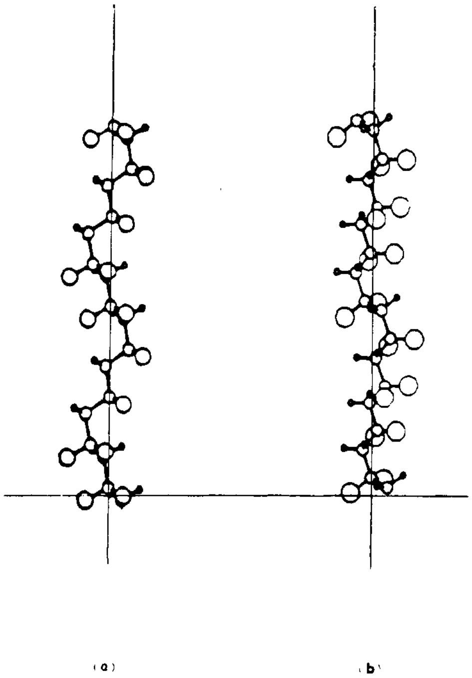

Figure 3. Ball-stick models of possible phase III PVF$_2$ chain conformations: (a) *TTTGTTTG'*; (b) *TGTG'TG'TG*.

Table III contains a description of the final two conformations we believe are most appropriate for phase III PVF$_2$. The phase I and II structures are also listed for comparison. Of the two possible phase III structures, *TTTGTTTG'* is preferred on the basis of FTIR data and also intrachain molecular energetics.

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A Study of Concentration Fluctuations during the Thermal Polymerization of Styrene Using Photon Correlation Spectroscopy

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ABSTRACT: The cooperative diffusion coefficient D_c for concentration fluctuations is studied as a function of polymer concentration during the thermal polymerization of styrene using photon correlation spectroscopy. Measurements were carried out from the semidilute region to approximately 90% polymer. From 2–10%, polymer D_c rose linearly with concentration. The value of D_c eventually reached a plateau with a value of 4.5×10^{-6} cm^2/s which corresponds to a minimum dynamic screening length between 10 and 15 Å. At higher polymer concentrations, the local viscosity increases sharply, and the value of D_c falls accordingly.

Introduction and Theory

The Rayleigh spectroscopy of dilute polymer solutions is now well understood.[1] The spectrum due to concentration fluctuations can be explained in terms of the dynamics of isolated polymer molecules. There has been considerable recent interest in the Rayleigh spectroscopy of semidilute and concentrated polymer solutions.[2–7] Experimentally, it has proven difficult to clarify such solutions sufficiently to study the intrinsic homodyne correlation function. However, a convenient technique exists to prepare optically clear polymer solutions. Stevens and co-workers[8,9] have studied the thermal polymerization of styrene using Rayleigh–Brillouin spectroscopy and have shown that the spectrum obtained can be accounted for by intrinsic thermal fluctuations. In the present paper, we report a study of the concentration fluctuations in semidilute and concentrated polymer solutions obtained

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by thermal polymerization of styrene at 90 °C using photon correlation spectroscopy.

The dynamics of the concentration fluctuations in polymer solutions have been presented by deGennes.[2] There are two important lengths that must be considered in the description of the concentration fluctuations: (1) the magnitude of the wave vector for the fluctuations q, and (2) the hydrodynamic screening length ξ_h. In the present paper we consider only the case where $q\xi_h \ll 1$. The relaxation function for the concentration fluctuations is given by

$$\phi_c(t) = \exp(-D_c q^2 t) \tag{1}$$

where $D_c = kT/6\pi\eta\xi_h$ is a collective diffusion coefficient, k is Boltzman's constant, T is the absolute temperature, and η is the local shear viscosity. For dilute solutions, the value of ξ_h is taken to be the radius of gyration, R, of an isolated polymer molecule. When the concentration increases beyond the point where the macromolecules begin the overlap (c^*), the hydrodynamic length is predicted[2] to change according to

$$\xi_h = R(c/c^*)^{-\nu/(3\nu-1)} \tag{2}$$

where $\nu \sim 0.6$. There must also be some concentration beyond which ξ_h becomes independent of concentration, since the hydrodynamic screening length cannot be smaller than the size of a monomer unit in the chain. In the present experiments, observations were begun only after the concentration exceeded c^*. In this regime, the screening length is independent of molecular weight, and the broad molecule weight distribution characteristic of thermally polymerized styrene is not a problem.

The collective diffusion coefficient also depends on the local viscosity η. In a recent paper,[9] the local viscosity during the thermal polymerization of styrene was studied using depolarized Rayleigh spectroscopy. The collective orientational relaxation time increased only 50% during the first 80% of the reaction. Thus most of the solutions would be expected to be characterized by a local viscosity near that of the solvent. Only near the end of the reaction when the glass–rubber relaxation of the solution is approaching would the local viscosity be expected to increase sharply.

Light scattering at some finite angle is due to fluctuations in the dielectric constant of the medium with wave vector magnitude $q = (4\pi n/\lambda) \sin(\theta/2)$ where n is the refractive index for light of vacuum wavelength λ scattered through an angle θ in the scattering plane. Concentration fluctuations lead to light scattering because there is a difference in refractive index between the solute and the solvent. There will also be light scattering from polymer solutions which is due to thermal density and optical anisotropy fluctuations.

Photon correlation spectroscopy measures the quantity

$$C(t) = \langle I(t)I(0)\rangle / \langle I(0)\rangle^2 \tag{3}$$

where $I(t)$ is the intensity of light scattered at time t and the brackets denote a time average. For a Gaussian random process, the homodyne correlation function can be represented as

$$C(t) = 1 + |\phi(t)|^2 \tag{4}$$

where $\phi(t)$ is a relaxation function determined by the dynamics of the fluctuations which lead to the light scattering. The relaxation function for the concentration fluctuations was given in eq 1. The total relaxation function will also include the contributions due to density and anisotropy fluctuations. However, experimentally, only those components which contribute to the relaxation function at times longer than 10^{-7} s will be observed using present photon correlators.

The density fluctuations should relax much faster than 10^{-7} s until the glass–rubber relaxation of the solution is approached. The same is also expected for the anisotropy fluctuations in the semidilute regime. However, as the solution becomes more concentrated, there will come a point when the anisotropy fluctuations of the polymer molecules will contribute to the observed relaxation function, and it may be difficult to separate the contribution due to concentration fluctuations from the part due to anistropy fluctuations. Also, the value of the correlation function $C(t)$ at 10^{-7} s depends on the square of the fraction of the scattered light with long relaxation times. In the semidilute regime, the scattering is dominated by the concentration fluctuations, but as the reaction proceeds and the concentration of polymer increases, the intensity due to concentration fluctuations becomes a rapidly decreasing fraction of the total. These effects limit the ultimate concentration at which accurate measurements of the collective diffusion coefficient can be made. In the present paper we restrict attention to the concentration fluctuations. The following paper discusses the anisotropy fluctuations in concentrated solutions of polystyrene in styrene.

Experimental Section

1. Sample Preparation. The styrene was dried with calcium hydride and degassed under vacuum. The monomer was then vacuum distilled through a Millipore filter directly into the square quartz scattering cell, and the sample was sealed under vacuum. The samples were stored in dry ice until the start of the experiment.

2. Light-Scattering Spectrometer. The incident light was at 5145 Å and was vertically polarized. The intensity was regulated to better than 1%. The scattered light was observed at 90° and was not analyzed for polarization. The sample was held in a temperature-controlled aluminum block at 90 °C, and the temperature was regulated to ±0.2 °C. The scattering volume was defined by a pair of matched lenses followed by a 50 μm pinhole. The coherence area of the scattered light was adjusted to optimize the signal-to-noise ratio with a second aperture placed between the two lenses. The effect of finite coherence area was fully taken into account in the analysis of the data. The light was detected with a Channeltron photomultiplier, optimized for low dark current and minimum intrinsic correlations due to afterpulsing. The output of the PMT was converted to a series of standard digital pulses and analyzed with a 96-channel Malvern digital correlator.

The correlation function actually obtained with the Malvern correlator is the single clipped autocorrelation function

$$C_k(t) = \frac{\langle I_k(t)I(0)\rangle}{\langle I_k(0)\rangle\langle I(0)\rangle} \tag{5}$$

where $I_k(t)$ is the clipped intensity which equals 1 if the number of counts observed during the time window of the correlator exceeds the clipping level k and equals 0 otherwise. The single clipped autocorrelation function is related to the relaxation function $\phi(t)$ according to

$$C_k(t) = N_b\left[1 + \frac{1+k}{1+\langle n\rangle} f(A) g(T) \phi^2(t)\right] \tag{6}$$

where $\langle n\rangle$ is the average number of counts per sample time, $f(A)$ accounts for the finite scattering volume, A, $g(T)$ depends on the finite sampling interval, T, and N_b is a term of order 1 which accounts for small misnormalizations of the real data. In order to accurately obtain $\phi(t)$, all the factors which affect the correlation function must be taken into account. The function $f(A)$ was determined for the apertures used in the present experiments. The sampling interval T was chosen to be short enough that the function $g(T)$ was near 1. The measured correlation function $C_k(t)$

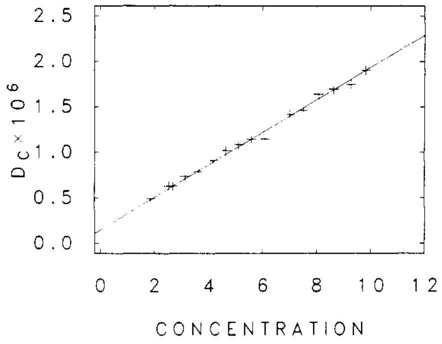

Figure 1. Plot of collective diffusion coefficient D_c vs. concentration. The units of D_c are cm^2/s, and the concentration is expressed as percent polymer.

was then modified by subtracting 1 and dividing by the terms that multiply the square of the relaxation function. The resulting function was then fit with a nonlinear least-squares program to a function of the form

$$F(t) = \delta + P\phi^2(t) \tag{7}$$

During the initial stages of the polymerization, the collective diffusion coefficient was changing significantly during the time necessary to collect a correlation function. As a result, the observed correlation function was not a single exponential decay. In order to obtain an average diffusion coefficient, the early data were analyzed by the method of cumulants. When the collective diffusion coefficient became less sensitive to the concentration of polymer, the data fit very well to a single exponential decay. Near the end of the polymerization, the relaxation time associated with the anisotropy fluctuations became long enough to observe, and the correlation functions could no longer be fit to a single exponential decay. For a short while, the concentration fluctuations could still be studied by discarding the first few points in the observed correlation function, but when the magnitude of the anisotropic scattering became comparable to the concentration fluctuations, the two contributions could not be accurately separated because the anisotropy fluctuations do not lead to a single exponential relaxation function.

Results and Discussion

During the initial stages of the polymerization, the correlation function changed rapidly with time (concentration). It has previously[9] been determined that the rate of the reaction during this period is 0.99% per hour, so that the concentration of polymer can be calculated from the elapsed time. A plot of D_c vs. c for the first 10% of reaction is shown in Figure 1. These results were also all collected using exactly the same experimental parameters (pinhole size, clipping level, and time step (1 μs)). The dependence of D_c on c appears linear, and a fit of the data to a power law relation confirms the linearity. The prediction of the deGennes theory is that there should be a power law relation between D_c and c with an exponent of 0.75. However, we believe that our results are neither a contradiction to the prediction of deGennes nor a confirmation of any other theory that might predict a linear relation between D_c and c.

The collective diffusion coefficient actually depends on many other variables than those displayed in eq 1. In particular, the rate of concentration fluctuations depends on the quality of the solvent (the value of the osmotic virial coefficients), on the friction constant, and on the occupied volume of the polymer. In the dilute region (which we do not probe in this study), the value of D_c can increase, decrease, or remain constant with concentration, depending on the actual nature of the solvent and polymer. This intrinsic behavior persists into the semidilute region and must be taken into account in the analysis of data near c^*. It has also been found[10] that the pseudogel behavior assumed in the deGennes theory is only progressively established in the semidilute region and does not just switch from independent molecule diffusion to pseudogel diffusion at c^*. Thus, the rapid rise in D_c with increasing concentration is a good indication that the screening length is indeed decreasing with increasing polymer concentration, but the exact nature of the power law is obscured by the other factors that affect the observed value of D_c. Under our experimental conditions, the solvent is expected to be very good, probably better than the usual room temperature studies. As a result, the collective diffusion coefficient is expected to rise with increasing concentration in the dilute region, and this effect is expected to persist well into the semidilute region. This could account for the power law exponent being greater than predicted by the pseudogel theory. If the solvent were very bad, the apparent power law exponent could even be negative, due to the low value of the second virial coefficient. Thus, it may be very difficult to actually test the detailed predictions of the deGennes theory with real materials of finite molecular weight.

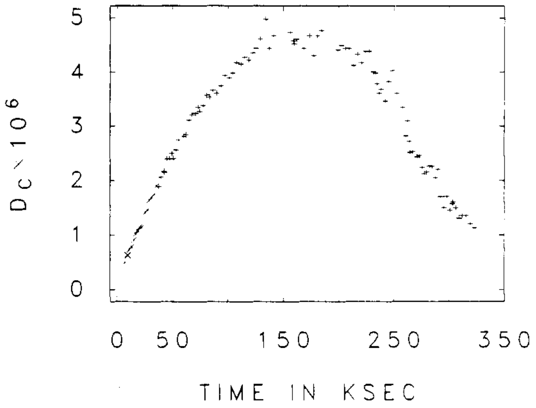

Figure 2. Plot of collective diffusion coefficient D_c vs. elapsed time for all the data.

For times (concentrations) greater than those shown in Figure 1, the data were analyzed using a single exponential relaxation function. All the calculated values of D_c are plotted vs. elapsed time in Figure 2. The calculated value of D_c continued to rise with increasing concentration, but more slowly than the initial linear dependence, and eventually reached a constant region with a value near 4.5 × 10^{-6} cm^2/s. If this value of D_c is used to calculate an apparent value of the hydrodynamic screening length, and the viscosity is taken to be the initial solvent viscosity, then a minimum screening length of approximately 15 Å is obtained. In a previous study of the local viscosity which determined the reorientational relaxation time of the styrene monomer during the polymerization, it was found[9] that the local viscosity increased by only 50% after 80% of the reaction was complete. Thus, the minimum screening length is greater than 10 Å and probably somewhat smaller than that calculated above. This is quite reasonable for polystyrene. No concentration of other polymer molecules will be able to dynamically screen the motion of neighboring monomer units, and the minimum screening length corresponds to about the size of two monomer units in polystyrene.

After approximately 3 days, the average diffusion coefficient started to decrease. The decrease was followed until it was not possible to rigorously separate the concentration fluctuations from the anisotropy fluctuations. The behavior of the anisotropy fluctuations near the end of the reaction forms the subject of the following paper. We attribute the decrease in D_c to the approach of the glass-rubber relaxation and the consequent large increase in the local viscosity of the solution. The pseudogel behavior with high local mobility dominates most of the concentration range; only for concentrations above 80% at our temperature (90 °C) will there be a manifestation of the glass transition. This has important implications for the bulk polymerization of monomers like styrene. The local mobility and hence the reactivity remain high to very large conversions. If the reaction were carried out at temperatures well above the glass transition temperature of the bulk polymer, the local mobility could be maintained at a high level indefinitely.

The use of photon correlation spectroscopy to study the pseudogel behavior of polymer solutions during polymerization appears to be a very promising tool. It should be applicable to virtually all bulk polymerizations where the system remains a true solution. The qualitative ideas expressed by deGennes[2] appear to be correct, but a quantitative test of the theory seems remote at this time. Applications of this technique to other polymers are presently in progress.

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Depolarized Rayleigh Spectroscopy of Concentrated Solutions of Polystyrene in Styrene

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ABSTRACT: The depolarized Rayleigh spectrum of polymerizing styrene is studied as a function of time near the end of the reaction. The average relaxation time changes over five orders of magnitude as the reaction proceeds to its end point. The relaxation function observed for the anisotropy fluctuations is not a single exponential. The same form used to fit data for bulk polystyrene near the glass transition is indicated in this study as well. Thus dilution has a similar effect on the dynamics of the anisotropy fluctuations as heating above the glass-rubber relaxation.

Introduction and Theory

In the previous paper[1] (herein denoted I), we reported a study of the concentration fluctuations during the thermal polymerization of styrene using photon correlation spectroscopy. When the reaction was approximately 90% complete, a feature began to appear in the observed correlation function which had a faster relaxation time than the concentration fluctuations and which became an increasing fraction of the scattered light intensity. A typical spectrum showing the two components is presented in Figure 1. By examining the depolarized Rayleigh scattering, this feature was found to be due to slowly relaxing collective reorientation fluctuations of the units of the fluid. In the present paper, we report a study of this slowly relaxing component of the depolarized Rayleigh scattering as the reaction proceeded from greater than 90% to near completion.

We have previously published[2] a study of the depolarized Rayleigh spectroscopy of bulk amorphous polystyrene near the glass-rubber relaxation using photon correlation spectroscopy. The average relaxation time determined by this technique increases very dramatically as the fluid is cooled toward T_g. Another important feature of the results for bulk polystyrene is that the relaxation function could not be described by a single exponential decay. The observed relaxation function was of the form

$$\phi(t) = A \exp(-(t/\tau)^{\beta}) \qquad (1)$$

where τ is the lag time at the $1/e$ point and β is a parameter which characterizes the width of the distribution of relaxation times implicit in the above empirical form. In the present work, the polystyrene solutions approach the glass transition by converting styrene to polystyrene. Thus the effect of small amounts of diluent on the dynamics of the polystyrene fluid is examined.

In a recent study[3] of the orientational relaxation times of the styrene molecules during the first 90% of the thermal polymerization reaction, it was found that the styrene molecules continue to relax very fast even at high conversions. Thus the intensity observed in the present experiments is attributed mostly to the polymer motions. Also, at high conversions most of the total intensity of depolarized Rayleigh scattering is due to the polymer segments and they would be expected to dominate the correlation function. The collective orientation fluctuations are governed by the local viscosity, the temperature, and the size of the reorienting unit. In the case of bulk polystyrene, the results were interpreted primarily as due to a rapid change in the local viscosity as the glass-rubber relaxation is approached. It is expected that the addition of diluent would also act to decrease the local viscosity and hence to shorten the orientational relaxation time.

Experimental Section

All conditions are the same as described in I except that the incident light was polarized horizontally with respect to the scattering plane. The temperature was maintained at 90 °C. In our previous studies of bulk polystyrene, data were collected at

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