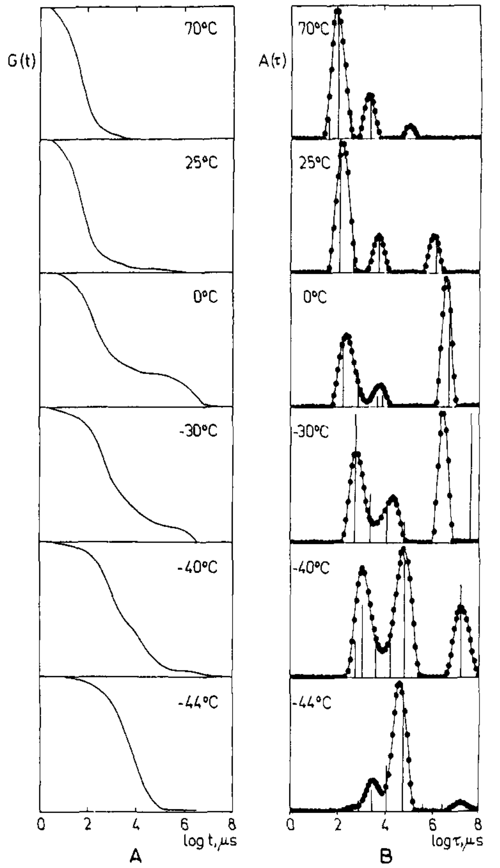

Figure 3. (A) Time-correlation functions at various temperatures for a PS sample at a concentration $C = 0.053$ g mL^{-1} measured at $\theta = 60°$. (B) Distribution of relaxation times obtained from the curves in Figure 3A by inverse Laplace transformation. Full line, CONTIN[22] results; vertical lines, PES[24] results.

We emphasize here the necessity of recording the "entire" time correlation function. Use of an autocorrelator with a single sampling time facility and with an inappropriate setting for a particular decay process in the spectrum may not reveal its presence if it is of low amplitude. The earlier papers[29,30] on the semidilute PS/ethyl acetate system at ambient temperature apparently failed to register the participation of the slower modes even though these become the dominant feature as the temperature is reduced. However, a large value of the second cumulant was noted[29,30] when the diffusion coefficient was evaluated by using the cumulants method, and this is an indirect acknowledgment of the complexity of the decay function.

The decay times and relative amplitudes of the constituent modes were determined from the moments of the CONTIN inversion peaks. The values of the decay times for the fast mode were always well-defined and with low scatter, whereas the scatter associated with the middle and slow modes was considerably larger. Improved results could be obtained for the slow mode when the correlation function was limited to delay times longer than that of the middle mode. A single-exponential function was force-fitted to this part of the curve. It is noted that the resulting decay time did not change significantly when the position of the first point of the partial curve was varied somewhat.

The dynamic correlation length, ξ_H, has been evaluated as

$$\xi_H = kT/(6\pi\eta_0 D) \qquad (1)$$

where η_0 is the viscosity of ethyl acetate taken from the

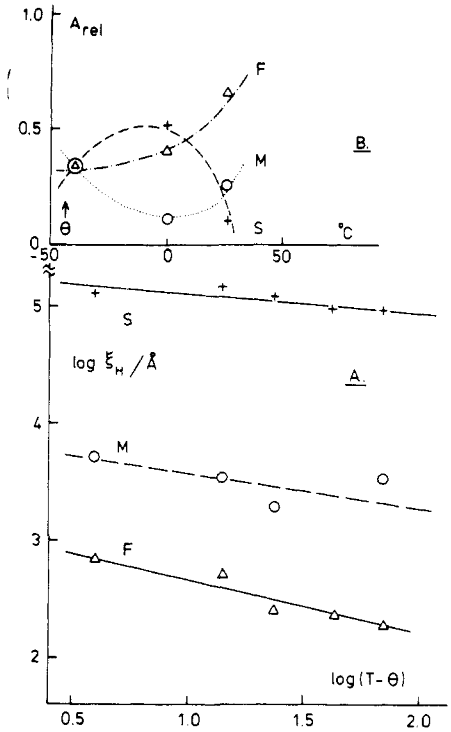

Figure 4. (A) log–log diagram of the dynamic correlation length (ξ_H) from eq 1 versus ($T - \Theta$) where Θ is the Θ temperature. Data are for $C = 0.0227$ g mL^{-1} and measurement angle 60°. (B) Change in the relative amplitude of fast (F), middle (M), and slow (S) modes with temperature; Θ temperature $\cong -40$ °C.

literature[32] within the range −5 to +70 °C. Extrapolated estimates were used for the lower temperatures taken from a log η_0 versus log T diagram. D is the diffusion coefficient ($=\Gamma/\mathbf{K}^2$) determined from the relaxation rate (Γ) for each mode, since the latter are approximately $\mathbf{K}^2$ dependent (see below).

The change in the dynamic length with temperature for each mode is shown in Figure 4. In semidilute solutions one anticipates[26,27,33,46] an increase in ξ_H with decreasing temperature, and the predicted relationship between ξ_H and the reduced temperature τ (where $\tau = (T - \Theta)/\Theta$) is

$$\xi_H \sim \tau^{-b_H}$$

The value $b_H = -0.25$ has been predicted[26] for good solvents and has received support from neutron scattering measurements.[27] Adam and Delsanti[46] give a value of −0.33 for the PS/cyclohexane system in the vicinity of the Θ temperature. The values of the exponents taken from Figure 4 are

$$\text{slow:}\quad b_H = -0.16$$
$$\text{middle:}\quad b_H = -0.3$$
$$\text{fast:}\quad b_H = -0.44$$

Using mean field theory, Schaefer et al.[30] predict $b_H = -0.5$ for marginal solvents, and experimentally they have determined[31] a value of −0.49 for the PS/cyclopentane system at a volume fraction PS of 0.025.

The relative amplitudes of the modes are shown as a function of temperature in Figure 4B. These data reveal a complicated interdependence, with the fast mode dominating at the highest temperature. When the measured total intensity is apportioned between the modes according to the moments of the peaks (see ref 14), this quantity is found to be almost temperature invariant for the three modes, except in the vicinity of the Θ temperature, where the middle mode displays a strong increase.

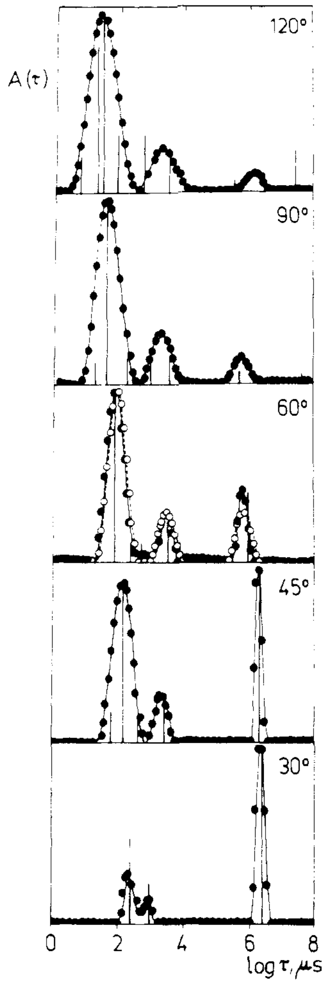

Figure 5. Distribution of relaxation times at 26 °C measured at different angles on a sample with $C = 0.053$ g mL^{-1} ($\simeq 31C^*$): (●) from multi-τ correlation curves; (○) from composite correlation curves; vertical lines, PES results.

The dependence of the inverse relaxation time on the scattering vector $\mathbf{K}$ ($\mathbf{K} = 4\pi/\lambda$) sin ($\theta/2$), where λ is the wavelength of the light in the medium and θ is the scattering angle) can provide further information as to the nature of the individual modes. Multi-τ correlation curves were taken up as a function of angle at each concentration. The corresponding CONTIN inversion results and PES analyses are shown for the data obtained at ambient temperature (26 °C) at $C = 5.3 \times 10^{-2}$ g mL^{-1} in Figure 5. The three modes are most clearly represented at intermediate angles (e.g., $\theta = 60°$), but there is a clear progressive trend from fast mode domination at the high-angle limit to domination by the slow modes at $\theta = 30°$.

The fast mode is well represented at 26 °C at all concentrations. These data are depicted in Figure 6A, which shows the relaxation frequency as a function of sin^2 ($\theta/2$). The fast mode is diffusive (i.e., $\Gamma_F \sim \mathbf{K}^2$) and is considered to reflect the dynamics of the transient network. This conclusion is also supported by the value of the concentration exponent discussed below.

The middle and slow modes (Figures 6B and 6C) are of comparatively low intensity at 26 °C (see also Figure 4B), and there is a correspondingly large scatter in the data. The QELS runs were of long duration to obtain an improved resolution, and a more detailed grid of fixed components (90–120 instead of the standard 30 components) was used in the CONTIN analyses. The middle mode, however, shows a finite intercept in the Γ versus sin^2 ($\theta/2$) plots, which suggests contamination with another relaxa-

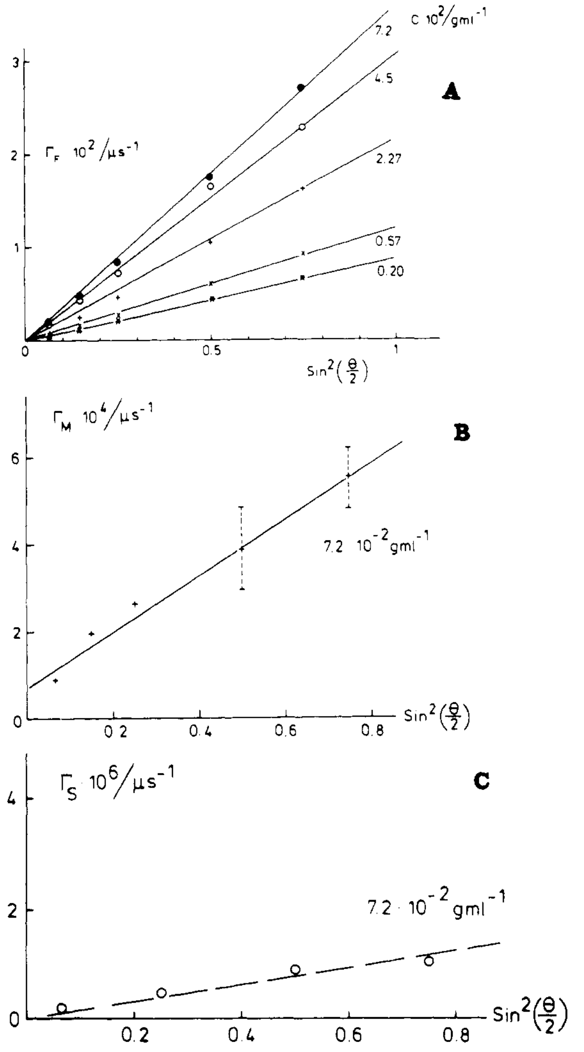

Figure 6. Relaxation rate ($\Gamma/\mu s^{-1}$) as a function of $\sin^2(\theta/2)$ at different concentrations for the fast mode (A), middle (B), and slow (C) modes at 0.072 g mL^{-1}.

tion process. The angular dependence is too poorly defined to allow conclusions as to the source of this mode.

The relaxation rate of the slow mode is approximately $\mathbf{K}^2$ dependent. Data for the long-time portion of the curve were also evaluated by a single-exponential forced fit. It is stressed that with currently available apparatus, the middle and slow modes lie at the limit of characterization possibility. But even if certain questions remain regarding their precise nature, the existence of the slower modes is clearly established: they are physical entities that are essential aspects of semidilute solution behavior. We note that earlier QELS studies on Θ systems[13,34] have interpreted the slowest mode detected as a structural relaxation, i.e., **K** independent. The uncertainties attending the precise definition of this mode are such that its **K** dependence may be more complicated than envisaged. Takahashi and Nose[35] have recently described the behavior of PS in cyclohexane in the crossover region from Θ to critical temperature. In semidilute solution the time correlation function was fit with a bimodal model, the line width of the fast mode being $\mathbf{K}^2$ dependent, while a finite intercept was found for the slow mode relaxation rate.

Figure 7 shows data from intensity light scattering measurements (Sofica instrument, Prague). The reduced intensity function decreases strongly toward low angles, suggesting the presence of transient clusters of chains.

Figure 8 depicts the angular dependence of the quantity $1/(A_i \sin\theta)$ where A_i is the intensity attributed to each mode. The latter quantity was estimated by combining the relative intensities calculated from the moments of the CONTIN peaks and the measured integral intensity. This procedure is only approximate, however, since correction should be made[36] for the difference in weighting caused by the size polydispersity of the scattering particles. The term sin Θ is introduced to compensate for the variation in scattering volume. The quantity $(A_i \sin\theta)^{-1}$ has a much stronger angular dependence in the case of the slow mode, indicating that this is the major source of the angular dependence of the integrated intensity in Figure 7.

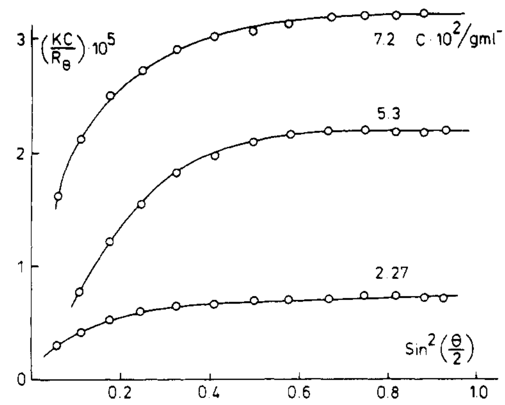

Figure 7. Intensity light scattering data: $\mathbf{K}C/R_\Theta$ versus $\sin^2(\theta/2)$ at different PS concentrations in ethyl acetate as shown, at 26 °C.

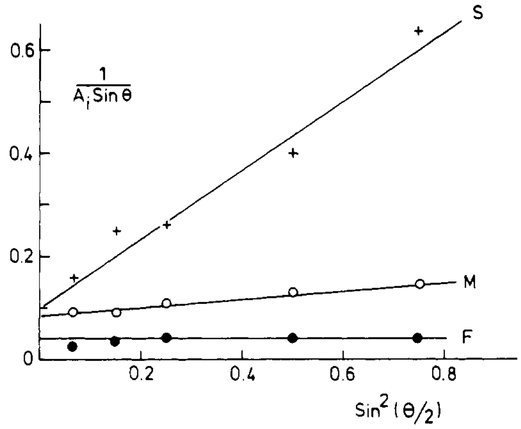

Figure 8. Dependence of the reciprocal intensity (obtained by apportioning the measured integral intensity between the modes by using the relative amplitudes from CONTIN results) on $\sin^2(\theta/2)$ at 26 °C.

Figure 9A illustrates typical time correlation functions measured at semidilute concentrations from C^* to $42C^*$. Distinct changes in their shape are apparent with increasing concentration. Figure 9B shows the corresponding CONTIN inversions of the curves in Figure 9A, and these confirm the qualitative observation that three decay processes exist. Below the overlap concentration ($\simeq 0.2 \times 10^{-2}$ g mL^{-1}) the correlation function is, to a first approximation, a single exponential. It may be noted here that an extensive investigation[37,38] of a very high molecular weight PS ($\bar{M}_w = 15 \times 10^6$) in the Θ solvent cyclopentane (21 °C) has also revealed three modes. The inference is that several modes are a general feature of semidilute solution structure in poorer solvents. Future work will be directed to a reinvestigation of good solvent systems at high concentration for which bimodal behavior has earlier[10] been reported.

Figure 10 shows the concentration dependence of the individual decay rates (Γ) in a log–log diagram at 26 (Figure 10A) and −40 °C (Figure 10B). At 26 °C the fast

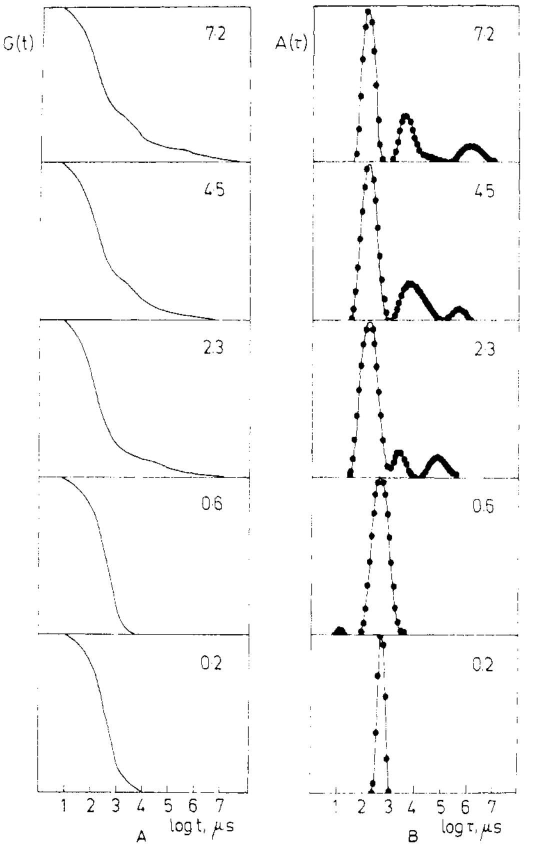

Figure 9. (A) Correlation functions ($G(t)$ versus log $t/\mu s$) at the concentrations shown (10^2C/g mL^{-1}) for PS in ethyl acetate at 26 °C and $\theta = 60°$. (B) Corresponding distribution of relaxation times using CONTIN.

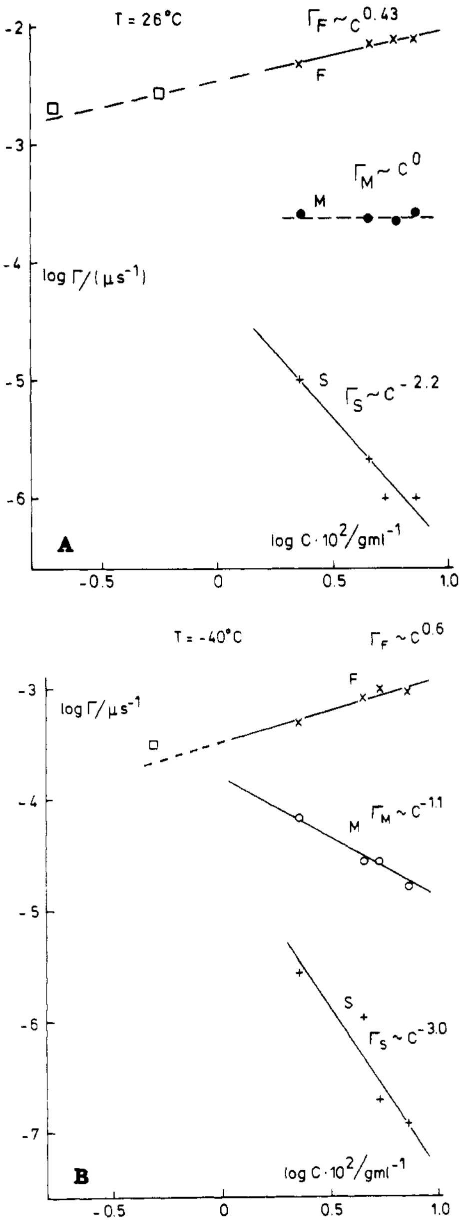

Figure 10. (A) log–log plots of the relaxation rate ($\Gamma/\mu s^{-1}$) versus concentration for the three modes at 26 °C. The concentration exponents are as indicated. The symbol □ denotes data for the single-exponential correlation function below or approximately at C^*. (B) Data at −40 °C; symbols are as in A.

mode has a concentration dependence given by $\Gamma_F = C^{0.43}$, and this value agrees well with previous findings for the network mode in semidilute marginal solvents. An exponent of 0.5 was predicted by Schaefer et al.[30] by application of mean-field theory. They found an experimental value of 0.4, which was referred to the average relaxation rate that had been evaluated using a cumulants method. It was noted that the time correlation functions were strongly nonexponential. Brown has subsequently reported[12] a value of 0.43 using a similar evaluation procedure but also interpreted the nonexponentiality in terms of a bimodal model. All experimental approaches to marginal solvent systems have indicated a substantially lower exponent than that predicted (0.75) by scaling theory[1] in termodynamically good solvents (see, for example, ref 28). At −40 °C the exponent for the fast mode is found to be greater ($\Gamma_F \sim C^{0.65}$), but the value of the Θ-state gel mode concentration exponent appears to be controversial (cf. ref 34 and 52). In a parallel investigation of the PS/cyclopentane Θ system[38] an exponent of 0.6 was also found. Takahashi and Nose[35] also find a very low fast mode exponent in the PS/cyclohexane system, as do Amis et al.[39]

The middle mode appears to be approximately concentration independent at 26 °C, whereas the concentration exponent has the value −1.1 at −40 °C close to Θ conditions.

The slow mode relaxation rate exhibits a stronger negative dependence on concentration than the middle mode. The exponents are −2.2 at 26 °C and −3 at −40 °C. While the value at ambient temperature is somewhat greater than predicted for reptation in a good solvent (−1.75), we are not aware of the value to be expected in a marginal solvent. The exponent at −40 °C agrees with that predicted by scaling theory[1] for Θ systems. However, in spite of this agreement, the accumulated data for the slowest mode do not support a reptation mechanism. Deschamps and Leger[6] have recently reported self-diffusion coefficients for PS in a Θ system. An estimation by extrapolation from their data indicates that the present slowest mode is nearly 2 orders of magnitude slower than that corresponding to hydrodynamic motion of a single chain. This and the $\mathbf{K}^2$ dependence of its decay rate suggest that the slow mode may instead derive from translational motions of transient clusters of chains. A similar phenomenon has been demonstrated[21] in semidilute solutions of poly(ethylene oxide) by a comparison of QELS and pulsed field gradient NMR data. It was shown there that both the concentration and molecular weight dependences of the diffusion coefficients paralleled those predicted by using the reptation model (also showing that these indices can provide only partial evidence that such a mechanism may be operative). One may also note that Kolinski et al.[40–42] and Rendell et al.[43] have recently discussed alternative transport mechanisms in entangled systems that also lead to the same scaling behavior as predicted by the reptation model. We also

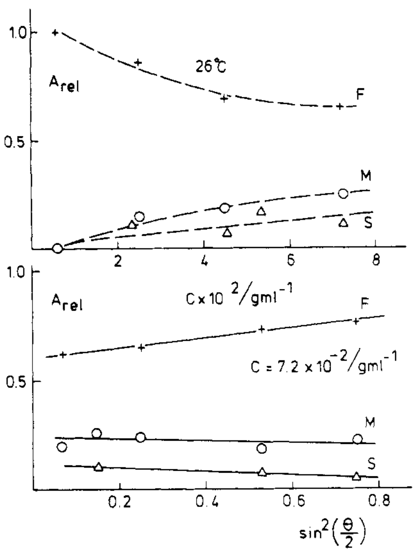

Figure 11. Relative intensity (A_{rel}) for the three modes derived from the moments of the CONTIN peaks, shown as a function of (top) concentration at angle $\theta = 60°$ and (bottom) angle at a concentration of $C = 0.072$ g mL^{-1}. Data are at 26 °C.

note the similar analysis of the problem made by Chang and Yu.[44]

In this context we would draw attention to the interpretation of QELS data for the poly(vinylpyrrolidone)/H_2O system[45] in semidilute solution, where support is found for cluster formation as a source of the slow mode. The viewpoint was subsequently expressed[47] that the clusters represent the precursor stage in network formation.

The above discussion, although speculative, finds support in the intensity light scattering data in Figure 7, where the reduced intensity function decreases strongly at low angles. This is consistent with the presence of large particles, which increasingly dominate the scattering pattern as the concentration is increased. We exclude dust as a contributing factor from the method used to prepare the solutions. Furthermore, the measurements at +70 °C display only a very small relative amplitude of this mode, but it becomes increasingly emphasized in the same solution as the temperature is lowered. Were dust responsible for the slow mode, it would be most in evidence at the high-temperaure end, where the scattering from the polymer is lowest.

Figure 11 shows the relative intensities of the modes as a function of (top) concentration and (bottom) $\sin^2(\theta/2)$. At low concentrations, i.e., below 0.02 g mL^{-1} ($\sim 10C^*$ at 26 °C), only the fast mode has a significant amplitude (see also Figure 9A). The middle and slow modes are more accentuated toward higher concentration. The relative intensities are, however, strongly dependent on temperature as shown in Figure 3B, the middle mode increasing strongly toward the Θ temperature. The relative intensities all show a weak angular dependence.

The previous reports[11,12] dealing with the behavior of semidilute PS solutions in ethyl acetate used a bimodal model to interpret the correlation curves. We note that these correspond rather closely to the presently determined fast and middle modes, the slowest mode not having been resolved from the base line in the first-named papers.

Conclusions

The presence of three relaxational modes is established in the decay time spectra of semidilute solutions ($\sim C^* \rightarrow 42C^*$) of PS in ethyl acetate over a range of temperatures extending from moderately good solvent quality at +70 °C to Θ conditions at about −44 °C.

Although the methods used (CONTIN and PES) provide only semiquantitative information on the distributions, the agreement between the two intrinsically different analyses is very encouraging (Figures 3B and 5). More recently, we have performed complementary analyses of correlation functions using the maximum entropy method, the use of which is known not to introduce spurious peaks.[49-51] Using both simulated data and experiments selected from those reported here, we have found consistent agreement with the distributions resulting from the CONTIN inversion.

As (a) temperature, (b) concentration of PS, and (c) measurement angle are varied, there are systematic trends in the distribution of relaxation times, showing that the observed phenomena are not artifacts. It has been shown that the alternative use of either computer splicing of successive runs of increasing sampling time or the use of a broad-band multi-τ autocorrelator is essential for establishing the complete distribution, which ranges over 6–8 decades on the time scale. Although one should be very careful in drawing conclusions from a single CONTIN inversion, the separation of the modes is quite unambiguous when large series of angular and temperature dependences of correlation curves are compared. However, the low intensities of the slower modes, in combination with the general use of autocorrelators with a limited resolution width, has inhibited a broad approach in terms of the simultaneous recording of several relaxation processes in earlier studies.

The present fast mode corresponds to the motions characterizing the interentanglement points of the transient gel. We have been unable to unequivocally establish the origins of the two slower modes. The middle mode (which is possibly a mixture of modes) is too poorly defined for present characterization.[48] The slow mode is considered to characterize the translational motions of clusters of chains.

The presence of three modes discussed here has also been established in the decay time spectra of semidilute solutions of very high molecular weight PS ($\bar{M}_w = 15 \times 10^6$) in the Θ solvent cyclopentane (21 °C) over a much more extended range of concentration (up to 0.14 g mL^{-1}). These results show that the qualitative features of the decay time distribution are a general aspect of the dynamics of semidilute solutions in poorer solvents. The nature of the slower modes is a subject of ongoing work, although their resolution seems to lie at the limit of feasibility with current apparatus. Theoretical approaches have tended to oversimplify the situation that exists, for reasons of tractability. Thus current theory of semidilute solutions is predicated on the model of the (homogeneous) transient network. However, slower modes of self-diffusion (e.g., reptation, Stokes–Einstein translation motions) are aspects that have received both theoretical and experimental support in studies on binary and ternary polymer solutions. There is also much evidence for the interpretation of the slowest mode observable as deriving from the translation of polymeric clusters, see, for example, the discussion of Huber et al.[47] What has been insufficiently recognized is the complex interweaving of the relaxational processes in real systems.

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Noncooperative Relaxations

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ABSTRACT: Dynamic mechanical studies have revealed a large class of internal motions having activation entropies close to zero which appear to involve well-defined structural units acting in a noncooperative manner. Examples include rotations of methyl groups, certain side-group motions, and local-mode relaxations which are restricted to short polymethylene sequences. Other cases, including grain boundary relaxations in metals, are associated with crytalline phases.

Introduction

The relationship between the frequency and the temperature of a viscoelastic relaxation can be expressed as an Arrhenius equation:

$$f = Ae^{-E_a/RT} \tag{1}$$

An alternative relationship is derived from the theory of absolute reaction rates.

$$f = \frac{kT}{2\pi h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R} \tag{2}$$

The relationship between the Arrhenius activation energy, E_a, and the activation enthalpy, $\Delta H^{\ddagger}$, is

$$E_a = \Delta H^{\ddagger} + RT \tag{3}$$

From eq 2 and 3, it follows that

$$E_a = RT[1 + \ln (kT/2\pi hf)] + T\Delta S^{\ddagger} \tag{4}$$

If the activation entropy, $\Delta S^{\ddagger}$, is zero, the relationship between the activation energy and T', the temperature at which the frequency of the relaxation is 1 Hz, becomes

$$E_a = RT'[1 + \ln (kT'/2\pi h)] = RT'(\ln T' + 22.922) \tag{5}$$

If the energy difference between the potential minima is small, there can be an additional term of up to $RT' \ln 2$.[1] This is roughly equivalent to the width of the points

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