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Dynamic light scattering measurements on the polystyrene/ethyl acetate system at semi-dilute concentrations as a function of temperature

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Summary

Measurements of autocorrelation functions extending over a broad time range are reported for a sample of polystyrene in ethyl acetate as a function of temperature between -44°C (Θ-temperature) and 70°C. The corresponding spectra of decay times are obtained by two mathematical methods. The existence of three dynamic processes is shown and their temperature and angular behaviour is studied.

Introduction

Earlier quasielastic light scattering (QELS) measurements on polystyrene (PS) dissolved at semidilute concentrations in the marginal solvent ethyl acetate (1-4) indicated that the correlation functions deviate substantially from the single exponential decay more typical of thermodynamically good solvents. PS in ethyl acetate has been studied (5) in detail using a multiexponential method to analyze the correlation function. It was subsequently shown that the complexity of the correlation function increases progressively with decreasing solvent power, by making experiments in mixtures of ethyl acetate and the isorefractive non-solvent ethanol (6). Similar complexity of the decay time spectrum has recently been demonstrated by Štěpánek et al (7) in the PS/cyclohexane system using different methods to analyze the correlation function.

In order to examine more systematically the way in which the decay time spectrum changes with solvent quality in a single medium, we have made measurements on the PS/ethyl acetate system over a broad range of temperature. The quality of the solvent was varied from moderately good at +70°C to *theta* solvent conditions at -44°C (8). This preliminary report describes the results obtained on a single semidilute (15c* at 25°C) concentration of PS ($M=3\times10^6$) as a function of the temperature and scattering vector.

Experimental

1. Solutions:

Two solutions of a nearly monodisperse PS standard (Toyo Soda Ltd., Tokyo) were prepared ($M_w=2.95\times10^6$ and $M_w/M_n = 1.05$). Ethyl acetate was of spectroscopic grade. Initial experiments showed that even trace amounts of water in the solutions caused phase separation (clouding) at temperatures below -30°C. Water-free, essentially dust-free, semidilute solutions were

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prepared as follows:
A stock solution of PS in spectroscopic grade cyclopentane was prepared at a concentration of 0.5 wt% and centrifuged at 10,000 r.p.m. for one hour. Measurement cells linked to the vacuum line were flushed with acetone vapour to remove dust, dried and then filled with a known amount of the PS/cyclopentane solution taken from the upper half of the centrifuge cell. The cyclopentane was evaporated. The measurement cells were coupled to the vacuum line, as well as to a container with previously dried ethyl acetate (CaH_2 for 48 hours). The ethyl acetate was de-gassed by repeated freezing in liquid nitrogen under high vacuum followed by thawing. Still under vacuum, a predetermined amount of ethyl acetate was condensed 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 then flame-sealed at -70°C without freezing the solvent (freezing point -82°C). The final concentration was then determined by weighing. The solutions were allowed to homogenize for several months with occasional shaking.

2. *Apparatus*

Complementary measurements were made on photon correlation spectrometers in Prague and Uppsala. Both have been described elsewhere (9,10). The light source in each was an Ar-ion laser. With the first apparatus (Prague) a real-time, single-bit 96-channel digital correlator (constructed in Prague) was used for sampling times shorter than 1 ms and a 100 channel analog correlator (Hewlett-Packard 3721-A) for the longer sampling times. With the Uppsala apparatus an ALV multi-bit, multi-tau correlator was opearated with 23 simultaneous sampling times typically covering the range 1 µs to 50 s (ALV-Langen Co. FRG). The sample cell was placed in an index-matching liquid. The temperature could be regulated within -140°C to +120°C (Prague) and -20° to +70°C (Uppsala).

3. *Data treatment*

While the ALV correlator directly yields a correlation curve covering nearly 8 decades in delay time, the correlation curves obtained with the Prague apparatus were computer-spliced to produce the composite curve having 800-1100 points as described in ref.7. The multi-tau and composite correlation curves, measured under identical conditions on the same solution, were found to be superimposable, and differences in the spectra of decay times negligible, see the curves for the angle 60° in Fig.4. This gives confidence in the use of the different apparatus and the method used to obtain the composite curves.

Two different mathematical methods were used to analyze the correlation curves:
(a) The positive coefficients exponential sum (PES) method (11), which uses floating components and in successive steps finds the absolute minimum of the sum of squares of residuals.
(b) CONTIN (12) which uses a grid of fixed components (typically 90 - 120 components) and finds their amplitude. In a recent comparative test, Stock and Ray (13) found that CONTIN tends to oversmooth the spectrum of decay times. However, the testing was confined to a narrow region (about 2 decades). One of us (14) performed a further test which showed that for a wide

spectrum of decay times CONTIN seriously under-smoothed in the region of short decay times and over-smoothed on the long-time side. This behaviour could be eliminated by setting IQUAD=1 in the CONTIN programme and this led to a different penalizing compared to the standard IQUAD=3. It was also found that even small systematic errors (of a fraction of root-mean-square noise) in the correlation curves may lead to false peaks in the so-called chosen solution. We have thus preferred solutions with a regularization parameter greater than that of the chosen solution.

Results and Discussion

The extrapolated estimate (8) of the Θ-temperature for the PS/ethyl acetate system (Θ=-44°C) was checked using a solution with $c=0.0227\ g.ml^{-1}$. This concentration is close to the crossover concentration, c_Θ^*. Assuming that the empirical relationship: $c_\Theta^*=40/\sqrt{M}$, as used in ref.15 for the PS/cyclohexane system, is also valid for the PS/ethyl acetate system, we obtain $c_\Theta^*=0.023\ g.ml^{-1}$ for the present sample. In the same reference (15) the expression $\Delta T=3000/\sqrt{M}$ 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 ΔT=1.7°C.

Fig.1 shows the reciprocal intensity of light scattered at an angle of 60° by this solution as a function of temperature. The intercept with the T-axis, corresponding to infinite scattered intensity and thus demixing, occurs at a temperature T_D=-46°C ±1°C. This gives for the Θ-temperature an estimate of Θ=-44.3°C ±1°C.

The accessible temperature range in solutions of PS in ethyl acetate is thus ca -45°C to 77°C (B.Pt. of the solvent). Composite correlation curves were measured at several temperatures between +70°C and -44°C for a solution of PS concentration $c=0.053\ g.ml^{-1}$ at an angle of 60°. The changes in the correlation function are depicted in Fig.2a. In addition to a shift to longer delay times due to the increasing viscosity, distinct changes in the shape of the correlation function are observed. As the temperature is lowered, a slow decay becomes observable but almost disappears again as the temperature -44°C is approached. The CONTIN inversion of the curves together with

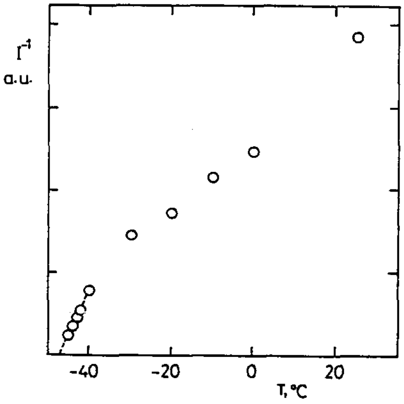
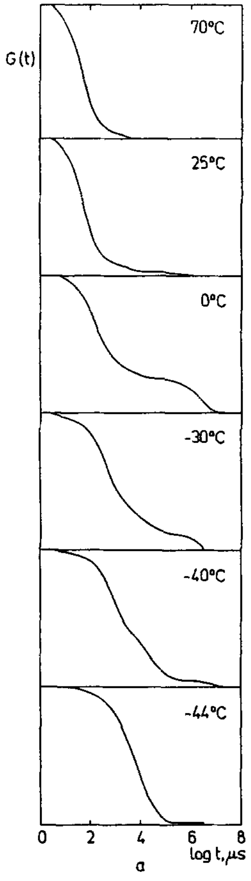


Fig.1 Temperature dependence of the reciprocal intensity of light scattered at an angle of 60° of a sample with concentration c=0.0227 g/ml.



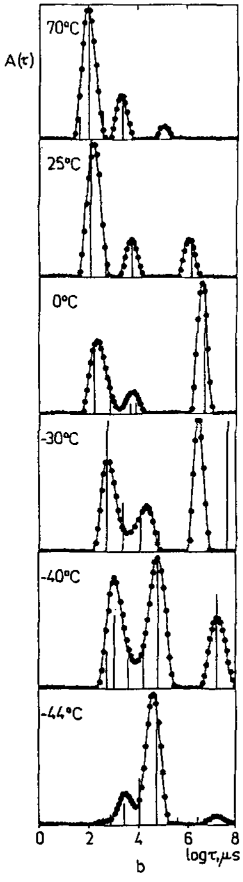


Fig.2a Composite correlation curves for various temperatures for a sample with concentration c=0.053g/ml measured at an angle of 60°.

Fig.2b Distribution of decay times as obtained from correlation curves in Fig.2a. Full line - CONTIN results, vertical lines - PES results.

the PES results are shown in Fig.2b. Three different decay processes are observed throughout even if the contribution of the slowest one is sometimes comparable to the noise level. These three components are present in the decay time spectra obtained with CONTIN even with a regularization parameter which is larger by two orders of magnitude than that of the so-called chosen solution. We thus consider that the three components correspond to real physical processes. They will be referred to as the fast, middle and slow modes. Fig.2b not only confirms the general trend in Fig.2a but also demonstrates a transfer of intensity from the fast to the middle mode.

The decay times and relative intensities of the three modes were determined from the moments of the peaks in Fig.2b. Values of the decay time for the slow mode were rather scattered. Improved results were obtained 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. The resulting decay time did not change significantly when the position of the first point of the partial curve was slightly varied. The decay times of the different modes were normalized using the factor T/η, to account for the change in temperature and viscosity of the solvent (literature data (16) were used for viscosity values in the range -5°C to 70°C and extrapolated values used for the lower temperatures). The results are plotted as a function of temperature in Fig.3a.

As the temperature is lowered to the Θ-point, the three modes are slowed by a factor larger than T/η. The uncertainity introduced by the extrapolated viscosities at low temperatures cannot account for this discrepancy. We are currently determining these viscosities directly at low temperatures.

Both CONTIN and the PES method only give the relative intensities of the components. Absolute intensities were estimated by determining the integral intensity of light scattered at the same temperature and angle, and assigning the corresponding fraction to each component. The results are shown in Fig.3b. The intensity of the fast mode increases smoothly as the Θ-temperature is approached, while the intensity of the middle mode shows a concomitant strong increase. The slow mode varies little in intensity.

Further information regarding the characterization of the individual modes may be obtained from the dependence on the scattering vector K (K=(4π/λ) sin(θ/2), where λ is the wavelength in the medium and θ is the scattering angle).

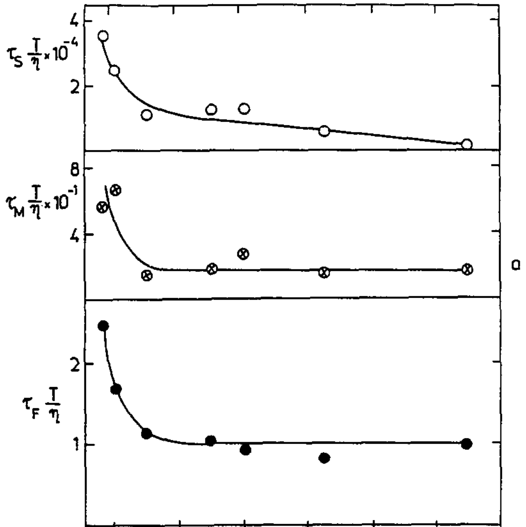


Fig.3a Temperature dependence of the decay times of the fast (τ_F), middle (τ_M) and slow (τ_S) modes, reduced by the factor T/η. τ is in seconds, T in °K, η in Pa.s.

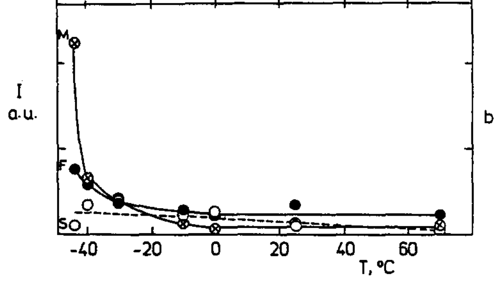


Fig.3b Temperature dependence of the intensity of the fast (F), middle (M) and slow (S) mode at an angle of 60°.

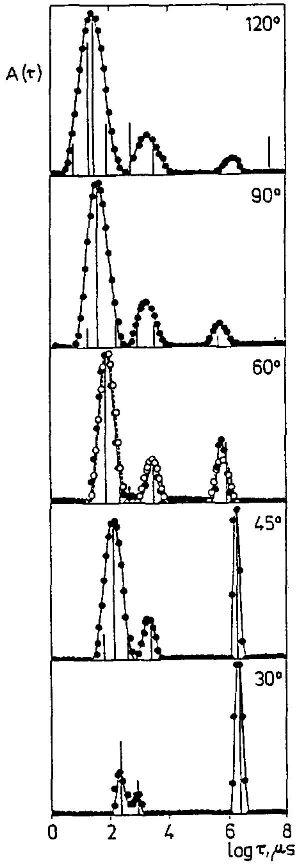


Fig.4 Distribution of decay times obtained at T=26°C for various angles with the sample of concentration c=0.053 g/ml; ● from multi-tau correlation curve, ○ from composite correlation curve, vertical lines - PES results.

For a diffusive process:

$$\tau^{-1} = 2DK^2 \tag{1}$$

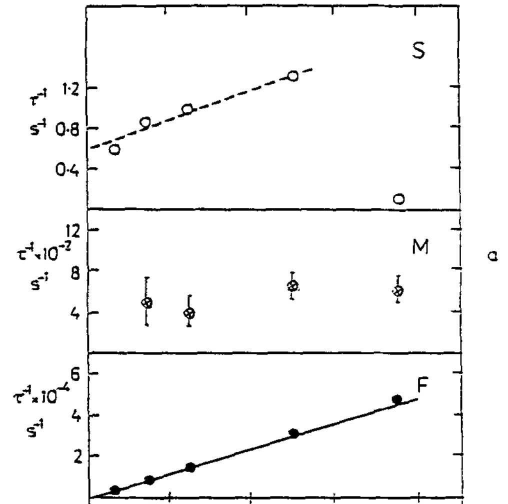
and for a structural relaxation the reciprocal decay time should be independent of K.

Multi-tau correlation functions were measured at ambient temperature at various angles; the corresponding CONTIN and PES analyses are shown in Fig.4. A net angular dependence is found for the fast mode, while the variation of the position of the other peaks is less clear.

The inverse decay times of the modes are plotted as a function of angle in Fig.5a. The reciprocal decay time of the fast mode clearly has a K^2-dependence and the line intercepts the origin. The slope corresponds to $D = 2.5\times10^{-7}$ cm^2 s^{-1}. In a semidilute solution D is related to the mesh size of the transient network through the Stokes-Einstein relationship:

$$\xi = k_BT/6\pi\eta_oD \tag{2}$$

where k_B is Boltzmann's constant. Here we find ξ = 20.7 nm.



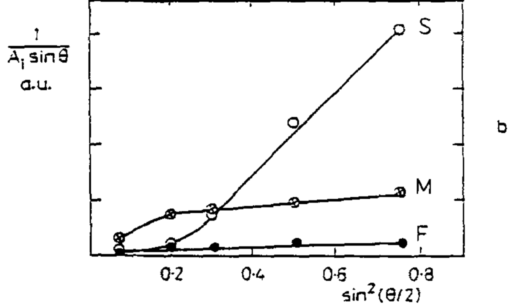


Fig.5a Dependence of the reciprocal decay times τ^{-1} of the fast, middle and slow modes on $\sin^2(\theta/2)$, at T = 26°C.

Fig.5b Dependence of the reciprocal intensity of the fast, middle and slow modes on $\sin^2(\theta/2)$ at T = 26°C.

The points for the decay time of the middle mode are scattered with relatively large error bars which could not be reduced by analyzing a part of the correlation curve as was done for the slow mode. The character of this mode is at present uncertain, but new data on other concentrations strongly suggest a K^2-dependence for this mode. The slow mode has (except for the point at θ=120°) a decay time which is proportional to K^2, but the line does not pass through the origin. This may indicate (19) contamination of a diffusional mode by a structural relaxation. It is thus not compatible with the description of the slowest mode in refs. 7 and 18 as a purely structural relaxation. See also ref.20, where an anomalous K^2-dependence of the reciprocal decay time of the slow mode was also observed. The overall pattern of behaviour is nevertheless consistent with that found earlier in the PS/cyclopentane (17) and the PS/cyclohexane (7, 18) systems.

The angular dependence of the intensity for the different modes, A_i, was found by measuring the integral intensity on a Sofica instrument and attributing to each mode the fraction calculated from the moments of the appropriate peaks in Fig.4. To remove the effect of the variation of the scattering volume with angle, the quantity $1/A_i\sin\theta$ is plotted in Fig.5b. The points for the fast mode follow a line with a small positive slope. The angular dependence of the slow mode is much more pronounced. Speculations about the origin of such effects must await future experiments to elucidate the nature of the middle and slow modes.

Conclusions

We confirm that the Θ-temperature for the PS/ethyl acetate system is -44.3 ± 1°C. Furthermore it is established that a composite correlation curve is equivalent to a multi-tau correlation curve.

With high probability, the existence of three distinct dynamic processes has been demonstrated in this system, covering a considerable range of solvent quality, and this substantiates the earlier indications that semidilute solutions have a greater complexity than hitherto thought.

The fast mode is identified as the gel mode characterizing the transient network. Further information is required for interpretation of the middle and slow modes. As the solvent quality diminishes from good to *theta* the intensity of the middle mode increases strongly, that of the fast mode increases slightly while the slow mode intensity does not change significantly.

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References

1. Munch,J.P.,Candau,S.J.,Herz,J., J.Phys.(Paris),38,971 (1977)
2. Mathiez,P.,Mouttet,C.,Weisbuch,G., J.Phys.(Paris), 41,519 (1980)
3. Schaefer,D.W.,Joanny,J.F.,Pincus,P., Macromolecules, 13, 1280 (1980)
4. Brown,W.,Johnsen,R.M., Macromolecules, 18, 379 (1985)
5. Brown,W., Macromolecules, 19, 1083 (1986)
6. Brown,W.,Johnsen,R.M., Macromolecules, 19, 2002 (1986)
7. Štěpánek,P.,Koňák,C.,Jakeš,J., Polymer Bull.16, 67 (1986)
8. Saeki,S.,Konno,S.,Kuwahara,N.,Nakata,M.,Kaneko,M., Macromolecules, 7, 521 (1974)
9. Koňák,Č.,Štěpánek,P.,Sedláček,B.,Czech.J.Phys.A.34,497(1984)
10. Brown,W., Macromolecules, 17, 66 (1984)
11. Jakeš,J.,Štěpánek,P., to be published
12. Provencher,S.W., Makromol.Chem. 180, 201 (1979)
13. Stock,R.S.,Ray,W.H.,J.Polym.Sci. Polym.Phys.Ed.23,1393(1985)
14. Jakeš,J., to be published
15. Cotton,J.P.,Nierlich,N.,Boué,F.,Daoud,M.,Farnoux,B., Jannink,G.,Duplessix,R.,Picot,C.,J.Chem.Phys.65,1101 (1976)
16. Beilsteins Handbuch der organischen Chemie, Springer, Berlin, 1972.
17. Brown,W., Macromolecules, 19, 3006 (1986)
18. Adam,M.,Delsanti,M., Macromolecules, 18, 1760 (1985)
19. see, for example, Štěpánek,P.,Koňák,Č., Adv.in Coll. and Int.Sci. 21,195 (1984) and references cited therein.
20. Takaheshi M.,Nose,T., Polymer, 27, 1071 (1986)

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