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Distribution of Relaxation Times from Quasi-Elastic Light-Scattering Experiments: High Molecular Weight Polystyrene in Cyclopentane at θ Conditions

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ABSTRACT: Time correlation functions have been measured over extended spans of delay time for the θ system polystyrene ($M = 15 \times 10^6$) in cyclopentane as a function of angle and over a range of semidilute concentrations. Measurements were also made on solutions at two other temperatures. Distributions of relaxation times were obtained by using CONTIN and the maximum entropy method (MAXENT). This treatment allows a qualitatively new picture of the dynamic processes in semidilute θ systems. Three relaxational modes are found to be present. The fast mode (K^2 dependent) characterizes the transient gel network and is described by a concentration exponent of $C^{0.62}$. The slow mode (K independent) corresponds to a structural relaxation. From the present data it has not been possible to accurately characterize the middle mode. The results, together with those on other solvent systems, establish a complex solution structure in semidilute solutions in thermodynamically poorer solvents.

Introduction

The dynamic behavior of θ solutions at semidilute concentrations has been relatively little studied. From the viewpoint of testing the predictions of hydrodynamic theories for this concentration region, such systems present an unusual level of difficulty in experiments since, even with very high molecular weight fractions, asymptotic behavior as regards relationships between various quantities may not be attained.

A further complication met when using quasi-elastic light scattering (QELS) is the marked departure of the time correlation function from a single exponential. This aspect was discussed by Chu and Nose[1,2] in a series of papers on the polystyrene (PS)/transdecalin θ system. They were the first to point out that the large variance observed at semidilute concentrations most probably derives from contributions from a small number of discrete modes of relaxation. Chu and Nose employed a histogram method and a bimodal fit to separate a fast (gel) mode and a slow (translational) mode having comparable time scales, these assignations being made from the nature of the concentration dependences of the separated relaxation rates. There was subsequently a number of reports[3-8] dealing with semidilute θ systems where different modes were isolated by using, for example, optimized sampling times[3] for limiting decay processes and forced single-exponential fits[5,6] to approximate different parts of the correlation function. While there is a general consensus regarding the origins of the fast mode, only the value of its concentration dependence is discussed. Large discrepancies remain concerning the nature and properties of the slow process(es): for example, the angle, concentration, and molecular weight dependences. There is thus ample experimental evidence to show that at least two discrete modes are required to adequately describe the θ state semidilute solution structure on short time (τ) scales $\tau < T_R$, where T_R is the disentanglement[9] time associated with the transient network of polymer chains. Not surprisingly, the properties of the modes as isolated (e.g., the concentration dependence of the observed relaxation rate) vary between the different investigations since the procedures used to separate them differ considerably. Much uncertainty remains regarding the level of experimental support for the current models which have been advanced to describe these systems.

Brochard[10] and de Gennes and Brochard[11] treated the dynamics of semidilute θ-state polymer solutions. Brochard predicted two modes because the self-entangled chain forms a micromesh with characteristic length much shorter than the correlation length. At sufficiently high K values such that $\Gamma_K T_R > 1$ (where K is the scattering vector and Γ_K is the determined relaxation rate ($=DK^2$ where D is the diffusion coefficient)), the high-frequency motion corresponds to the gel mode. The slow mode is a hydrodynamic component at sufficiently low K that $\Gamma_K T_R < 1$. As regards the concentration dependence of the gel mode, which concerns us here, Adam and Delsanti[6] find $\Gamma_F \sim C^1$, both experimentally and also by modification of the earlier theory of semidilute θ solutions by Brochard.[10]

It is thus expected that the pattern of relaxation behavior will depend on the time scale over which the measurements have been made, and this may be the seat of some discrepancies between different investigations on θ systems. Earlier QELS studies employed autocorrelators with a single time setting. This limited time "window" will permit registration of only part (or none) of the slower part of the spectrum, and this may seriously distort the overall picture of the solution structure.

The present study was directed toward elucidation of the dynamics of semidilute θ systems by experimental registration of the "entire" (from the viewpoint of light scattering) time correlation function. This has been made possible by the use of a broad band autocorrelator allowing coverage of a wide span of delay times (here typically 6–9 decades) in the multi-τ mode with up to 23 simultaneous sampling times. The distribution of relaxation times may thereafter by obtained by use of a suitable analytical procedure such as the modified form of the CONTIN program[12] described by Jakes[13] or the maximum entropy method[14,15] referred to as MAXENT.

A recent investigation[16] using a similar approach was directed toward the PS/ethyl acetate system at moderately good conditions down to θ solvent conditions at −44 °C. It was shown there that over the whole temperature range studied the distribution of relaxation times consisted of several components. The peak decay times and amplitudes

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varied systematically with angle, concentration, and temperature.

In the present investigation it was anticipated that the use of a very high molecular weight fraction might more closely approximate the hypothetical model of the homogeneous transient gel. Furthermore, overlap of chains will be achieved at $T = \theta$ at a concentration well below that at which the local friction becomes significant, and thus the system is amenable to study under conditions which meet the assumptions underlying the model used. The QELS measurements were made as a function of angle on two molecular weights ($\bar{M}_w = 3.8 \times 10^6$ and 15×10^6) and also as a function of concentration and temperature on the higher molecular weight.

Experimental Section

Polystyrene solutions were prepared by using polymer from Toya Soda Ltd., Japan: $\bar{M}_w = 15 \times 10^6$, $\bar{M}_w/\bar{M}_n = 1.30$; $\bar{M}_w = 3.8 \times 10^6$, $\bar{M}_w/\bar{M}_n = 1.05$. The sample of higher molecular weight was a nominal 20×10^6 fraction with reported MW = 15×10^6.

The cyclopentane was spectroscopic grade from Merck, Darmstadt, FRG, and was used without further purification, except for drying over 3-Å molecular sieves. Samples and solvents were sealed in glass vials and allowed to slowly rotate for 4 months. The solutions were then filtered through 3-μm Fluoropore filters (except for the highest concentration of 13.4×10^{-2} g·mL^{-1}, which was too viscous). The solutions were bled off into 10-mm precision NMR tubes and placed in an oven at 50 °C for 6 months to homogenize after having been flame-sealed at −15 °C. A previous description of preliminary measurements on these solutions has been given in ref 7. The stability of the photon count at all angles indicated that the solutions were essentially dust-free.

Dynamic Light Scattering. The apparatus and procedure have been described previously.[7,16] The light source was a 488-nm Ar-ion laser. All measurements were made with an ALV-Langen Co. multibit multi-τ autocorrelator operated with 23 simultaneous sampling times (covering, for example, the delay times in the range 1 μs to 1 min) in logarithmic mode and 191 channels.

Two methods were used to analyze the correlation functions:

(1) CONTIN[12] uses a grid of fixed components and finds their amplitudes. The necessary modifications to the original program supplied by Provencher have been described by Jakes[13] and are summarized in ref 16. These allow reproducible relaxation time spectra covering very wide spans in delay time (typically 6–8 decades) to be obtained. The CONTIN analysis provides a number of solutions with different degrees of smoothing as well as a so-called "chosen" solution. For each solution the moments are given in the output, yielding the amplitude and relaxation frequency of each peak.

(2) MAXENT gives the distribution of relaxation times by using the maximum entropy method. Its applications to QELS has been described by Livesey et al.[14,15] and its particular advantages for handling the ill-conditioned Laplace transform to produce a unique solution using noisy data are discussed.

Static Light Scattering. These measurements were made by using a photon-counting apparatus from Hamamatsu to register the signal scattered as a function of angle. The light source was a He-Ne laser (3 mW). A liquid-filled light guide was used to connect the scattering cell to the photomultiplier. The instrument was calibrated with benzene, which produced a flat angular dependence of the reduced intensity, when angle-corrected, over the range 45–135°.

Results and Discussion

Intensity–intensity time autocorrelation functions ($G(t)$) were measured at different concentrations as a function of angle in the range θ = 30–120° (corresponding, respectively, to KR_g = 1.1–3.75, where R_g = 1180 Å at $T = \theta$ is the radius of gyration of the fraction $\bar{M}_w = 15 \times 10^6$). By use of ξ values from neutron scattering[24] (where ξ is the static correlation length) it is found that the product $K\xi < 1$ for all concentrations (see below) and angles (30–120°) except at the lowest value of concentration and θ=90° and 120°. The concentration range was 1 to 13.4×10^{-2} g·mL^{-1} corresponding to 2.7C^* and 36.2C^*, where C^* has been given by $C_\theta^* = 3M/(4\pi R_g^3 N_A)$ ($C_\theta^* = 0.37 \times 10^{-2}$ g·mL^{-1} for $M = 15 \times 10^6$). The correlation curves were measured by using an ALV-Langen multi-τ autocorrelator adapted to encompass widely spaced delay times (extending up to 8 decades in delay time) as described in the Experimental Section. Figure 1A shows autocorrelation functions $G(t)$ versus log t at the θ temperature (21 °C) at different angles for a solution with $C = 9.4 \times 10^{-2}$ g.mL^{-1}. A progressive change in the shape of the correlation function can be distinguished with reducing angle.

The CONTIN inversion of the curves in Figure 1A is depicted in Figure 1b. The latter distributions were obtained by using a program that had been modified[13] to permit the analysis of autocorrelation functions of a very wide time span. This includes extending the number of data points to 2000 and the number of grid points to 140 and setting the integration control variable IQUAD to 1.

Moreover, as demonstrated and discussed by Jakeš,[13] the presence of a pronounced, narrow peak in the spectrum of decay times seriously distorts the remainder of the spectrum. The present distributions have such a dominant peak as seen in Figure 1B. Therefore, after an initial analysis of a particular correlation curve, the following procedure was adopted: A simulated, noiseless, single-exponential function having a decay rate and amplitude corresponding to that of the fast, strong, narrow component was subtracted from the correlation function. The remainder was then reanalyzed by the CONTIN method.

The CONTIN solutions presented in Figure 1B and throughout the paper are composites consisting of the peak representing the fastest component taken from the initial analysis and the remainder from the second analysis giving only the middle and slow part of the decay time spectrum. Correct normalization is maintained with this procedure. The distorted (middle and slow) part of the spectrum from the initial analysis is not shown since it has no physical value.

The three relaxation processes which can be discerned in the spectra of decay times are referred to below as the fast, middle, and slow modes. It may be noted that the overall form of the distributions is similar to that previously obtained by a similar analysis of data for the PS/ethyl acetate system,[16] suggesting multiple modes in poor solvent systems.

Figure 1C gives the distributions of relaxation times obtained by using maximum entropy analysis (MAXENT), based on the Shannon–Jaynes entropy.[18] This is a new technique for data analysis and has been applied with success to a variety of problem areas involving image reconstruction, e.g., radio astronomical interferometry, medical imaging (CAT, MRI), NMR spectroscopy, optical deconvolution, and Raman spectroscopy[14,15]—see a review by Gull and Skilling.[19] Its application to QELS data has been described in detail by Livesey et al.[14,15] and the power of the technique to deal with single and multiple peaks and broad distributions was demonstrated by using both simulated data and experimental correlation curves for colloidal systems. The program, based on the Cambridge maximum entropy suite (MEMSYS) of subroutines, provides a unique solution which is robust to noise and only shows features if demanded by the data.[14] A full description of the algorithm has been given by Skilling and Bryan.[20]

The MAXENT solutions in Figure 1C are in fair agreement with the distributions obtained by using the modified CONTIN program and the procedure described above (Figure 1B) both as regards peak localization on the decay time scale and the relative amplitudes (which are shown

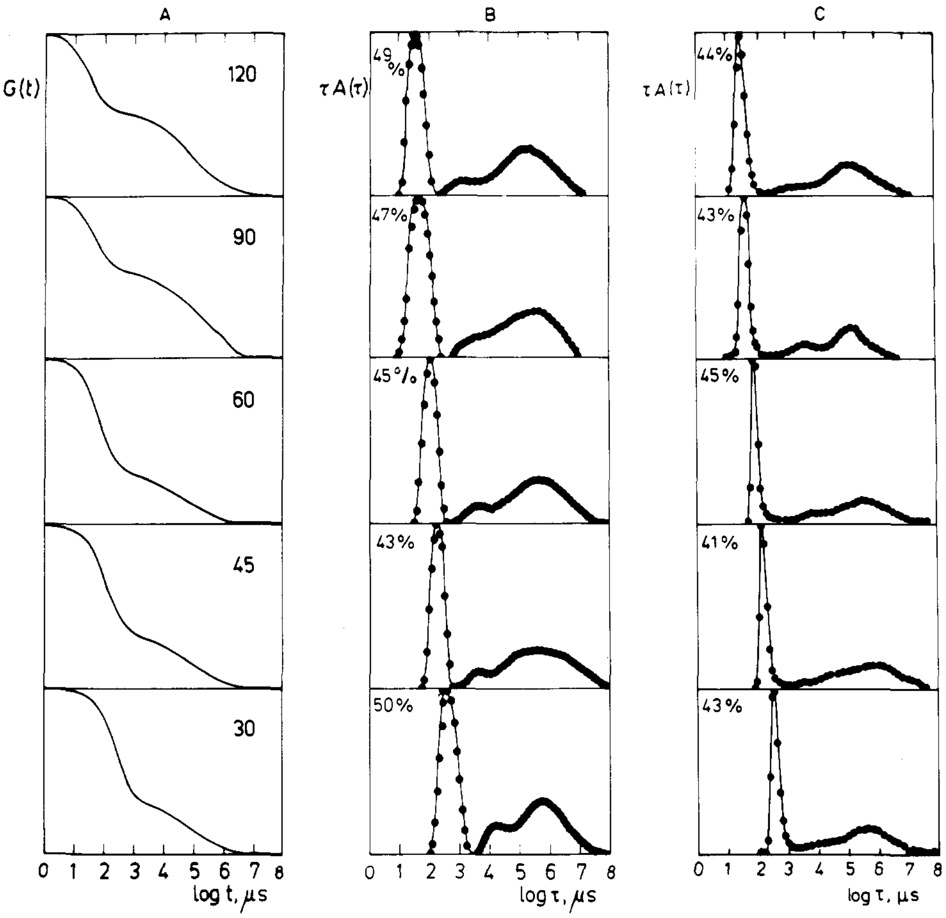

Figure 1. (A) Normalized second-order intensity-intensity time correlation functions ($G(t)$) plotted as a function of log time (μs) for PS ($M = 15 \times 10^6$) at a concentration of 9.4×10^{-2} g·mL^{-1} in cyclopentane. The data encompass the angular range 30–120° as indicated. (B) Distribution of relaxation times with CONTIN[12] inversion of the data in Figure 1A. $K\xi < 1$ for all data except those for $C = 1.0 \times 10^{-2}$ g·mL^{-1} (see below) at $\theta = 90°$ and 120° (where $K\xi = 1.3$ and 1.6, respectively). The quantity $\tau A(\tau)$ is plotted to account for the log scale of the figures. This also applies in Figures 2, 3, and 5. The relative amplitude is shown in percent. (C) Distribution of relaxation times using maximum entropy analysis (MAXENT).[14,15] *Relative amplitude of the fast mode as shown.*

in the figures for the well-defined fast peak) computed from the moments provided in the outputs of both methods. Decay rates evaluated in this way correspond closely to the maxima of resolved peaks. The agreement between the two methods of data analysis with real (noisy) data provides a high degree of confidence in the overall structure of decay times since the procedures are intrinsically different in their approach to the Laplace transformation of data. The fast mode is well-defined at all angles. This remark extends to the other concentrations and temperatures (25 and 40 °C) used as shown in the subsequent figures. The decay times and relative amplitudes of the constituent peaks were determined from the moments of the CONTIN and MAXENT inversion peaks.

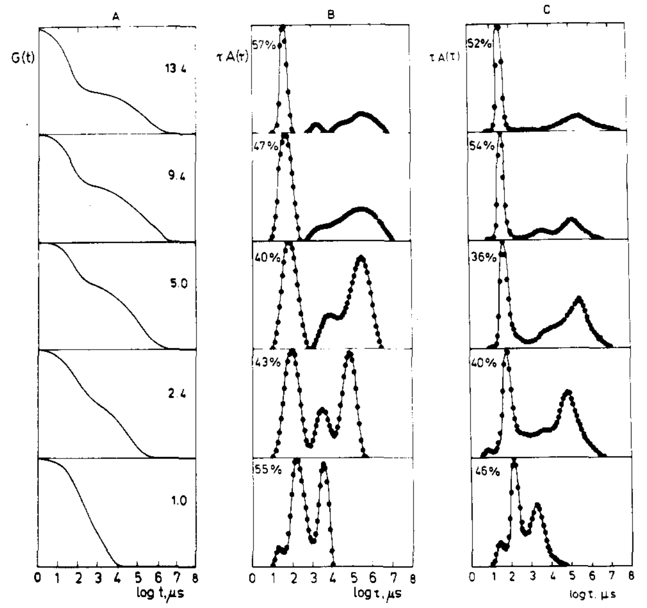

Figure 2. Data analogous to those in Figure 1, but referring to a range of semidilute concentrations. Measurement angle = 90°. The concentrations in part A are expressed as $C \times 10^2$ g·mL^{-1}.

Measurements were also made at a series of semidilute concentrations at each of the angles shown in Figure 1. The data in Figure 2 are at 21 °C (θ conditions) at a measuring angle of 90°. The correlation curves reveal an increasing complexity with increasing concentration (Figure 2A), and this was also true at the other angles. Parts B and C of Figure 2 show, respectively, the CONTIN and MAXENT inversions of the curves in Figure 2A. As a general rule, one may interpret the decay time spectra in terms of three components at all but the lowest concentration (close to C^*). Measurements were extended at the angles shown in Figure 1 and at the concentrations used in Figure 2 to the temperatures 25 and 40 °C. This was done in order to examine the influence of solvent quality on the relative amplitudes and also to examine the consistency of the trends observed under θ conditions when extended to a broader range of experimental parameters. Figure 3 shows CONTIN inversions of autocorrelation functions for data obtained at 25 and 40 °C. The relative amplitudes of the fast mode have been derived from the

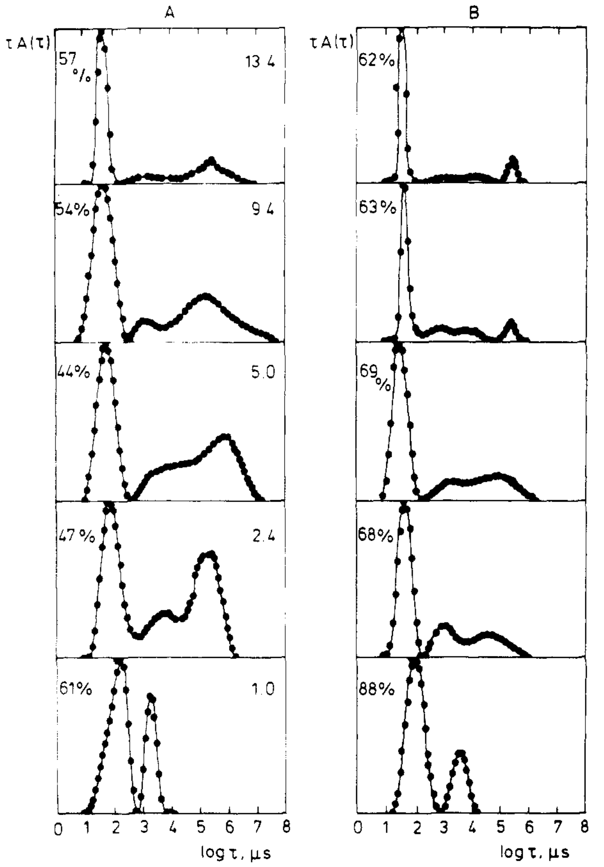

Figure 3. Distribution of relaxation times obtained from CONTIN for data collected on $M_w = 15 \times 10^6$ at an angle of 90°. Temperatures are 25 (Figure 3A) and 40 °C (Figure 3B). Percent fast mode as shown. The concentrations in part A are given as $C \times 10^2$ g·mL^{-1}.

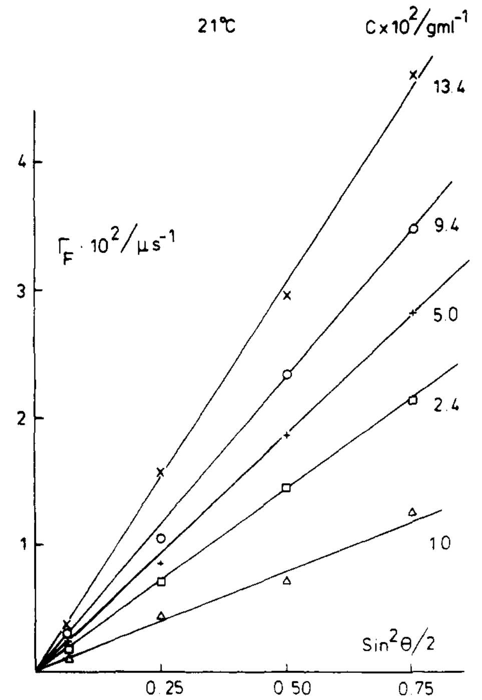

Figure 4. Relaxation rates for the fast mode (taken from Figure 2B). The moments of the peaks have been calculated from the chosen solutions in the CONTIN inversion of the data in Figure 2A.

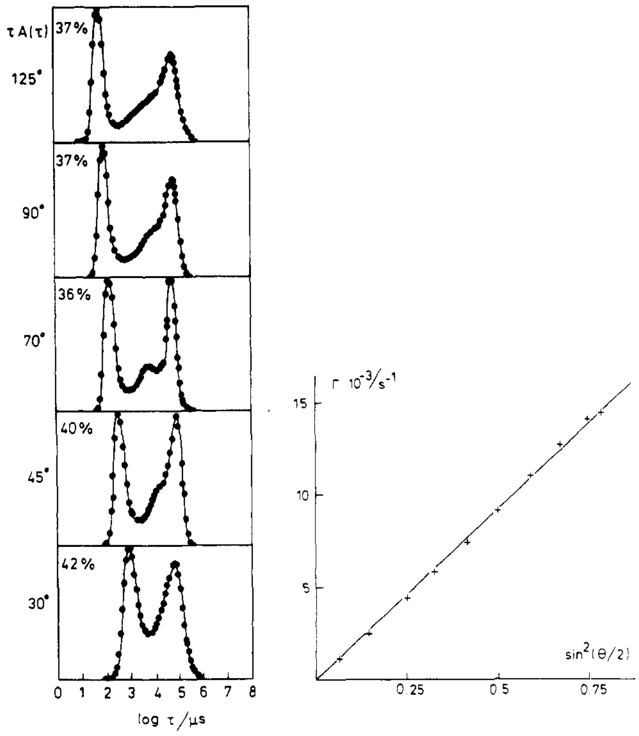

Figure 5. Data for a molecular weight $M = 3.8 \times 10^6$ in cyclopentane at a concentration of 6.0×10^{-2} g·mL^{-1}. The time correlation functions in Figure 5A refer to the angles shown at the left. $K\xi < 1$ applies for all data points. (A, Left) The distributions of decay times were calculated by using MAXENT.[14,15] The relative amplitude of the well-defined fast mode is indicated in percent. (B, Right) The decay rate for the fast mode, taken from the moments of the fast peak shown in Figure 5A, plotted as a function of $\sin^2(\theta/2)$.

moments of the peaks and are shown for the fast mode as a percentage. The fast mode amplitude increases with increasing temperature. However, when the total scattered intensity measured in a static light-scattering experiment is apportioned between the modes according to their relative intensities (see also ref 16), it will be noted that I_F decreases with increasing temperature—see Figure 9. This is a consequence of the smaller overall scattering at the higher temperature.

CONTIN data are depicted in Figure 4 and show the relaxation frequency (Γ_F) as a function of $\sin^2(\theta/2)$ for a series of semidilute concentrations at the θ temperature (21 °C). The linear relationship, passing through the origin, confirms that the fast mode is diffusive since $\Gamma_F = DK^2$, where D is the diffusion coefficient. This mode is considered to reflect the dynamics of the transient network.

Analogous linear relationships between relaxation frequency and angle were found for the data at 25 and 40 °C. The temperature dependence of the corresponding correlation lengths is also discussed below. The middle and slow modes are less well-defined and become increasingly so as the concentration is raised and the solutions more heavily entangled. However, both methods of data analysis agree semiquantitatively on the description of the slower part of the decay time spectrum. The slowest mode cannot be attributed to either dust or cluster formation (as was the case in the PS/ethyl acetate system). This is shown by the presence of only a small angular dependence in the static light-scattering experiments. Also, the relaxation time of the slow peak is more than an order of magnitude faster than that which was considered to characterize cluster diffusion for PS in ethyl acetate with a comparable sample. Visual inspection of the diagrams in parts B and C of Figure 1 suggests that the slow mode is angle-independent. This conclusion is reinforced by the analogous

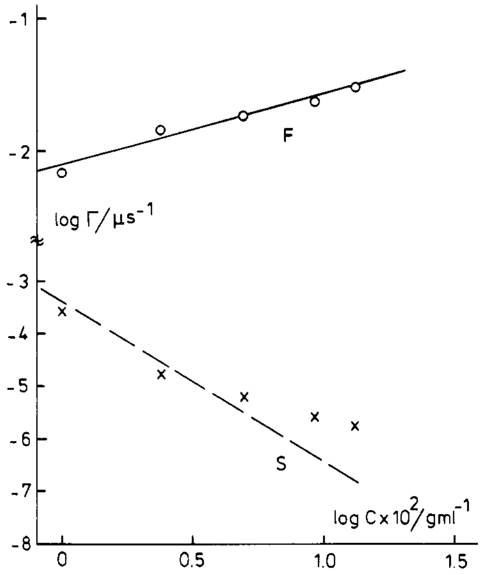

Figure 6. Concentration dependence of the fast and slow decay rates ($\bar{M}_w = 15 \times 10^6$/cyclopentane). Data are at the θ temperature (21 °C). Measurement angle = 90°. The decay rates were obtained from the moments of the CONTIN[12] inversions of the curves in Figure 2B. The relationship for the fast mode is $\Gamma_F \sim (1 - \phi)C^{0.62}$. A line of slope −3 is included as a guide with the slow mode data.

data for a PS sample of lower molecular weight ($\bar{M}_w = 3.8 \times 10^6$) shown in Figure 5. Figure 5A gives the distributions of decay times obtained with MAXENT. The middle peak is not well resolved. Figure 5B shows the relaxation rate for the fast mode as a function of $\sin^2(\theta/2)$. In addition, a parallel investigation of the PS/cyclohexane θ system, which also shows the presence of three components, revealed that the position of the slowest mode on the decay time axis is independent of measurement angle. With this lower molecular weight the slower peaks are much better defined. In both systems the relaxation spectra were also remarkably similar in overall character, e.g., in peak spacing on the time scale and their relative amplitudes.

Independence of Γ_S (the decay rate of the slow mode) of K suggests that it derives from a structural relaxation characterizing the lifetime (τ_R) of the transient gel. From theory,[9] $\tau_R \sim M^3$, while experimental data suggest a larger value of the exponent in the range 3–3.8.[25-27] From Figures 1–3 it may be concluded that it is difficult to assign a particular decay time to the broad peak of the slow component. Owing to the M^3 dependence, the theoretical distribution of τ_R will have a width of ca. 3 times that of the distribution of molecular weights, which is in itself not negligible ($\bar{M}_w/\bar{M}_n = 1.3$). The middle mode is insufficiently resolved to permit its characterization. Its low intensity and the proximity to two dominant modes further complicate the analysis.

Figure 6 includes the concentration dependence of the fast mode decay rate (Γ_F) in a log–log diagram at the θ temperature. When the relaxation rates are corrected for backflow by division by $1 - \phi$, where ϕ is the volume fraction of polymer,[21] the relationship $\Gamma_F/(1 - \phi) \sim C^{0.62}$ applies. Since this exponent applies to a fraction with $M = 15 \times 10^6$ and mostly in the concentration region well above C^*, it should not have been influenced by crossover effects. The value is similar to that found[16] in the PS/ethyl acetate system at −40 °C, which is close to θ-conditions, and also corresponds to exponents found for the fast mode in earlier studies.[1,8,29]

Assuming that a form of the Stokes–Einstein relationship as used for good solvents[9] as well as poor[30] can be used here, one can derive a dynamic correlation length for the fast mode data (ξ_H) where ξ_H is defined by $\xi_H = kT/(6\pi\eta_0 D_F)$ and D_F is the diffusion coefficient for the fast mode ($=\Gamma_F/K^2$). Figure 7 shows the temperature dependence of this characteristic length at the concentrations indicated. Figure 6 includes data for the concentration dependence of the decay rate Γ_S on C. For comparison, the broken line having a slope = −3 is included.[9] The points for the lower concentrations follow this line, but there is a pronounced deviation at the higher concentrations at which the peaks have become broad and poorly defined. The present results broadly accord with the previous investigations[7] of the PS/cyclopentane θ system at semidilute concentrations where a bimodal fit with floating base line was used to describe the correlation functions. The two relaxation rates were then found to be K^2 dependent and were interpreted as the gel mode and a translational mode. Evidence was also provided[7] for an even slower mode at the tail end of the time spectrum, which was K independent. The results qualitatively accord with those of Adam and Delsanti[5,6] for the PS/cyclohexane θ system using a single-exponential forced fit analysis. At short times a K^2-dependent relaxation which was linearly related to concentration was found, and at long times a K-independent structural relaxation (strongly concentration and molecular weight dependent) was assigned. On the other hand, Takahashi and Nose[8] found that a slow mode with an abnormal angular dependence gives a nonzero intercept.

Amis et al.[3] obtained QELS data on the PS/cyclohexane system by making measurements at short and long sampling times in order to isolate the limiting decay rates characterizing the system. This procedure (which is very approximate due to inadequate separation) gave a fast mode dependent on molecular weight with a concentration exponent of less than 0.5. The slower mode was highly molecular weight and concentration dependent and was assumed to represent self-diffusion of the single coil in the semidilute solution. However, comparison with data interpolated from the forced Rayleigh scattering experiments of Deschamps and Léger[22] shows that the values of the slow mode[3] are more than an order of magnitude lower than those corresponding to self-diffusion of the single coil and

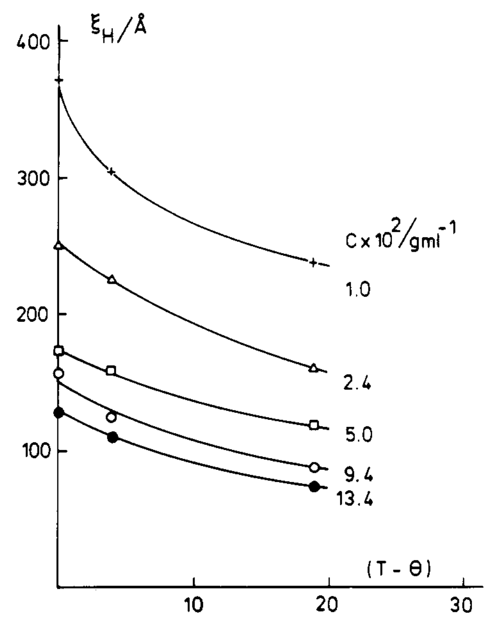

Figure 7. Temperature dependence of the dynamic correlation length (ξ_H) obtained from the fast mode data. Data are at an angle of 90° for the semidilute concentrations shown.

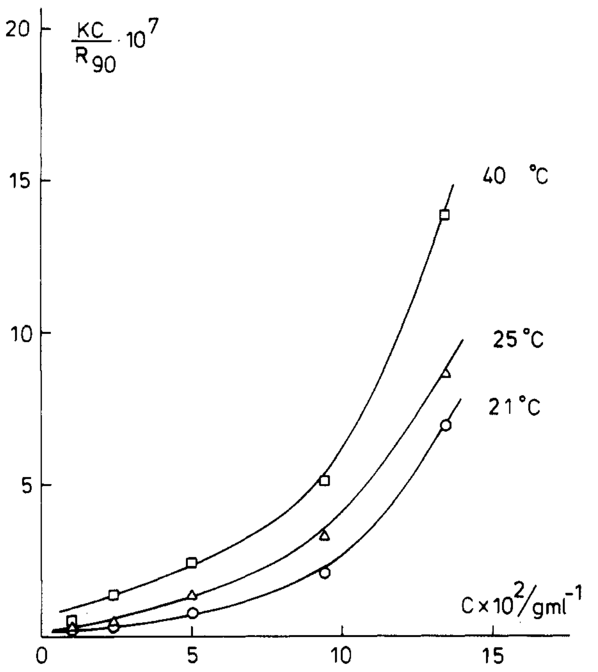

Figure 8. Reduced scattering function (KC/R_{90}) from static light-scattering measurements on the PS ($M_w = 15 \times 10^6$)/cyclopentane system.

thus more probably represent diffusion of clusters of chains.

More complete information can be obtained by measuring static light scattering since it then becomes possible to convert the relative amplitudes obtained from the Laplace inversions to absolute values. (It was not the purpose here to make a more detailed study of the static properties of the system, as this has already been described in a similar θ system.[28]) Static light-scattering measurements were made as a function of angle on the different concentrations at 21, 25, and 40 °C. These data are shown for the angle of 90° in Figure 8 as plots of the reduced scattering function, KC/R_θ, vs concentration. Using the corresponding relative amplitudes derived from the peak moments from the CONTIN inversion, the absolute intensity was estimated for the well-defined fast mode. These data are shown as a function of measurement angle in Figure 9A and of concentration in Figure 9B at three temperatures. A very small angular dependence is noted for the fast mode intensity, I_F. I_F decreases with increasing concentration as the slower modes develop in accordance with the data shown in Figure 1-3. Also, as expected, the absolute intensity increases toward the θ temperature at 21 °C.

Conclusions

Previous studies of θ systems have established pronounced deviation from a single-exponential decay of the autocorrelation functions recorded in QELS experiments, but the origin and nature of these deviations were not described. It may be generally acknowledged that the presence of multiple modes of relaxation implies severe problems both in the collection and the interpretation of data. The then current techniques dictated a limited approach to the problem. Data were collected by using narrow time windows, and this meant that only restricted regions of the time correlation function were monitored. Processing of data frequently followed comparatively unsophisticated patterns (e.g., a cumulants analysis), which was then considered adequate since the complexity of the problem had not been envisaged. The present investigation stresses the necessity of recording the "entire" autocorrelation function and of employing an analysis in terms of relaxation time distributions. Such an approach has now become feasible owing to the advent of multi-τ autocorrelators (or alternatively, the much more laborious computer-splicing of many successive runs), in addition to the recent extensions of powerful numerical techniques to yield distributions extending over 8 decades or more in delay time.

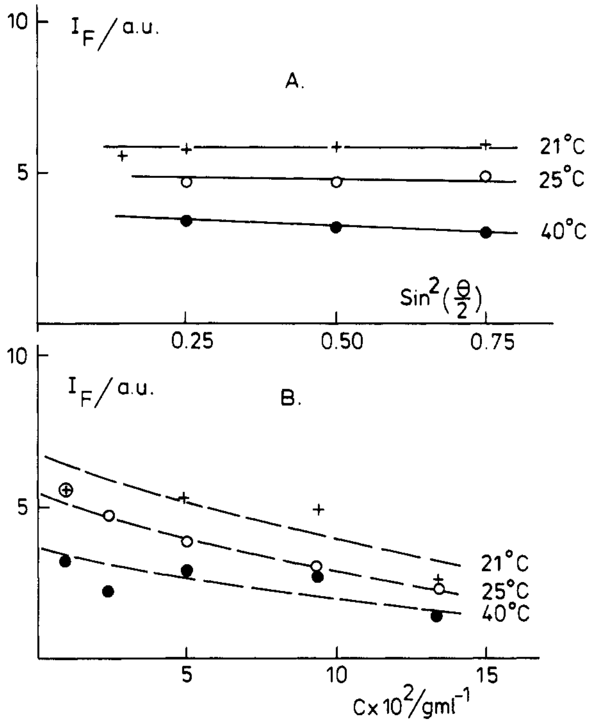

Figure 9. (A) Angular dependence of the intensity of the fast (gel) mode. The quantity I_F (arbitrary units) has been estimated by apportioning the measured (total) intensity from static light scattering according to the relative amplitude of the mode from the CONTIN[12] inversion. Concentration = 5.0×10^{-2} g·mL^{-1}. (B) Concentration dependence of the intensity (I_F) of the fast mode (arbitrary units) as estimated above (Figure 9A). Measurement angle = 90°.

We present a qualitatively new picture of dynamic processes in semidilute polymer solutions as seen by light scattering. The broad extent and complexity of the distributions explain discrepancies reported in earlier investigations.[3-8] In the PS/cyclopentane system studied here three relaxational modes have been distinguished. Systematic trends in the positions on the time scale of the respective peaks are observed with angle, concentration, and temperature. The fast gel mode (K^2 dependent), which is always well represented in the spectrum of decay times, characterizes the network: it exhibits a concentration dependence given by $\Gamma_F \sim (1-\phi)C^{0.62}$, which agrees substantially with earlier experiments but does not agree with the value of unity advanced in ref 6. The slow mode (K independent) corresponds to a structural relaxation.

With the present data, the middle mode is insufficiently resolved for detailed characterization of its angular dependence. Recent multiangle analyses suggest that it is also K independent. However, from the overall pattern of the concentration and temperature dependences in this and related systems examined,[16] the presence of this mode as an entity is clearly demonstrated. Although it had been anticipated that a molecular weight of 15×10^6 might approximate the hypothetical homogeneous transient gel used as a model[9] in semidilute solution work, this is not found to be the case. In comparison with the lower molecular weight fraction, the proportion of the slower modes does not decrease, but their identity becomes blurred into a very broad peak(s) at the slow end of the delay time spectrum, and this is more accentuated as the concentration is raised. This is in part due to the effects of polydispersity and also coupling of modes in the heavily entangled system.

These findings support the results obtained on semidilute solutions of polystyrene in ethyl acetate and also cyclohexane. Taken together the results establish a complex solution structure, at least in poorer solvents. The ongoing work is directed toward further elucidation of the character of the slower modes.

It is known that at high polymer concentrations (and in polymer melts) the photon correlation spectrum becomes K independent and may be interpreted as a wide distribution of internal modes.[31] Our interpretation of the middle and slow modes is that they represent cooperative internal relaxation modes of many entangled chains. At high segment concentrations, the internal modes have become slower than the collective diffusion motions of the network[32] and will eventually dominate the spectrum. A comprehensive theory for the relative amplitudes and relaxation times in concentrated solutions is not available, however.

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Thermotropic Liquid Crystalline Main-Chain Polyesters Containing Cyclooctyl Units. 4. Influence of the Methylene Spacer Length on the Nature of the Mesophase

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ABSTRACT: A series of polymers based on the novel mesogenic unit *cis*-1,5-cyclooctanediyl bis(*p*-hydroxybenzoate) have been synthesized with spacer units varying from 3 to 10 methylene units. Only smectic phases could be detected when 3, 4, and 10 methylene units were incorporated and this changed to nematic phases only when the space lengths were 5–9 units. The smectic phase could be changed to a chiral nematic one when an optically active molecule (+)-3-methyladipic acid was incorporated in the chain. An odd–even effect in the melting and clearing temperatures was detected as the spacer length changed, with higher values being obtained when there was an even number of methylene units in the spacer. Supercooling effects could also be observed.

Introduction

Rigid polymers which show a high degree of molecular order either in solution (lyotropic) or in the melt (thermotropic) are characterized by their unique optical properties analogous to low molecular weight liquid crystals.[1,2] Fibers spun from orientated liquid crystalline (LC) states are claimed to have superior mechanical strength[3] because of the orientation of the molecules and so this characteristic property can be very attractive in such systems. As a consequence, the relationships between the structure and the properties of liquid crystalline polymers have been extensively studied, and progress in this area has recently been reviewed.[4]

Main-chain liquid crystalline polymers usually consist of aromatic units which act as the rigid component, the mesogen, and the thermal transition temperatures of these

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