for poly(ethyl methacrylate).[9]

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Light Scattering Study of Gelation and Gels Formed during the Thermal Copolymerization of Styrene and Divinylbenzene

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ABSTRACT: The mutual diffusion coefficient D_c is determined by photon correlation spectroscopy during the thermal gelation reaction of styrene and divinylbenzene. The resulting gel is then studied as a function of temperature. The present results do not differ significantly from those obtained for solutions of polystyrene in styrene reported earlier. The quantity D_c is determined by the polymer concentration, the solvent quality, and the temperature T divided by the solvent viscosity η. No information specific to the gel is obtained from the light scattering data.

Introduction

We have recently reported[1] a study of the concentration fluctuations observed by photon correlation spectroscopy during the thermal polymerization of styrene. In the semidilute concentration range it has been suggested[2] that such data can be interpreted in terms of a pseudogel network. We have recently shown[3] that for polystyrene in good solvents, the existence of a pseudogel network should have little or no effect on the observed concentration fluctuations. In the present paper we report a study of the concentration fluctuations observed by photon correlation spectroscopy during the thermal copolymerization of styrene and divinylbenzene. In this way the effect of a solution undergoing gelation is studied. The resulting gel is then studied as a function of temperature.

Theory

The light scattering relaxation function due to concentration fluctuations is given by

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

where D_c is the mutual diffusion coefficient and $q = (4\pi n/\lambda)(\sin(\theta/2))$ is the magnitude of the scattering vector for light of incident wavelength λ traveling in a medium of refractive index n and scattered through an angle θ. The mutual diffusion coefficient for a polymer solution can be expressed as[4]

$$D_c = \frac{M}{N_a f}(1 - \bar{v}c)\frac{\partial \pi}{\partial c} \tag{2}$$

where M is the molecular weight, N_a is Avogadro's number, f is the friction coefficient, $\bar{v}$ is the partial specific volume of the polymer, c is the concentration, and π is the osmotic pressure.

A more general relation for the mutual diffusion coefficient would be[5]

$$D_c = E/\Phi \tag{3}$$

where E is the longitudinal modulus and Φ is the friction per unit volume. For a gel, $E = K + {}^4/_3 G$, where K is the modulus of compression and G is the shear modulus. The modulus of compression is given by $c(\partial\pi/\partial c)$, where the osmotic pressure now includes both the effects due to mixing of the polymer and the solvent and the elasticity due to swelling of the network. However, the contribution of elasticity to E is a small fraction of its total value for polystyrene and the observed concentration fluctuations are expected to be insensitive to the presence of the pseudogel or the real gel formed later in the reaction.

Experimental Section

Styrene and divinylbenzene were carefully dried and vacuum distilled into square quartz cells. The divinylbenzene concentration was nominally 8%. The samples were kept in dry ice until use. The thermal polymerizations were carried out at 90 °C as in previous studies.[1,6]

The incident light was as 5145 Å and the scattered light was observed at 90°. The homodyne correlation function $1 + \phi^2(t)$ was obtained with a Malvern correlator operated in the single-clipped mode. Data were collected as a function of elapsed time during the polymerization and as a function of temperature for the gel. The quantity D_c was obtained from a cumulant analysis of the correlation function. The sample time during the initial 5 h of the polymerization was 1 μs. The error in the determination of D_c increased at longer times due to the poorer signal-to-noise ratio obtained with shorter sample times.

Results and Discussion

The thermal copolymerization of styrene and divinylbenzene proceeds faster than that for pure styrene at 90 °C. Another important difference is that the sample undergoes a transformation to an opaque state after approximately 12 h. Examination of the product revealed that the sample was composed of many small clear regions and was a polygel. The reaction was stopped prior to formation of the polygel in order to study a clear gel. Also,

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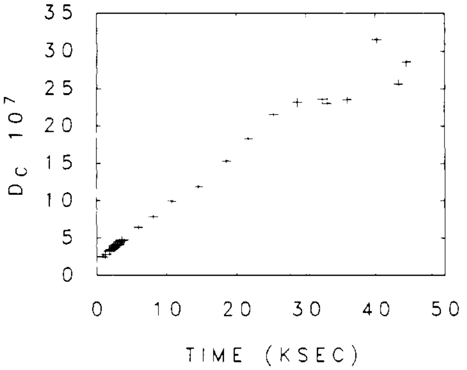

Figure 1. Plot of the mutual diffusion coefficient D_c vs. elapsed time for the thermal copolymerization of styrene and divinylbenzene.

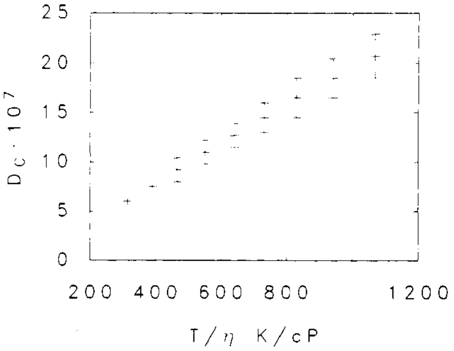

Figure 2. Plot of D_c vs. T/η for the polystyrene gel. The mutual diffusion coefficient is proportional to the absolute temperature divided by the solvent viscosity.

because the gelation reaction leads to permanent inhomogeneities in the sample, the data near the end of the run are probably partially heterodyned by the scattering from these gel defects. The results after 30 ks are probably affected by this problem.

The values of D_c observed during the polymerization are plotted vs. elapsed time in Figure 1. Even though a gel is being formed, there is no indication of any significant change from the homopolymerization results,[1] at least during the homogeneous part of the reaction. The effect of the gel elasticity would be to increase D_c. There is no indication of an increase in D_c over the pure solution results. This is consistent with the prediction that the concentration fluctuations are sensitive to the overall polymer concentration and not to the topology for these gels. The swelling ratio at the end of the polymerization was approximately 5. This was determined by weighing the fresh gel and a dried gel.

A clear gel sample was cooled and studied between 9 and 90 °C. Although the results were slightly affected by the part of the sample that was observed due to the presence of the gel defects, the trend of D_c with temperature was clearly determined. The ranges of D_c determined for the gel are plotted against the temperature divided by the solvent viscosity in Figure 2. The error limits reflect the uncertainty caused by the spatial variation in D_c in the sample. The modulus E depends linearly on the temperature and in a more complicated way on the solvent quality. Styrene is expected to be a very good solvent at all temperatures studied in this work. The friction per unit volume will depend linearly on the solvent viscosity and in a more complicated way on the polymer concentration. The mutual diffusion coefficient for the gel is then expected to be proportional to the quantity T/η. This relation is obeyed very well by the gel sample used in this study.

The present results suggest that no information about the detailed structure of the gel will be obtained from measurements of D_c under the conditions observed in this study. If the mutual diffusion coefficient is not measurably affected by the presence of a true network, then it should also not be affected by the presence of a pseudogel network. The actual value of D_c is determined by the balance of the osmotic restoring force, which depends on T and the solvent quality, and the friction, which depends on the solvent viscosity and the polymer concentration in this range. The present results do not support the notion that a dynamic screening length can be quantitatively extracted from measurements of the mutual diffusion coefficient in solutions and gels. Neither the solutions nor the gels obey the predicted[5] scaling law behavior in the range of concentrations observed here.

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Study of the Association of Anionic and Cationic Polymers by Nonradiative Energy Transfer[1]

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ABSTRACT: Nonradiative energy transfer was studied in aqueous solutions containing mixtures of naphthyl- and anthryl-labeled charged or uncharged polymers. An enhanced efficiency of energy transfer was observed when the donor and acceptor chromophores were attached to polymers carrying charges of the opposite sign. This effect decreased with an increasing ionic strength of the solution. However, in mixtures of an anionic copolymer of dimethylacrylamide and a cationic copolymer of vinylpyrrolidone, both hydrogen-bonding and hydrophobic interactions contributed to the stability of the polymer complex. Energy transfer was not found to reflect the repulsion between ionized poly(acrylic acid).

The phenomenon of nonradiative energy transfer between two fluorescing chromophores, discovered and subjected to theoretical analysis by Förster,[2] has been used extensively to characterize distances between donors and

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