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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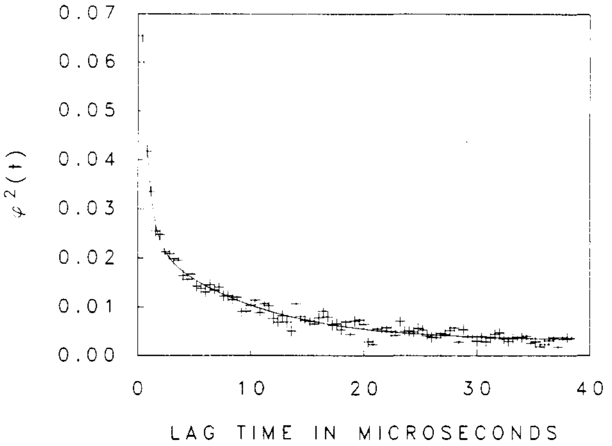

Figure 1. Polarized correlation function after 374.28 ks. The line is a fit to the square of the sum of two exponential relaxation functions whose relaxation times differ by over an order of magnitude. The fast relaxation time is due to anisotropy relaxation, and the slower time is due to concentration flucutations.

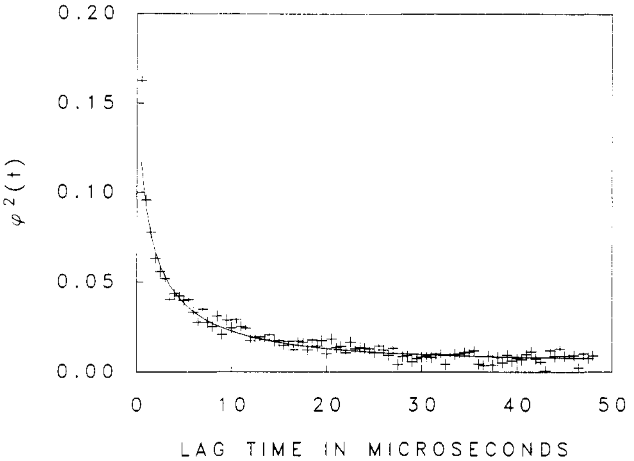

Figure 2. Depolarized correlation function after 403.26 ks. The line is a fit to the data using the relaxation function given in eq 1. The average relaxation time was found to be 1.6×10^{-5} s, and the value of β was 0.4.

each temperature over at least seven decades in time. In the present work, this was impractical since the relaxation times were changing with elapsed time. Thus the lag time in the correlator was chosen to give the $1/e$ point at a convenient position. The correlation function was then fit with the empirical relaxation function given in eq 1.

Results and Discussion

The first depolarized Rayleigh spectrum was collected after an elapsed time of 403.26 ks. The spectrum is shown in Figure 2. The data could not be fit with a single exponential decay, and the value of β necessary to achieve a satisfactory fit was 0.4. As the reaction proceeded, the average relaxation time changed very rapidly with time until the glass transition of the solution was approached. The reaction was carried out at 90 °C, and the glass transition temperature for polystyrene is 100 °C. Thus, the reaction did not go fully to completion at the lower temperature. The average relaxation times $\langle\tau\rangle$ are plotted against elapsed time in Figure 3.

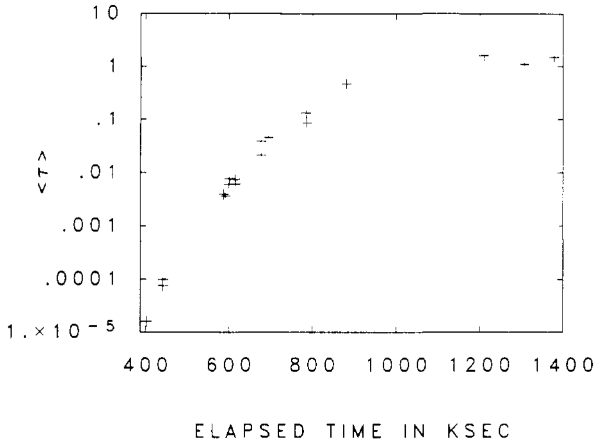

Figure 3. Average relaxation time $\langle\tau\rangle$ plotted vs. elapsed time in ks. The relaxation time changes by more than five orders of magnitude as the solution approaches its glass transition by converting styrene to polystyrene.

The values of β observed in the present experiments were near 0.4. This is consistent with the previous observations[2] of the depolarized Rayleigh spectrum of bulk polystryene. The fraction of the scattered light associated with the slowly relaxing component was also similar (60%). Thus it appears that dilution has the same qualitative effect on the dynamics of the anisotropy fluctuations as heating above the glass transition. The free volume is increased and the local viscosity is reduced.

The depolarized Rayleigh spectrum of large polymer molecules in dilute solution has been studied in detail by Bauer et al.[4] The longest relaxation time observed in that study for polystyrene molecules of molecular weight near 800 000 was in excess of 10 μs. The fact that the depolarized scattering did not interfere with the correlation function observed for concentration fluctuations during most of the reaction suggests that the dynamic screening ideas used to interpret the concentration fluctuations may be useful for the anisotropy fluctuations. Experiments are presently in progress to study the concentration dependence of the depolarized Rayleigh spectrum of polystyrene.

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