for the polymer diffusion. f is actually a crossover function and depends on the degree of confinement which is related to the ratio of the polymer size to that of the bottleneck. f assumes the limits (see ref 8 for details)

$$f \rightarrow \begin{cases} 1 & \text{weak confinement} \\ N^{-1}C^{(1/\nu)-1} & \text{strong confinement} \end{cases} \qquad (2)$$

The prefactor A appearing in eq 1 accounts for the modification of D_0 due to the screening of hydrodynamic interaction even in the absence of partitioning effects, as already addressed by Guillot et al.[12] A is less than 1 and is related to the ratio of the Rouse diffusion coefficient D_R to the Zimm diffusion coefficient D_0. It readily follows from eq 1 and 2 that a plot of $(1/M)\log(D_\infty/D_0)$ versus $1/M$ should show two linear regimes corresponding to weak and strong confinement with the slope for strong confinement greater than that for the weak confinement. Quantitative comparison with the predictions of the theoretical model requires specific knowledge of the length scales C_1 and C. Figure 4 is a plot of the data as $(1/M)\log(D_\infty/D_0)$ vs $1/M$. The graph clearly shows two linear regimes with a rather clear crossover between the two. The data for glasses R1866 and R703[6,7] though not as extensive as for R893, show the same qualitative features seen above. More recent data[12] in similar glasses with pore radii 275 and 75 Å, where the confinement is even stronger, also support this picture. Notice that while the crossover between the weak and the strong confinement regimes appears distinct in Figure 4, the data do not conform to any apparent power law in the double-logarithmic plot of Figure 3. Thus the data are in good agreement with the model of entropic barriers, indicating that a porous network with bottlenecks is a reasonable model for the structure of these CPGs and that the entropic barrier effects at these bottlenecks play an important role in polymer diffusion in these glasses.

Acknowledgment. I thank Professors K. H. Langley and M. Muthukumar for many useful discussions, F. E. Karasz and K. H. Langley for support and the use of experimental facilities at the University of Massachusetts, Amherst, MA, under the sponsorship of the U.S. Air Force Office of Scientific Research Grants AFOSR84-0033 and AFOSR87-001, and Smith College for support.

Registry No. Polystyrene, 9003-53-6.

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Spinodal Decomposition of an Aqueous Solution of Poly(*N*-isopropylacrylamide)

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Received November 14, 1988

A number of experimental studies have been performed on the spinodal decomposition of polymer mixtures. However, most of these studies were performed for organic solvent systems and very few for aqueous systems. To our knowledge, experimental studies for the latter systems have been reported only by Inoue and his co-workers,[3] for the aqueous solution of poly(vinyl alcohol). The present work has been devoted to measuring the spinodal decomposition of the aqueous solution of poly(*N*-isopropylacrylamide).

The polymer was synthesized by the radical polymerization of *N*-isopropylacrylamide in water at 0 °C with a monomer concentration 7.3 wt %, initiated with potassium persulfate (0.7 wt %) in the presence of a reaction accelerator, *N,N,N′,N′*-tetramethylethylenediamine (2 μg/L). The synthesized polymer had number- and weight-averaged molecular weights of 2.9×10^5 and 2.3×10^6, respectively. Aqueous solutions of the polymer at three different concentrations, 4.4, 5.9, and 7.3 wt %, were prepared and subjected to cloud-point and light-scattering measurements.

The cloud points were determined with thermal analysis, using a differential scanning calorimeter (Seiko I. SSC-5000) and also checked according to a common visual method. The experimental results are presented in Figure 1. Since the present system exhibits the behavior of a lower critical solution temperature,[2] phase separation occurs in a temperature region above the cloud points.

Light-scattering experiments were carried out with a light-scattering photometer (Otsuka Denshi Co., Model LS-601) equipped with a 488-nm Ar-ion laser source and a thermoregulated xylene bath. The xylene bath was maintained at a constant temperature above the cloud point. A sample cell of the polymer solution was placed in it and raised to the temperature of the bath. Then the intensities of light scattered from the sample were measured at appropriate intervals.

According to Cahn's linearized theory proposed for the initial stage of spinodal decomposition,[1] the variation of scattered light intensity with time is expressed as follows:

$$I(q,t) = I(q,0)\exp[2R(q)t] \qquad (1)$$

where

$$q = (4\pi/\lambda)\sin(\theta/2) \qquad (2)$$

and $I(q,t)$ is the scattered light intensity at wavenumber q and time t, $I(q,0)$ the initial value of $I(q,t)$, and $R(q)$ is the growth rate of composition fluctuation at wavenumber q, θ is the scattering angle of the light, and λ is its wavelength.

Figure 2 shows the time variations of scattered light intensity measured at various wavenumbers. The experimental temperature was 33.5 °C, and the polymer concentration of the sample used was 4.4 wt %. Figure 2 indicates that each set of data can be approximated by a linear relation until about 60 s. This linear relation is in accordance with the prediction of eq 1, and the same relation was also observed in the other experiments. Therefore the values of $R(q)$ were determined from the experimental data.

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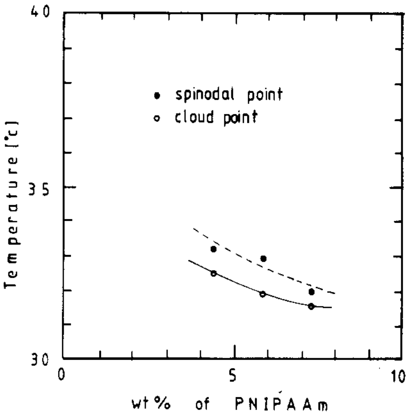

Figure 1. Cloud points and spinodal points for the aqueous solution of poly(*N*-isopropylacrylamide).

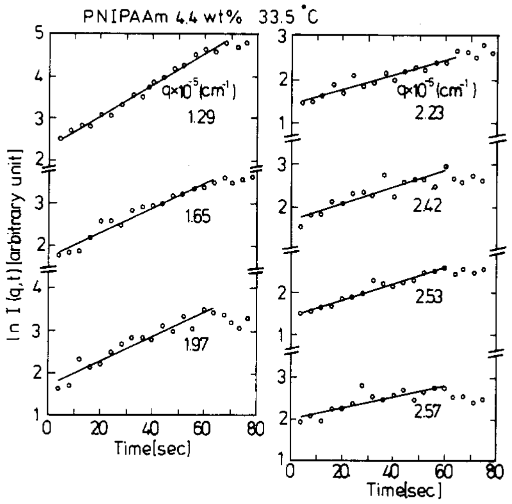

Figure 2. Time dependence of scattered light intensity from a 4.4 wt % solution at 33.5 °C.

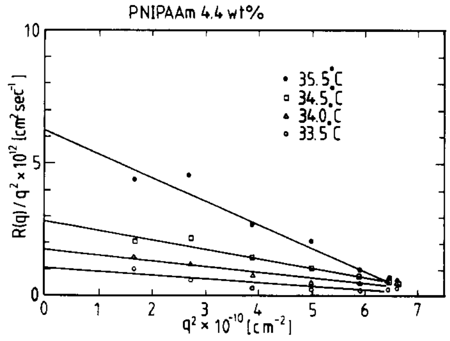

Figure 3. Plots of $R(q)/q^2$ vs q^2 for 4.4 wt % solutions at various temperatures.

The Cahn's theory, the following formula of $R(q)$ was derived:

$$R(q)/q^2 = D_{\mathrm{app}} - 2KMq^2 \qquad (3)$$

where D_{app} is the apparent diffusion coefficient, M mobility, and K a constant representing surface energy effect. To obtain the values of D_{app}, the experimental data of $R(q)/q^2$ were plotted against q^2. Some examples of such plots are shown in Figure 3.

All the values of D_{app} obtained for each polymer concentration are presented in Figure 4. This figure clearly shows that the extrapolation method can be adopted to determine a spinodal point at which the apparent diffusion coefficient equals zero. The determined spinodal points are shown in Figure 1. The spinodal point for each polymer concentration is slightly higher than the corresponding cloud point.

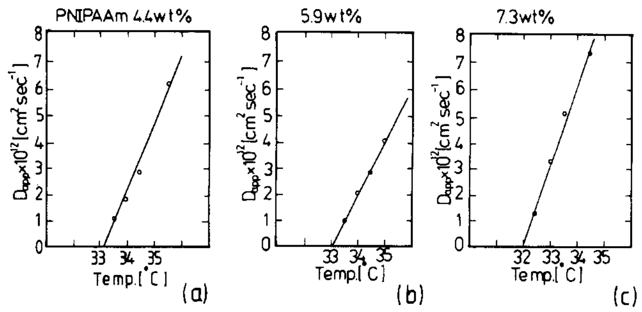

Figure 4. Temperature dependence of the apparent diffusion coefficient: (a) 4.4 wt % solution; (b) 5.9 wt % solution; (c) 7.3 wt % solution.

Thus in the present work, the occurrence of spinodal decomposition was confirmed for the aqueous solution of poly(*N*-isopropylacrylamide).

Registry No. Isopropylacrylamide, 25189-55-3.

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3-Vinylperylene: A Powerful Radical Trap

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Received October 4, 1988; Revised Manuscript Received January 5, 1989

3-Vinylperylene (3VP) has been previously prepared,[1] but there is no report of its polymerization or attempted polymerization in the literature. We now find that it cannot be polymerized or copolymerized (with styrene and maleic anhydride) and further that it strongly inhibits the radical polymerization of reactive monomers.

3VP was prepared from perylene via perylenecarboxaldehyde by Vilsmeier[2] and Wittig[1] reactions: mp = 162–164 °C (lit.[1] mp 153–154 °C); yield (overall) 62.0%. Anal. Calcd for $C_{22}H_{14}$: C, 94.93; H, 5.07. Found: C, 94.58; H, 5.07.

After attempts to polymerize or copolymerize 3VP under the normal free radical conditions failed, we investigated the effects of small quantities of added 3VP on the AIBN-initiated polymerizations of styrene, methyl methacrylate, 4-vinylpyridine, and vinyl acetate. The results are shown in Figure 1: the polymerization of vinyl acetate is completely inhibited when the 3VP molar concentration equals that of the initiator. For the other three monomers, the polymerization is strongly retarded by a concentration of 3VP double that of the initiator and completely stopped by three times the concentration.

Our results suggest that 3VP reacts with the initiator radicals as shown in Scheme I. The reactive vinyl group of 3VP traps $Me_2\dot{C}CN$ radicals, either immediately on their release from AIBN or in the early growth of the polymer chain, with the formation of radical **2**. **2** is insufficiently reactive to initiate polymerization. As further Me_2CCN is released, it reacts faster with radical **2** (to give **3**) than with the unreactive monomer vinyl acetate, but slower than with reactive monomers, such as styrene. Hence, an equal

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