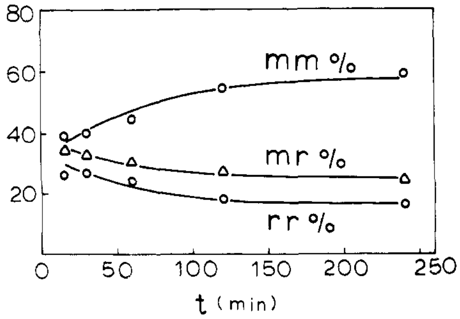

Figure 11. Relation between reaction time and sequence structure of PMMA initiated by *n*-BuLi at −21 °C. Molar ratio of solvents, THF/toluene = 10/90; M_0 = 0.972 mol/L; I_0 = 1.39 × 10^{-2} mol/L.

(or two sites) model for PMMA prepared in toluene. Müller et al.[17] claimed that the tacticity of PMMA in THF with Ce^+ as counterion assumes a first-order Markoff process.

According to our kinetic description, the sequence structures may fluctuate at the start of initiation for certain second-order Markoff processes, but this is not a necessary condition. To judge the order of the Markoff process, the decision equations in ref 6 are recommended. Our kinetic description is not intended to reject most statistics and/or other possible mechanisms but is intended to add some new ideas to this important topic. Because of the resolving power of the apparatus employed for the measurements, we have insufficient data to check our results for the order of the Markoff process. To use the decision equations in Tables II and III of ref 6, additional data for tetrads and pentads would be required.

7. Conclusions

From the above discussion, it can be seen that a non-steady-state stage exists at the beginning of the polymerization of vinyl polymers for both first- and second-order Markoff processes and, as a consequence, during this stage the configurational sequence structures of the products depend upon polymerization parameters. By contrast, for a Bernoulli process, once the vinyl monomer is initiated, there is no non-steady-state stage during polymerization. We thus obtain a simple method for judging the polymerization mechanism. The criterion for a Bernoulli process is that the plot of its sequence structures against any polymerization parameter (e.g., reaction time *t*, monomer conversion *Y*, *X*, and so on) during the whole reaction process be a horizontal line. If the polymerization does not satisfy this criterion, it should likely be ranked as a Markoff process.

Acknowledgment. This work has been supported in part by a NSERC of Canada grant in aid of research (to F.R.W.M.).

Registry No. MMA, 80-62-6; PMMA, 9011-14-7.

References and Notes

(1) Bovey, F. A. *Progress in Polymer Science*; Jenkins, A. D., Ed.; Pergamon: Oxford, 1971; Vol. 3, p 1.
(2) Bovey, F. A. *High Resolution NMR of Macromolecules*; Academic: New York, London, 1972; pp 65–80, 146–180.
(3) Fox, T. G.; Coleman, B. D. *J. Polym. Sci., Part A* **1963**, *1*, 3183; *J. Chem. Phys.* **1963**, *38*, 1065.
(4) Doi, Y. *Macromolecules* **1979**, *12*, 248.
(5) Price, F. P. *Markov Chains and Monte Carlo Calculations in Polymer Science*; Lowry, G. G., Ed.; Dekker: New York, 1970; pp 187–256.
(6) Yan, D. *Makromol. Chem.* **1983**, *184*, 91.
(7) Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173.
(8) Figni, R. V. *Makromol. Chem.* **1965**, *88*, 272.
(9) Yan, D. *J. Tongji Univ.* **1982**, *2*, 111.
(10) Wang, Z.; Yan, D. *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 2241.
(11) Galluccio, R. A.; Glasker, D. L. *Macromolecular Syntheses*; Fettes, E. M., Ed.; Wiley: New York, 1979; Vol. 7, p 1.
(12) Gilman, H.; Haubein, A. H. *J. Am. Chem. Soc.* **1944**, *66*, 1515.
(13) Scott, N. D.; Walker, J. F.; Hansley, V. L. *J. Am. Chem. Soc.* **1936**, *58*, 2442.
(14) Amerik, Y.; Reynolds, W. F.; Guillet, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1971**, *9*, 531.
(15) Yan, D.; Wang, Z. *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 2229.
(16) Peat, I. R.; Reynolds, W. F. *Tetrahedron Lett.* **1972**, *14*, 1359.
(17) Müller, A. H. E.; Höcker, H.; Schulz, G. V. *Makromol. Chem.* **1977**, *10*, 1086.

The Internal Modes of Polystyrene Single Coils Studied Using Dynamic Light Scattering

Taco Nicolai,* Wyn Brown, and Robert Johnsen

Institute of Physical Chemistry, University of Uppsala, Box 532, 751 21 Uppsala, Sweden.
Received June 14, 1988; Revised Manuscript Received November 23, 1988

ABSTRACT: Dynamic light scattering (DLS) has been used to examine the internal dynamics of polystyrene in cyclohexane at 34.5 °C (Θ solvent) and in toluene at 25 °C. Different procedures for evaluating the contribution from the internal modes to the decay time spectrum are used and compared: (a) fit to double-exponential function; (b) maximum entropy analysis (MAXENT); (c) CONTIN. It is found that the first internal mode (τ_1) is lower than the theoretical value given by the non-free-draining (Zimm) model for Gaussian chains.

Introduction

Dynamic light scattering is a powerful technique with suitable space and time resolution for the investigation not only of the overall movements of polymers in solution but also of the internal dynamics of the single coil, if the radius of gyration is not small compared to the wavelength of the light source used.

For dilute solutions of large polymers, Pecora[1] expressed the spectrum of the scattered light in terms of normal modes, using the so-called bead-spring model for flexible

0024-9297/89/2222-2795$01.50/0

coils. The frequencies of these modes have been calculated by Rouse[2] for the free-draining model and by Zimm[3] for the nondraining model using a preaveraged Oseen tensor. Pecora[1] calculated values for the amplitudes of the modes that contribute most to the correlation function for the free-draining case. Perico et al.[4] extended these calculations to cover both the nondraining case and a partly draining case using a realistic value for the draining parameter. It turns out that the amplitudes are not very sensitive to the degree of draining assumed in the model. The frequencies, on the other hand, do depend on whether the free-draining model or the nondraining model is used (although the partly draining model gives frequencies close to those of the nondraining model). Several authors have investigated the influence of polydispersity, but the effect appears to be small if the polymer sample is not very polydisperse.[5,6]

Thus, from a theoretical point of view, the problem of internal dynamics of large coils in solution would appear to be solved. Experimentally, however, matters are not so clear. Formidable difficulties have prevented the determination of relaxation times for higher internal modes than the first. But even for the first internal mode, there is a disconcerting large spread in the values reported for very similar systems.[6-13] The main problem lies in the difficulty in performing a correct analysis of the measured autocorrelation function because of the unavoidable noise in the data. The most common method for analysis used in the earlier studies has been a fit to a double-exponential function followed by extrapolation of the fast relaxation rate to low scattering angle where only the first internal mode has a significant amplitude. It will be shown, however, that this method has disadvantages when the exponential of interest has a small relative amplitude.

We have also used here other computational techniques that have recently become available to experimentalists, viz., CONTIN and MAXENT, which allow a much improved appraisal of the decay time distribution (see Data Treatment). The application of such methods becomes very powerful when applied to data taken with the recently developed multisampling time autocorrelators since one obtains access to the complete distribution of decay times in a single experiment. It will be shown that the uncertainties, inherent in a double-exponential fit, may be reduced significantly.

The main system used for this investigation is polystyrene in cyclohexane at the Θ temperature (34.5 °C) ($\bar{M}_w = 15 \times 10^6$, $C = 3.05 \times 10^{-4}$ g·mL^{-1}). The system has been chosen because relatively monodisperse polystyrene samples of high molecular weight can be obtained commercially. Furthermore, many previous investigations have been performed on similar systems, thus giving the possibility of making comparisons of the various derived quantities. In addition, a number of measurements have been performed on a solution of polystyrene in toluene at 25 °C ($\bar{M}_w = 3.8 \times 10^6$, $C = 1.9 \times 10^{-4}$ g·mL^{-1}).

Theory

The theory of internal modes as detected by dynamic light scattering was first given by Pecora,[1] and only a brief summary will be given here. The normalized electric field correlation function of scattered light from a dilute solution of large monodisperse coils may be written as a series of discrete exponents:

$$g^{(1)}(t) = e^{-D\mathbf{q}^2 t}(P_0 + P_{21}e^{-2t/\tau_1} + P_{12}e^{-t/\tau_2} + P_{22}e^{-2t/\tau_2} + P_4 e^{-4t/\tau_1} + ...) \quad (1)$$

where τ_1 and τ_2 are the relaxation times of the first two normal modes. The relative amplitudes of these terms depend strongly on a parameter $x = \mathbf{q}^2\langle R_g^2\rangle$, where $\mathbf{q}$ is the scattering vector and R_g is the radius of gyration. Only the first five terms that appear in eq 1 will be considered here because they are the dominant terms for values of x up to about 7. Furthermore, quantitative estimates of the amplitudes of subsequent exponents are lacking. The relaxation times are generally expressed either in terms of the intrinsic viscosity $[\eta]$ and the molecular weight M or in terms of the diffusion coefficient D and R_g. In the free-draining (Rouse) model, the relaxation time of the first mode is given by

$$\tau_1 = 1.21M[\eta]\eta_s/RT \quad (2a)$$

or

$$\tau_1 = 0.201R_g^2/D \quad (2b)$$

where η_s is the solvent viscosity and R is the gas constant. The relaxation time of the pth mode may be calculated from the first mode by using

$$\tau_p = \tau_1/p^2 \quad (3)$$

In the nondraining (Zimm) model, τ_1 is correspondingly given by

$$\tau_1 = 0.847M\eta_s[\eta]/RT \quad (4a)$$

or

$$\tau_1 = 5.84\eta_s R_g^3/kT \quad (4b)$$

where k is the Boltzmann constant. Higher modes are, in this case, given by

$$\tau_p = \tau_1/p^{1.5} \quad (5)$$

If the nondraining model is used without preaveraging the Oseen tensor, the calculated values for the relaxation times are increased by approximately a factor of 2 with respect to the values obtained after preaveraging.[14]

For the respective models, both ways of expressing the relaxation times are equivalent and should yield the same numerical values. In practice, however, when using experimental values for the intrinsic viscosity and the molecular weight, one obtains values for the relaxation times that differ significantly from those calculated employing the experimental values of the radius of gyration and the diffusion coefficient. In the case of polystyrene in a Θ solvent, the difference is relatively small (±15%) when the nondraining model is used but is still well outside the accuracy of the experimentally determined values of the used parameters (see ref 15 for a discussion of this point). However if the free-draining model is used, the difference may be larger (it becomes more than a factor of 2 for the present system). The reason is that the observed dependencies of D, R_g, and $[\eta]$ on molecular weight are close to those expected for the nondraining model but different from the values expected from the free-draining model.[16] In view of this discrepancy, it seems less reasonable to use the free-draining model to calculate the normal modes. We have therefore compared our data with theoretical values by using the nondraining model with and without preaveraging of the Oseen tensor.

A different approach to the internal modes is to examine their combined influence on the average relaxation time described by the correlation function. At large x values, the average relaxation time is expected to become proportional to $\mathbf{q}^3$ in the nondraining case and $\mathbf{q}^4$ for the free-draining case.[17] Experimentally, a cubic dependence on $\mathbf{q}$ has been found by various authors[18,19] for polystyrene in a Θ solvent, which again indicates that the free-draining model is not appropriate.

Data Treatment

In the homodyne mode, the measured normalized intensity autocorrelation function $g^{(2)}(t)$ is related to the normalized electric field correlation function $g^{(1)}(t)$ by the expression

$$g^{(2)}(t) = 1 + \beta|g^{(1)}(t)|^2 \qquad (6)$$

where β accounts for the deviation from ideal correlation. For monodisperse particles much smaller than the wavelength, experiencing Brownian motion, we have

$$\Gamma\ (=\tau^{-1}) = D\mathbf{q}^2 \qquad (7)$$

where D is the translational diffusion coefficient, τ the relaxation time, and Γ the relaxation rate.

The distribution of relaxation times $A(\tau)$ is related to $g^{(1)}(t)$ (and thus the measured function $g^{(2)}(t)$) by inversion of the Laplace equation:

$$g^{(1)}(t) = \int_0^\infty A(\tau)\exp(-t/\tau)\,\mathrm{d}\tau \qquad (8)$$

which is notoriously difficult to perform and ill-conditioned due to the finite range and precision of the experiments.

Analysis of the measured data was attempted by three distinctly different approaches, as described below. These methods were used to analyze both experimentally measured data and data simulated by using eq 1 with the addition of noise of the same size as detected in the experiments. The amplitudes and relaxation times used in the simulations were interpolated from theoretical values tabulated by Perico et al.[4]

Method 1. The data were fitted directly (*not* its square root) to the double-exponential model

$$g^{(2)}(t) - 1 = \beta[A_1\exp(-\Gamma_1 t) + A_2\exp(-\Gamma_2 t)]^2 + C \qquad (9)$$

where C is a floating base line. One decay rate (Γ_2) reflects the diffusive mode and the other (Γ_1) is assumed to include an average of all the internal modes. For low x values (i.e., low scattering angles), Γ_1 becomes equal to ($D\mathbf{q}^2 + 2/\tau_1$). p $2/\tau_1$). At low x values, however, the contribution of the internal modes is only a few percent of the total scattering, which strongly reduces the accuracy of the fit. To improve the situation, the first exponent may be fixed using a value for the diffusion coefficient obtained from measurements at very low angles where no contribution of internal modes is observed and the correlation functions are observed to be single-exponential functions. This is the method most often applied to this type of experiment. Simulations show that this method works well when the diffusion coefficient (and thus Γ_2) is known with high accuracy, but a slight error in D introduces large errors in the fast relaxation rate (Γ_1), especially when the amplitude of this component is small, which is the case if one wishes to be sure that the fast exponent reflects only the first internal mode. The results of a number of simulations are shown in Table I. Values for the amplitudes and relaxation times have been chosen, which are close to those expected for the system under investigation at lower x values ($1 < x < 2$). It is clear that in order to use this method successfully a very precise (deviation <1%) value for D is needed. This is particularly difficult for large molecular weight samples, because only at very low angles, where the influence of spurious scattering is largest, is the correlation function unaffected by internal modes.

Table I
Analysis of Simulated Correlation Curves[a]

	$A_1/[A_1 + A_2]$, %	$10^{-3}\Gamma_1$, s^{-1}	$10^{-3}\Gamma_2$, s^{-1}
		(A)	
(a)	3.76	2.38	0.307
	5.0	2.56	0.386
	6.8	3.15	0.469
	8.0	3.20	0.515
(b)	2.73	2.89	0.316
	3.76	3.24	0.398
	5.6	3.63	0.483
	6.6	3.68	0.530
(c)	1.86	3.99	0.326
	2.81	4.27	0.410
	4.56	4.20	0.497
	5.47	4.23	0.546
		(B) Expected Values	
	2.84	2.90	0.316
	4.34	2.97	0.398
	6.0	3.58	0.483
	7.1	3.69	0.530

[a] Relative amplitudes ($A_1/[A_1 + A_2]$) and relaxation rates (Γ_i) obtained from fits to a double-exponential function (see eq 9) using different fixed relaxation rates for the slower component (Γ_2). The results given in section A are for fits using (a) slightly too low, (b) correct, and (c) slightly too high fixed relaxation rates. The data in section B are the values expected from the simulations.

Method 2. Experimental correlation functions have been analyzed by the so-called maximum entropy method (MAXENT),[20,21] which yields a continuous distribution of relaxation times. The result of such analyses cannot be directly compared with theory due to the smoothing that is involved in the procedure. Only when the correlation functions are single exponential or consist of components that are widely separated on the time scale will true values for the fitted parameters be recovered. To make a comparison with theory possible, correlation functions have been generated by using eq 1 incorporating a noise level identical with that of the experimental data. The generated data were subsequently subject to the same analysis, making it possible to observe the effect of smoothing. If eq 1 correctly describes the physical situation, the obtained distribution of relaxation times will be identical with the experimental result. The method is therefore useful only for judging to what extent a theoretical expression for the correlation function is valid. The CONTIN program from Provencher[22] yields, for the systems investigated here, results that are close to MAXENT results when a smoother solution than the chosen solution of CONTIN is selected. However, even the less smoothed solutions of CONTIN cannot be directly compared to theory.

Method 3. The main obstacle to a correct analysis of the correlation function obtained at low x values is the small relative amplitudes of the internal modes. To substantially eliminate the influence of the translational diffusion relaxation on the minor components (from the internal modes), the correlation functions have been divided by $\exp(-2\mathbf{q}^2Dt)$, yielding what might be called a "reduced correlation function". If the correct D value has been chosen, the result should reflect only the contribution of the internal modes. As the relaxation times of the latter are independent of scattering angle, one may sum the reduced correlation functions derived from data measured at different angles to decrease the noise level. Contrary to force fitting to a double-exponential function with a fixed D value, this procedure is not particularly sensitive to the accuracy of the chosen D value, as long as the latter is not larger than the true value. A value for D that is too high is easily detected by an upward curvature of the base line. Choosing a slightly too low value for D only introduces a very slow relaxation time without significantly influencing the fast relaxation time. This procedure thus greatly reduces a major source of error. A significant disadvantage of this method is that the noise in the baseline is divided by small numbers and is therefore

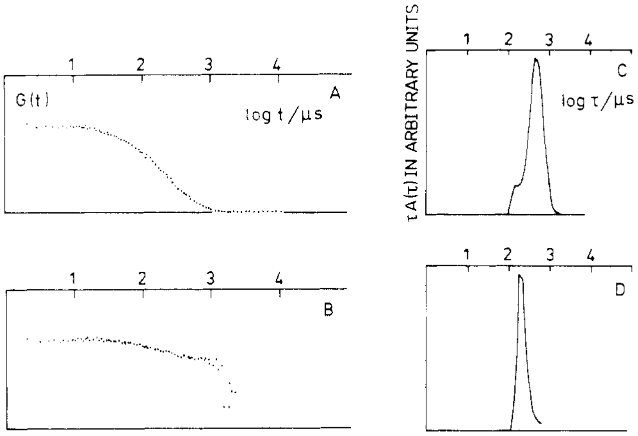

Figure 1. Example of an autocorrelation function $g^{(2)}(t)$ with the corresponding relaxation time distribution obtained from MAXENT, before (A,C) and after (B,D) division by $\exp(-2D\mathbf{q}^2t)$. The sample used consists of polystyrene in toluene ($\bar{M}_w = 3.8 \times 10^6$, $C = 1.9 \times 10^{-4}$ g·mL^{-1}) with $(\mathbf{q}R_g)^2 = 2$.

greatly enhanced. This means, in practice, that the correlation function has to be cut off at the point at which the noise becomes too large. This artificial cutoff, plus the noise in the tail, is the reason why, even after division by the correct value of D, a very slow relaxation time is obtained in addition to a large base-line value. In Figure 1, an example is shown of a correlation curve before and after division by $\exp(-2\mathbf{q}^2Dt)$ together with the corresponding relaxation time distributions obtained from MAXENT. It is clear that data collection for a long time is required to obtain a reasonable noise level after division. The results from simulated data obtained using the same set of simulated curves as used in method 1 are shown in Table II. The diffusive term was not fixed here but divided out before analysis with MAXENT. In all cases, only one peak was recovered, which is an average of all four components containing internal modes (see eq 1) used in the simulation. This shows that for lower x values MAXENT cannot separate components from the different internal modes. The results show that this method of analysis is less sensitive to uncertainties in the D value, but it seems to slightly overestimate the relaxation rate and underestimate the amplitude, depending, of course, on the noise level.

In conclusion we can say that, to obtain a quantitative value for τ_1, the best method is a forced fit to a double-exponential function by fixing the first exponent using a very accurate D value and extrapolating the fast decay time to zero angle. Lacking such a precise value for D (which is the usual experimental situation), the correlation curves should be divided by $\exp(-2\mathbf{q}^2Dt)$, which makes the results less sensitive to the used value of D but also reduces the accuracy of the resulting parameter τ_1.

Experimental Section

Polystyrene solutions were prepared using polymers from Toya Soda Ltd. Japan: $M_w = 15 \times 10^6$, $M_w/M_n = 1.30$, $M_w = 3.8 \times 10^6$, $\bar{M}_w/\bar{M}_n = 1.05$. Solvents were spectroscopic grade materials from Merck, Darmstadt, FRG, and were used without further purification except for drying over 3-Å molecular sieves. The solutions were flame sealed at −15 °C and were allowed to mature for 3 months prior to use.

Dynamic Light Scattering. The experimental arrangement has been described previously.[23] The light source was either a 488-nm Ar laser or a 632-nm He-Ne laser. An ALV-Langen Co., multibit, multi-τ autocorrelator was operated with 23 simultaneous sampling times (covering, for example, delay times in the ranges 1 μs to 1 min) in the logarithmic mode and 191 channels. The stability of the photon count at all angles indicated that the solutions were essentially dust free. The data were analyzed by successive fitting to discrete exponential functions using a program in which it was possible to fix chosen parameters. The use of the latter is discussed below under Results and Discussion.

Table II
Analysis of Simulated Curves[a]

	A, %	$10^{-3}\Gamma$, s^{-1}	$10^{-3}D\mathbf{q}^2$, s^{-1}
		(A)	
(a)	2.9	2.47	0.307
	3.8	2.87	0.386
	5.3	3.24	0.469
	6.6	3.19	0.515
(b)	2.56	2.7	0.316
	3.8	2.87	0.398
	5.2	3.26	0.483
	6.65	3.16	0.530
(c)	2.1	3.24	0.326
	2.76	3.68	0.410
	4.3	4.1	0.497
	5.26	3.8	0.546
		(B) Expected Values	
	2.84	2.58	0.316
	4.34	2.57	0.398
	6.0	3.10	0.483
	7.1	3.16	0.530

[a] Relative amplitudes and relaxation times rates from fits using MAXENT. Before fitting, the curves were divided by $\exp(-2D\mathbf{q}^2t)$. In all cases, only one peak was obtained, which reflects the average of all four terms containing internal modes used in the simulation (see eq 1). The results given in section A are for fits using (a) slightly too low, (b) correct, and (c) slightly too high values for $D\mathbf{q}^2$ (given in the third column) in the division. The data in section B are the values expected from the simulations.

Distributions of relaxation times were also obtained by using the maximum entropy analysis (MAXENT), which is a comparatively new technique for DLS data analysis and which has been successfully applied to a variety of problem areas involving image reconstruction. Its application to DLS data treatment has been described by Livesey et al.,[20,21] and the power of the method to deal with distributions containing single and multiple peaks was demonstrated using both simulated data and experimental correlation curves for colloidal systems. It is particularly relevant in the present context that MAXENT provides a unique solution that is robust to noise and only shows features (peaks) if demanded by the data. Resolution is limited, however, such that when two components differ in relaxation time by less than a factor of about 2 they are no longer resolvable. (This curtailment appears to be a general one. Only if the form of the distribution is known (e.g., bimodal) can a better resolution be obtained.)

Some analyses have also been made by using CONTIN, a constrained Laplace inversion program provided by Provencher.[22] It 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 relative amplitude and relaxation rate (Γ) of each component. Since, in general, the distributions from CONTIN (chosen solution) and MAXENT are practically identical, we have emphasized the latter procedure.

Results

Polystyrene ($\bar{M}_w = 15 \times 10^6$) in Cyclohexane at 34.5 °C. Correlation functions have been measured in the angular range 20–140°. The sequential use of two lasers with wavelengths of 488 and 633 nm made it possible to scan a large range of x values ($0.4 < x < 15$). Relaxation time distributions have been obtained by using MAXENT. Examples are shown in Figure 2 for different values of x. For $x < 0.8$, the correlation curves are close to single-exponential functions. From these curves, an average value for the diffusion coefficient $D = 3.3 \pm 0.1 \times 10^{-12}$ m^2·s^{-1} was obtained. By use of a now well-established relation between D at infinite dilution and R_g ($R_g = kT/14.8\eta_s D_0$),[25] the radius of gyration was calculated to be 1140 Å. The value 1140 Å has been used in the calculation of x. Other

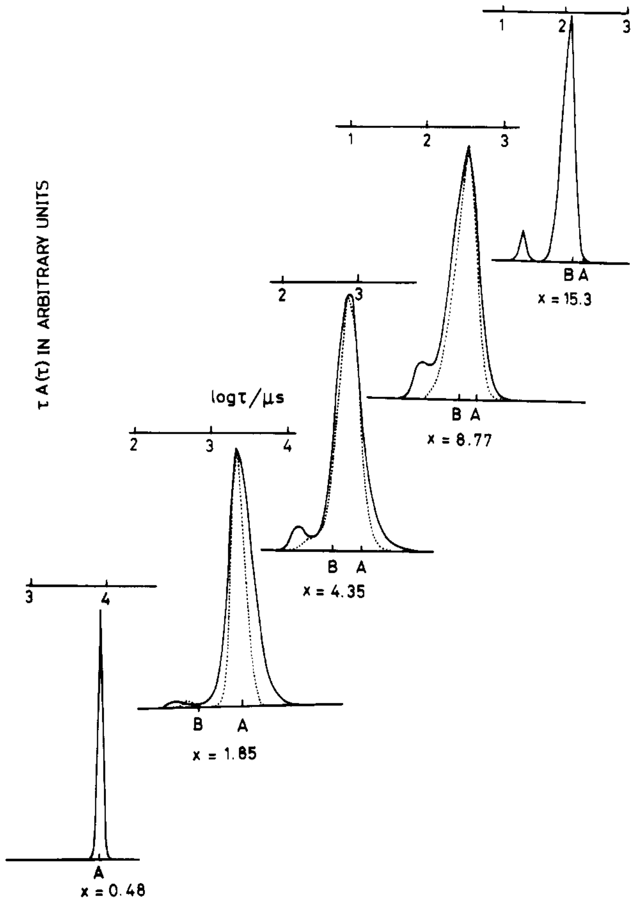

Figure 2. Results of some analyses of autocorrelation functions of polystyrene in cyclohexane ($\bar{M}_w = 15 \times 10^6$, $C = 3.05 \times 10^{-4}$ g·mL^{-1}) using MAXENT, for various values of $x = (\mathbf{q}R_g)^2$ (full lines). For comparison, some results of simulations using eq 1 have been added to the plots (dotted lines). The first two relaxation times used in the simulation are indicated, where $A = 1/(D\mathbf{q}^2)$ and $B = 1/(D\mathbf{q}^2 + 2/\tau_1)$. For $x > 5$, the simulations show only one peak, while the experiments show two peaks.

well-established relationships have been used to calculate the molecular weight ($R_g = 0.29M^{0.5}$ Å),[24] yielding $M = 15 \times 10^6$ g/mol, and the intrinsic viscosity ($[\eta] = 0.091M^{0.5}$),[25] yielding $[\eta] = 354$ cm^3 g^{-1}. One may query why experimental values for M, R_g, and $[\eta]$ were not used. The reason is that the diffusion coefficient is the parameter that can be obtained with the highest accuracy for high molecular weight samples. Rather than using a single experimentally determined value for the other parameters, we judged that better values are obtained when reasonably well-established relationships from the literature are used.

Using the above parameters in eq 4 and 5 gives the values $\tau_1 = 1330$ μs and $\tau_2 = 470$ μs when M and $[\eta]$ are used and $\tau_1 = 1570$ μs and $\tau_2 = 554$ μs when R_g is used. With the latter values for τ_1 and τ_2 and the amplitudes tabulated in ref 4, correlation functions were simulated according to eq 1, incorporating the same noise as in the actual experiments. These curves were then fitted by using MAXENT, and each distribution of decay times was compared with that derived from the corresponding experiment. Figure 2 shows examples of these comparisons for various x values. Peak positions for the pure diffusion mode (A) and for the first internal mode mixed with the diffusion mode (B) are indicated in the plots. Semiquantitatively there is agreement between the simulated data and the experimental curves. However, it is clear that for large x values more exponential terms than those given in eq 1 are needed to adequately describe the experimental results. It is also clear that it is impossible to obtain a satisfactory value for τ_2 from these fits, as the exponential terms containing τ_1 and τ_2 are too close on the time scale for separation using MAXENT. The same qualitative result is obtained by using CONTIN; i.e., even the least smoothed solution does not allow separation of the exponents containing τ_1 and τ_2.

Table III
Experimental Results for Polystyrene in Cyclohexane from Fits to a Double-Exponential Function with the Slow Relaxation Rate Fixed, for Various Values of x[a]

x	A, %	$10^{-3}\Gamma$, s^{-1}	A, %	$10^{-3}\Gamma$, s^{-1}	A, %	$10^{-3}\Gamma$, s^{-1}
1.21	4.6	1.61	3.1	2.15	2.0	3.03
1.85	7.3	2.20	5.7	2.66	4.3	3.09
2.03	8	2.52	6	2.81	5	3.40
2.58	10	2.96	8.9	3.25	7.4	3.62
3.40	17	3.13	14.7	3.36	12.8	3.59
4.35	26	4.27	25	4.4	23	4.64

[a] The fixed relaxation rate has been set equal to $D\mathbf{q}^2$ for three different values of D. From left to right, D equals respectively 3.2×10^{-12}, 3.3×10^{-12}, and 3.4×10^{-12} m^2/s.

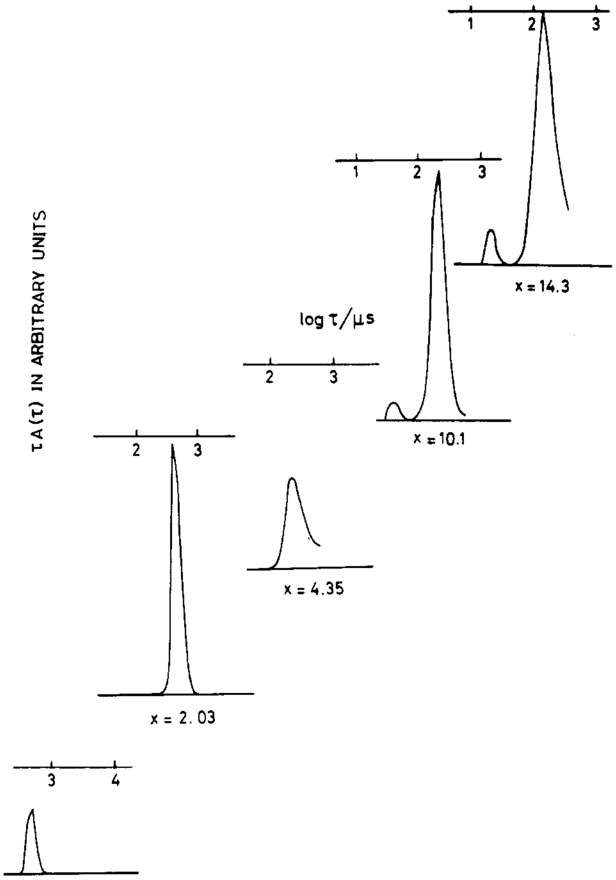

Figure 3. Results of some analyses of autocorrelation functions using MAXENT, after dividing out the diffusive term, for various values of $x = (\mathbf{q}R_g)^2$. The positions of the peaks, which reflect only internal modes, are given in Table IV. The absolute heights of the peaks do not have any significance. System as in Figure 2.

In order to obtain a better quantitative value for τ_1, the experimental data have been force fitted to a double-exponential function using three slightly different values for D; see Table III. The results show that there is a strong dependence upon the D value both for the relaxation times and for the amplitudes, which confirms the conclusion drawn from the simulations. From the relaxation times at low angles, a value for τ_1 may be estimated. $\tau_1 = 1350$, 1000, or 770 μs with $D = 3.2 \times 10^{-12}$, 3.3×10^{-12}, and 3.4×10^{-12} m^2·s^{-1}, respectively.

Table IV
Experimental Values for Polystyrene in Cyclohexane Obtained for Various x Values Using MAXENT after Dividing the Curves by a Fixed Diffusion Term: $\exp(-2D\mathbf{q}^2t)$

x	A_1, %	$10^{-3}\Gamma_1$, s^{-1}	A_2, %	$10^{-3}\Gamma_2$, s^{-1}
1.21	2.4	2.3		
1.85	5.0	2.38		
2.03	6.1	2.34		
2.58	9.6	2.58		
3.40	12.9	2.8	0.3	19.2
4.35	13.6	4.42		
8.77	40.1	5.26		
10.1	51.5	4.85	2.1	23.2
11.6	51.2	5.97	1.8	30.8
14.3	66.0	5.95	3.4	40.2

Table V
Experimental Values for Polystyrene in Toluene for Various x Values Using MAXENT after Dividing the Curves by a Fixed Diffusion Term: $\exp(-2D\mathbf{q}^2t)$

x	A, %	$10^{-3}\Gamma$, s^{-1}
1.5	2.7	4.46
2.0	5.4	4.52
2.17	9.3	4.66
3.16	16.6	4.6

As mentioned above, after the correlation functions are divided by $\exp(-2\mathbf{q}^2Dt)$, the results for the fast mode become much less sensitive to the choice of the D value as long as the chosen D value is not larger than the true value. Curves treated in this way were analyzed by using MAXENT. Figure 3 depicts some results for different x values, employing $D = 3.3 \times 10^{-12}$ m^2·s^{-1} in the division. For low x values ($x < 4$) MAXENT yields a single peak, as well as a peak at very long relaxation times (not shown) due to noise in the data and inaccuracy in the chosen D value, as explained above. This peak comprises a mixture of the first internal mode plus the higher modes which become increasingly more important at higher x values. At high x values, a second, faster peak appears, characterized by a small amplitude and much shorter relaxation time. Peak positions are tabulated in Table IV. The results for $x < 2$ have been used to calculate an average value for τ_1, yielding 870 μs. In order to improve the definition of the modes, we have summed the correlation function (previously dividing out the diffusive term) taken up at the different (low) angles and again analyzed the multiangle sum with MAXENT. This procedure yields $\tau_1 = 900$ μs. By use of $D = 3.2 \times 10^{-12}$, the same value of τ_1 is found within the uncertainty of the method. Using $D = 3.4 \times 10^{-12}$, on the other hand, gives a somewhat lower value of τ_1. An upward curving residual after division indicates that the D value employed was too large. The relative amplitude of the sum of all the internal modes is given in Table IV. As in the case of the relaxation times, these values are much less sensitive to the choice of D.

Polystyrene ($\bar{M}_w = 3.8 \times 10^6$) in Toluene. Correlation functions have been measured for a number of selected angles. The diffusion coefficient determined from measurements at low scattering angles is 6.2×10^{-12} m^2·s^{-1}, which is in agreement with D values found by Appelt and Meyerhoff[26] and Nemoto et al.[13] By use of this value for D, correlation functions obtained at higher angles have been analyzed in the same way. The results are given in Table V. Averaging the values at the lowest three x values, we obtain $\tau_1 = 440$ μs. Values for R_g and $[\eta]$ have been calculated by using the empirical relationships between $R_g = 0.122M^{-0.595}$ Å[27] and $[\eta] = 7.8 \times 10^{-3}M^{0.75}$.[28] These gave respectively $R_g = 1000$ Å and $[\eta] = 671$ mL·g^{-1}. Using this value for $[\eta]$ in eq 4a (the prefactor in eq 4b may not be correct for good solvents), one obtains $\tau_1 = 478$ μs.

Discussion

Strongly differing values for τ_1 have been reported in the literature. The three groups reporting values for τ_1 for polystyrene in cyclohexane at the Θ temperature used a forced fit to a double exponential, fixing one exponent using the diffusion coefficient measured at very low angle.[6-9] However, use of slightly different values for D fully accounts for the different findings. Jones and Caroline[9] and King and co-workers[6,8] determined the molecular weight dependence of τ_1. For a fraction with $\bar{M} = 15 \times 10^6$ as used here, $\tau_1 = 1193$ μs (ref 9) and $\tau_1 = 645$ μs (840 μs before corrections for polydispersity) (ref 6, 8). These values may be compared to our value, 900 μs, lying in between. However, as has been shown above, our method of analysis may somewhat underestimate the true value, which is probably closer to Jones' value. Values of τ_1 found for polystyrene in other solvents are either close to the value calculated by using the nondraining model or lower.[10-13] Here, too, forced fits to a double-exponential function have been used. In one case, the so-called histogram method has been applied.[12,13] In the latter case, two exponents were obtained for x values between 0.75 and 10. The slow exponent was observed to be $\mathbf{q}^2$ dependent over the entire range of x and was considered to consist solely of the diffusion mode. The amplitude of the fast mode increased strongly with increasing angle and was thought to comprise all the internal modes together. This seems improbable, however, as the difference between the relaxation rate deriving from the first internal mode and from the pure diffusion mode (i.e., B and A in Figure 2) becomes smaller (less than a factor of 2 for $x > 6$) than the difference between the first internal mode (B) and the average of all internal modes. This means that τ_1 will not, in general, be resolvable from the diffusion peak at $x > 6$ (see Figure 2) and also that a tendency to split into two peaks at high values of x reflects the separation of different *groups* of internal modes. The additional very fast mode observed in the present investigation at high x values was not observed by Tsunashima et al.[12] Division into two modes over the whole x range constitutes a gross oversimplification.

Comparison with theory has given rise to some confusion, as has already been noted by Jolly and Eisenberg.[29] Usually, the theoretical expressions for τ_1 are given either in terms of the molecular weight and the intrinsic viscosity or in terms of the radius of gyration (and the diffusion coefficient). In the case of polystyrene, the only comparison between these two ways of expressing τ_1 is made by Huang and Frederick[7] using the free-draining model. Unfortunately, their expression in terms of D and R_g differs from eq 2b by a factor of 2, giving a fortuitous and misleading agreement between the alternative ways of expressing τ_1 for this model.

The values of τ_1 that have been found in the present investigation are smaller than the theoretical value calculated from either eq 4a or 4b for both systems investigated but are closest to theory when the intrinsic viscosity is used. Preaveraging the Oseen tensor is not the reason for the discrepancy between theory and experiments, as nonpreaveraging would increase the theoretical value for τ_1. Using a realistic draining parameter does reduce the theoretical value for τ_1, but it is not enough to explain the difference with the experimental value. Before drawing any conclusions, however, one must realize that, although we feel that the use of method 3 reduces the sensitivity to the value used for D, the errors may still be quite large. Also, in the calculation of the theoretical values, errors are

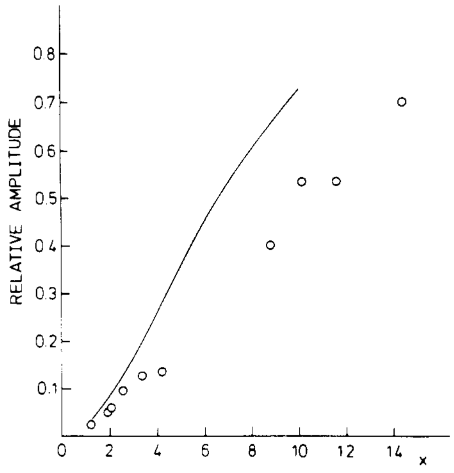

Figure 4. Comparison of relative amplitudes of the collected internal modes with theory values for the nondraining case (full line), as a function of $x = (\mathbf{q}R_g)^2$. System as in Figure 2.

introduced in conjunction with the parameters used. Furthermore, concentration effects on D and τ_1 have been neglected, but they are expected to be small for the concentrations that have been used.[12] We are planning to investigate the concentration effects on internal dynamics of single coils and semidilute systems at a later stage.

As in the case of the relaxation times, there is a large variation in the observed values of the relative amplitudes of the internal modes as a function of x. Amplitudes that lie both above[9,10] and below[7,8,12,13] the theoretical values have been reported. In Figure 4, the relative amplitudes of the internal modes have been plotted as a function of x together with the theoretical prediction. The contribution of the internal modes to the scattered light is thus observed to be lower than expected from theory for all x values.

With the nondraining model, a $\mathbf{q}^3$ dependence of the average relaxation rate $\bar{\Gamma}$ is expected for large x values.[17] In Figure 5, values of $\bar{\Gamma}/(\mathbf{q}^3kT/\eta_s)$ are plotted as a function of x for the polystyrene in cyclohexane system. For large x values, the curve reaches a plateau value. For the case of Θ solvents, the plateau value of $\bar{\Gamma}/\mathbf{q}^3(kT/\eta_s)$ is expected to be 0.053 with a preaveraged Oseen tensor.[19] The plateau in Figure 5 yields $\bar{\Gamma}/\mathbf{q}^3(kT/\eta_s) = 0.043$. A value which is lower by about 15% with respect to theory is usually observed for these systems.[19] An explanation for this phenomenon is lacking, however (not using a preaveraged Oseen tensor yields an even higher theoretical value). The observed $\mathbf{q}^3$ dependence demonstrates that the very fast relaxation time observed at high angles is caused by the concerted effect of the higher internal modes. Why these higher internal modes group into a single, well-defined peak is not clear. One needs values for the contribution of higher internal modes to the correlation function in order to determine whether this separation is expected by theory.

The present results highlight the difficulties in obtaining precise estimates of the normal modes using current apparatus and numerical techniques. The experimental error is unavoidably large, owing to the small contribution of the normal modes in the low x range. In the high x range, present methods are unable to separate the various modes, which are practically superimposed in the decay time spectrum.

Unless the diffusion coefficient is known with very high accuracy, the preferred procedure is to divide out this term from the correlation function prior to analysis. However, this requires data of very low noise level in order to give precise values of τ_1. Improvement may be obtained by making a multiangle summation in the low x range where only τ_1 is significant.

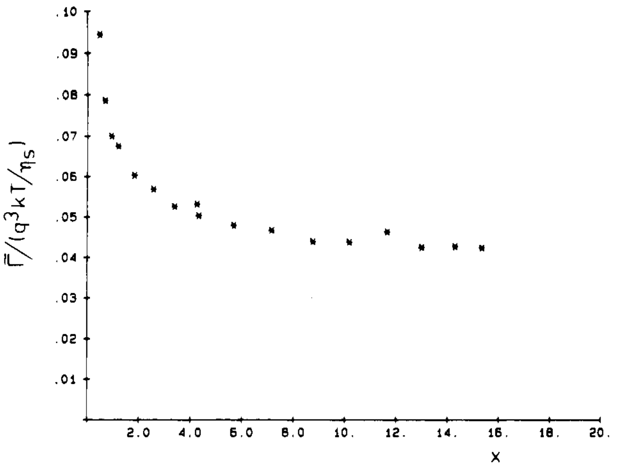

Figure 5. Values of $\bar{\Gamma}/(\mathbf{q}^3kT/\eta_s)$ for polystyrene in cyclohexane, as a function of $x = (\mathbf{q}R_g)^2$. System as in Figure 2.

With regard to theory, it is unclear as to which experimental parameters are to be used to estimate relaxation times with existing expressions. The free-draining model appears to be an unrealistic approach for calculating the relaxation times for flexible coils since the nondraining approximation more closely describes the molecular weight dependence of the coil parameters. Taken together, the weight of the accumulated data shows that the nondraining model overestimates τ_1. This is apparently a more general problem; quantitative differences with nondraining theory for other experimental parameters in dilute polystyrene solutions are well-known.[15,16]

References and Notes

(1) Pecora, R. *J. Chem. Phys.* **1965**, *43*, 1562.
(2) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
(3) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(4) Perico, A.; Piaggio, P.; Cumberti, C. *J. Chem. Phys.* **1975**, *62*, 2690, 4911.
(5) Tagami, Y.; Pecora, R. *J. Chem. Phys.* **1969**, 3293.
(6) King, T. A.; Treadway, M. F. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1473.
(7) Huang, W.; Frederick, J. E. *Macromolecules* **1974**, *7*, 34.
(8) McAdam, J. D. G.; King, T. A. *Chem. Phys.* **1974**, *6*, 109.
(9) Jones, G.; Caroline, D. *Chem. Phys.* **1979**, *37*, 187.
(10) Jones, G.; Caroline, D. *Chem. Phys.* **1979**, *40*, 153.
(11) Nishio, I.; Wada, A. *Polym. J. (Tokyo)* **1980**, *12*, 145.
(12) Tsunashima, Y.; Nemoto, N.; Kurata, M. *Macromolecules* **1983**, *16*, 584, 1184.
(13) Nemoto, N.; Makita, Y.; Tsunashima, Y.; Kurata, M. *Macromolecules* **1984**, *17*, 425.
(14) Bixon, M.; Zwanzig, R. *J. Chem. Phys.* **1978**, *68*, 1890.
(15) Fujita, H. *Macromolecules* **1988**, *21*, 179.
(16) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.
(17) Dubois-Violette, E.; de Gennes, P. G. *Physics (Long Island City, N.Y.)* **1967**, *3*, 181.
(18) Adam, M.; Delsanti, M. *Macromolecules* **1977**, *10*, 1229.
(19) Han, C. C.; Akcasu, A. Z. *Macromolecules* **1981**, *14*, 1080.
(20) Livesey, A. K.; Delaye, M.; Licinio, P.; Brochon, J. E. *Faraday Discuss. Chem. Soc.* **1987**, *No. 83*, 247.
(21) Livesey, A. K.; Licinio, P.; Delaye, M. *J. Chem. Phys.* **1986**, *84*, 5102.
(22) Provencher, S. W. *Makromol. Chem.* **1979**, *180*, 201.
(23) Brown, W. *Macromolecules* **1986**, *19*, 1083.
(24) Schmidt, M.; Burchard, W. *Macromolecules* **1981**, *14*, 210.
(25) Miyaki, Y.; Fujita, H.; Fukada, M. *Macromolecules* **1980**, *13*, 588.
(26) Appelt, B.; Meyerhoff, G. *Macromolecules* **1980**, *13*, 657.
(27) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180.
(28) Einaga, Y.; Miyaki, Y.; Fujita, H. *J. Polym. Sci.* **1979**, *17*, 2103.
(29) Jolly, D.; Eisenberg, H. *Biopolymers* **1976**, *15*, 61.