

Physical Properties

Quasielastic light scattering from semidilute solutions in Θ -solvent: Distribution functions of decay times

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Summary

Measurements of composite autocorrelation functions extending over a broad time range on semidilute theta solutions of polystyrene in cyclohexane are reported. Three mathematical methods were used to obtain the corresponding distribution functions of decay times, $F(\tau)$. Results of the different methods are in mutual agreement. It is found that $F(\tau)$ consists of several separated bands. The shortest and longest decay times have been extracted from $F(\tau)$ and, on the basis of their concentration and angular dependences, attributed to the gel mode and reptation process, respectively.

Introduction

The dynamic properties of semidilute polymer systems are now known to be very complex, as well documented by dynamic light scattering (1-11) in particular in Θ conditions. The shape of the correlation function is found to deviate from single exponential and to span a more or less wide interval of decay times depending on the polymer concentration and molecular weight, and on the quality of the solvent. The complex character of dynamic processes in the semidilute domain is then generally interpreted in terms of two relaxation times, a fast and a slow mode. These are resolved from the correlation measurements using either very different sampling times (6,11), a double exponential fit (1,2,9,10), the histogram method (1,2), or by studying the variation of the apparent decay time determined by a single exponential forced fit as a function of the correlator sample time (7,8,12). Particularly in Θ conditions the results obtained by different authors are in conflict in some aspects as to both the properties of the two decay times (e.g., their concentration and angular dependences) and their interpretation. We have previously reported (13) the possible existence of several relaxation times under these conditions.

The theoretical description of the dynamics of a semidilute Θ solution was given by Brochard and de Gennes (14) and Brochard (15). Subsequently, a modified version was proposed by Adam and Delsanti (8). A common feature of these theories is that they predict the existence of two relaxation times corresponding to two elastic moduli of the semidilute solution. Another qualitative picture of the dynamic processes in these solutions was proposed by Hwang and Cohen (16) who predict the existence of three relaxation times corresponding to a diffusive gel mode, a center-of-mass translational mode, and the slowest internal mode. Adachi et al. (17) assume the existence of three kinds of motion for the chain in the tube model: motion of the chain ends, stretching of the chain, and reptation.

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The aim of the present contribution is to elucidate in more detail the character of the correlation curves in semidilute Θ systems.

Experimental

Polystyrene standard F-380 was obtained from Toyo Soda Company (Japan) with stated values of molecular weight, $M_w = 3.84 \times 10^6$ and index of polydispersity, $M_w/M_n = 1.05$. The solvent, cyclohexane, and the auxiliary solvent, cyclopentane (both spectroscopic grade) were dried over calcium hydride before use.

Dustfree semidilute solutions were prepared in two steps: a) dustfree dry polymer was obtained by evaporating the solvent (cyclopentane) from a centrifuged dilute solution of polystyrene directly in the scattering cell (the separated upper half of the solution in the centrifuge cell was used). b) A corresponding amount of filtered cyclohexane was then added into the measuring cell and this was then flame sealed without freezing. The cells were kept in an oven at 50°C for several months with occasional shaking. The concentration of the solutions ranged between 0.002 g/cm^3 and 0.087 g/cm^3 , corresponding to $0.1 < c/c^* < 5$, where c^* is the overlap concentration

$$c^* = \frac{M_w}{R_G^3 N_A} \quad (1)$$

$R_G = 59 \text{ nm}$ being the radius of gyration of the polymer in cyclohexane at 34.5°C as obtained from elastic light scattering and N_A the Avogadro number.

The photon correlation spectrometer was operated in the homodyne regime and is fully described elsewhere (18). The light source was a Spectra Physics model 125A HeNe laser with output power of 40 mW. An analog 100 channel Hewlett Packard correlator model 3721A (for measurements with sample times $> 1 \text{ ms}$) or a RT digital, single clipped 96 channel correlator (19) (for measurements with sample times in the range $0.1 - 1000 \mu\text{s}$) were used. To obtain composite autocorrelation function (CACF) over a broad delay time range, several simple autocorrelation curves were measured with different sampling times (eg. 1, 3, 10, ... μs) and matched by means of a microcomputer to form a unique CACF containing 400-900 points by a least-squares adjustment (affinity plus translation).

All the measurements were performed at $34.5^\circ\text{C} \pm 0.05^\circ\text{C}$ and the solutions were allowed two hours to reach thermal equilibrium.

Data treatment

In polydisperse or complex systems, the autocorrelation function is given by the integral

$$G(t) = \int_0^\infty F(\tau) \exp(-t/\tau) d\tau \quad (2)$$

where $F(\tau)$ is the distribution function of decay times τ . Many efforts have been devoted (20) to develop a reliable method for inverting the Laplace equation (2). Here in this paper we have used the following procedures:

1. The regularization method known as CONTIN (21) modified to handle 2000 experimental points and to yield 50 exponential components. Solutions with the automatically chosen value of the regularization parameter α are always presented.
2. The linear programming (LP) method (ref. 22) which uses fixed components equidistant on a logarithmic scale and minimizes the sum of absolute values of residuals.
3. The positive coefficients exponential sum (PES) method (23) which fits the experimental curve to the expression

$$\sum_{i=1}^N c_i e^{-t/\tau_i} + b \quad (3)$$

with all c_i , τ_i and b adjusted by least squares with constraints $c_i > 0$, $\tau_i > 0$. The number N of components is increased until no new τ_i with positive c_i can be added.

These methods differ from each other. The CONTIN and LP methods are pseudo-continuous with fixed components and yield an estimate of the distribution of decay times, while the PES method is discrete with floating components. On the other hand, the PES and CONTIN methods use the sum of squares of residuals, while the LP method uses the sum of absolute values. The PES method finds the absolute minimum of the sum of squares of residuals.

Results and discussion

Composite correlation curves were measured for solutions of different concentrations that are listed in Table 1, at two scattering angles θ , 30° and 90° . The position of these scattering experiments in the KR_G vs. c/c^* diagram is shown in Fig.1. Here K is the scattering vector, $K = (4\pi n/\lambda)\sin(\theta/2)$ (n is the refractive index and λ the wavelength of light). The master curves in Fig.1 are reproduced from ref.8. The scattering experiments thus refer mainly to the gel regime and to its transition across the badly defined region around the point P (see Fig.1) to the dilute regime.

Table 1 Characteristics of the studied solutions. Polystyrene $M_w = 3.8 \times 10^6$ in cyclohexane; c_0^* corresponds to eq.(1). Characteristic times for structural relaxation τ_R are derived from data in ref. 27.

No.	$c \cdot 10^2$ [g/ml]	c/c_0^*	τ_R [ms]
1	0.20	0.27	-
2	0.40	0.54	-
3	0.92	1.24	-
4	1.8	2.43	-
5	2.5	3.37	11
6	3.7	5.00	32
7	4.1	5.53	42
8	6.4	8.64	140
9	8.7	11.7	320

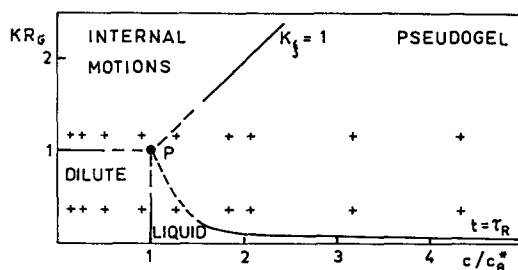


Fig.1 Localization of the individual experiments in the KR_G vs. c/c_0^* diagram. The master curves are reproduced from ref.8. ξ is the mesh size of the polymer network, τ_R is the characteristic time of the structural relaxation of the transient gel (ref.27).

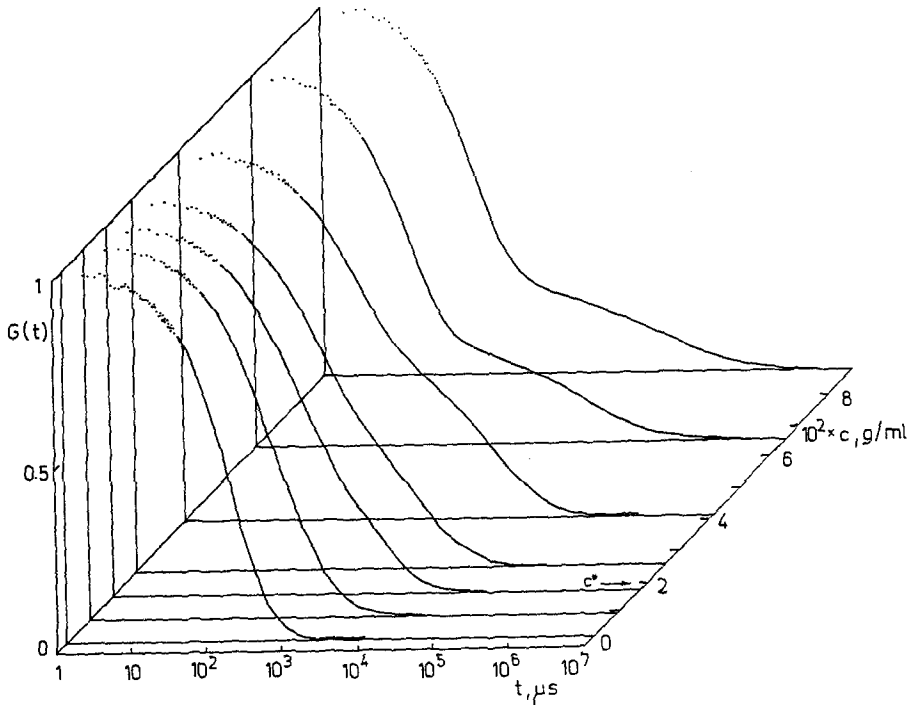


Fig. 2 Composite autocorrelation functions at different concentrations

Composite correlation functions $G(t)$ measured at $\theta = 90^\circ$ are plotted in Fig.2 against $\log t$ for different concentrations. With increasing concentration the curves are seen to become more complex and span a broader interval in time. A short time process is however always distinguishable in contrast to the situation known to exist in concentrated or bulk systems (24,25). It can also be seen that the long time part of the correlation function that begins to appear above c^* does not simply represent an additional single exponential component of the CACF.

The three methods described above were used to obtain the distribution function $F(\tau)$ for solutions collected in Table 1. Figs 3a (scattering angle 90°) and 3b (scattering angle 30°) summarize these distributions in three-dimensional diagrams where the third axis is linear in concentration.

For clarity, results for samples 2,4 and 6 from Table 1 are not shown, although they are included in the subsequent treatment, and only one distribution (alternately CONTIN and LP) is shown for measurements where the sample concentration was close to c^* .

The two methods yielding a pseudocontinuous distribution $F(\tau)$ (linear programming and CONTIN) give very similar results with several separate bands. The results of the PES method agree well as to the centres of bands of the pseudocontinuous distributions. Moreover, the PES method has the advantage of using floating components and it can thus localize the individual peaks in Fig.3 more precisely. Resolution of the CONTIN and LP methods cannot be better than the grid spacing on the τ axis. Within the resolution of the methods the position of bands is reproducible and virtually independent of setting of sampling times used for construction of CACF.

The large number of bands in Figs 3a and 3b in the region of higher concentrations is somewhat unexpected and a question may arise whether some of them are not artifacts due to the Laplace inversion itself. The mathematical methods themselves can create more bands (peaks) in the distribution of decay times than would correspond to physical reality. The term "overfitted distribution" was introduced in ref. 18 and a test based on sequence statistics was suggested to detect such situation. All results presented here are underfitted in this sense which means that not all information has been extracted from the curve. The CONTIN method was recently extensively tested (20) and it was shown to rather oversmooth the results. However, the simulated data used for the test spanned only two

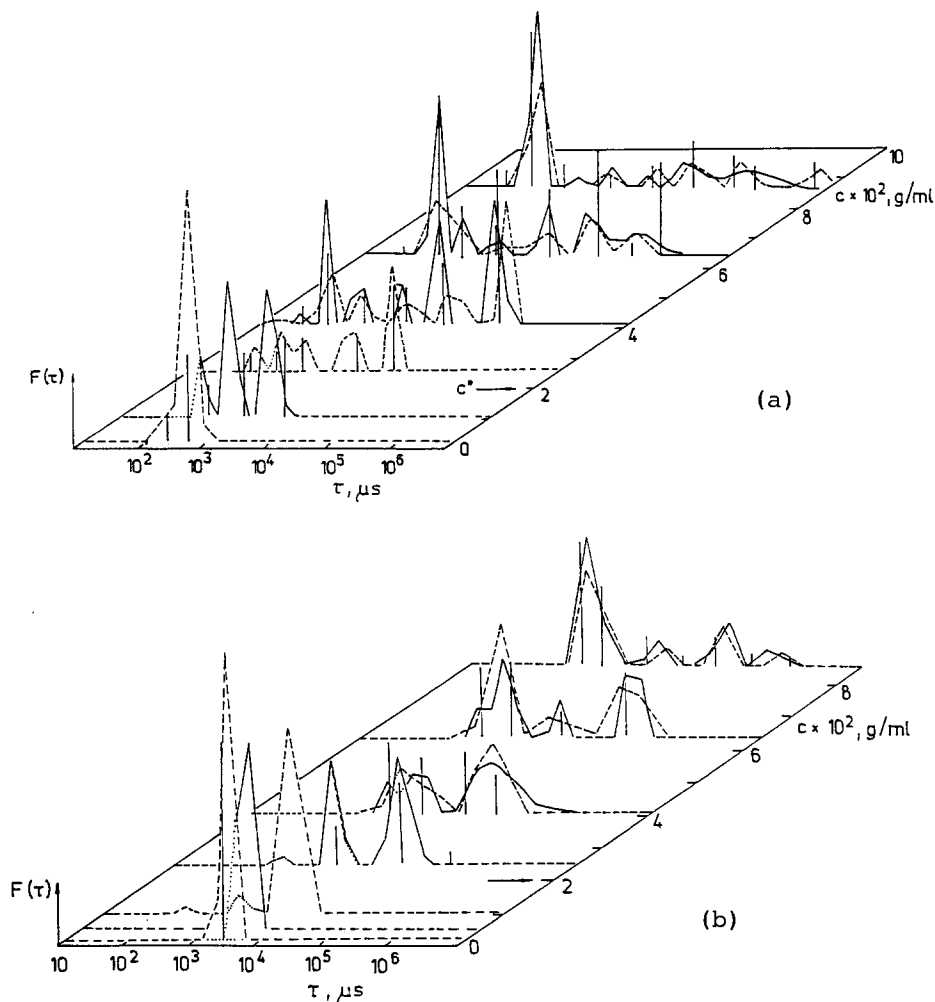


Fig.3 Distribution of decay times as a function of concentration (full line - CONTIN, broken line - linear programming, vertical lines - PES) a) angle $\theta = 90^\circ$, b) angle $\theta = 30^\circ$.

decades; behaviour of the different methods when applied to data spanning a very large interval (7 or more decades in time) is as yet unknown and should be tested. Therefore, we cannot be sure that the real distribution is not more smooth than that obtained by the CONTIN method.

Several features are evident in Figs 3a and 3b. The increasing complexity and range of the distribution functions with increasing concentration c apparent in Fig.2 is again fully reproduced here. In dilute solutions a single decay time is found, corresponding to the translational diffusion of the polymer chains. As concentration increases, a second slower process appears for $c > c^*$ and gains quickly on influence.

Two characteristic decay times, τ_S and τ_L can be introduced, corresponding to the respective bands in $F(\tau)$ at the shortest and longest decay times. In this communication we shall restrict ourselves to the properties of these two decay times; the discussion of the central part of $F(\tau)$, whose origin and exact structure is less evident, is postponed to a forthcoming paper. The decay time τ_L is angle-independent (see Fig.3) and can be thus assigned to a structural relaxation. On the other hand, τ_S is proportional to K^2 and has thus a character of a quantity related to a diffusive process. Values of τ_S and τ_L collected from the distribution functions for all solutions are represented as a function of concentration in a double-logarithmic scale in Fig.4. The quantity τ_S is only slightly concentration dependent and at higher concentrations ($c > c^*$) approaches a power law with exponent -1 (see Fig.4); it can be therefore identified with the gel mode of the semidilute Θ solution as described e.g. in refs. 14, 15, where a value of -1 is predicted for the corresponding exponent

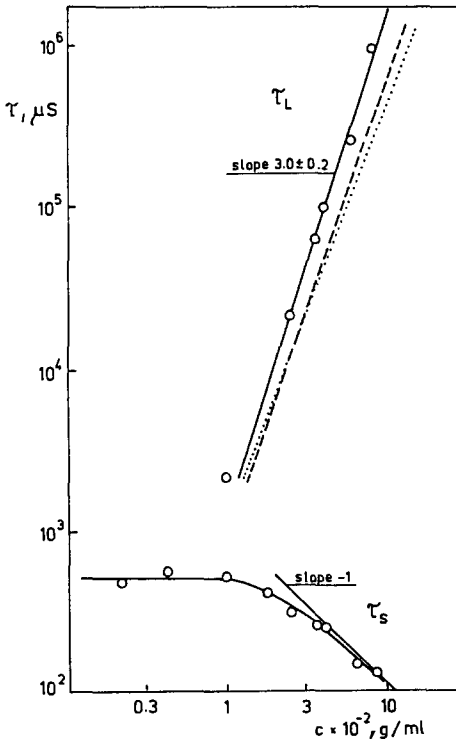


Fig.4 Concentration dependence of the shortest (τ_S) and longest (τ_L) decay times. Dotted line - results for τ_R from ref. 27, broken line - results for τ_L from ref. 8.

at $c > c^*$. On the other hand τ_L which follows a power law with an exponent $x_L = 3.0 \pm 0.2$ can be related to reptation time τ_R of a chain in the tube model (26), for which a theoretical prediction gives $x_L = 3$. For comparison, the dotted line in Fig.4 represents the results for τ_R obtained in ref. 27 by mechanical measurements, the broken line those from ref. 8 obtained by a heterodyne technique with a single exponential fit to the correlation curves.

Conclusion

We present here the first results of measurement of homodyne composite correlation functions on semidilute θ systems and the corresponding distribution of decay times calculated by three different methods. These distributions become more complex as concentration is increased; only properties of bands at the shortest and longest times were examined in this contribution. They were ascribed to the gel mode and structural relaxation, respectively.

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