Macromolecules **1991,** *24,* 3962-3963

Notes

Spinodal Decomposition of *N*-*n*-Propylacrylamide Gel. Effect of Hydrophobic Interaction

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*Received November 15, 1990;
Revised Manuscript Received February 13, 1991*

The volume phase transition of hydrogels has been treated extensively in the literature mostly, however, with respect to the swelling equilibria of the gels.[1-4] Very limited works have been reported on the dynamic aspect of the transition in spite of its significance for practical applications of the gels.

Tanaka et al.[5] measured the temperature dependence of the fluctuation of gel networks in equilibrium using a light-scattering method and determined, by extrapolation, the critical temperature at which the collective diffusion coefficient began to slow down. Recently, we directly measured the time evolution of spinodal decomposition with a thermoresponsible hydrogel, *N*-isopropylacrylamide gel.[6] During the spinodal decomposition, the intensities of light scattered from the gel were measured to examine the applicability of Cahn's linearized theory,[7] proposed for the initial stage of spinodal decomposition. In the present work, we have performed experiments on the spinodal decomposition of *N*-*n*-propylacrylamide gel and have discussed the effect of hydrophobic interaction on the dynamics of phase transition by comparing the present experimental data with those of *N*-isopropylacrylamide gel obtained in the previous work.[6]

N-*n*-Propylacrylamide monomer was synthesized according to the method reported by Itoh.[8] Then, gel samples were prepared for the light-scattering measurements. The sample preparation method was described in our previous work.[6]

Prior to the experiments, the phase-transition temperature of the gel was determined by differential scanning calorimetry (DSC). The transition temperature was 24 °C, which agreed with the value reported by Inomata et al.[9] from the swelling measurement.

The experiments were performed with a light-scattering apparatus (Otsuka Electronics Co., Model DLS700) equipped with a 633-nm He–Ne laser source and a thermoregulated bath. A photocell containing the gel sample, which was first kept at room temperature, was transferred into a bath that was maintained at a constant temperature above the phase-transition temperature. The intensities of light scattered from the gel were measured every 2 s at temperatures 25, 25.5, and 26 °C. The accuracy of temperature regulation was within ±0.05 °C.

For the initial stage of spinodal decomposition, Cahn's linearized theory was proposed, which predicted that the time evolution of elastic scattered light intensity during the decomposition should be expressed as

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

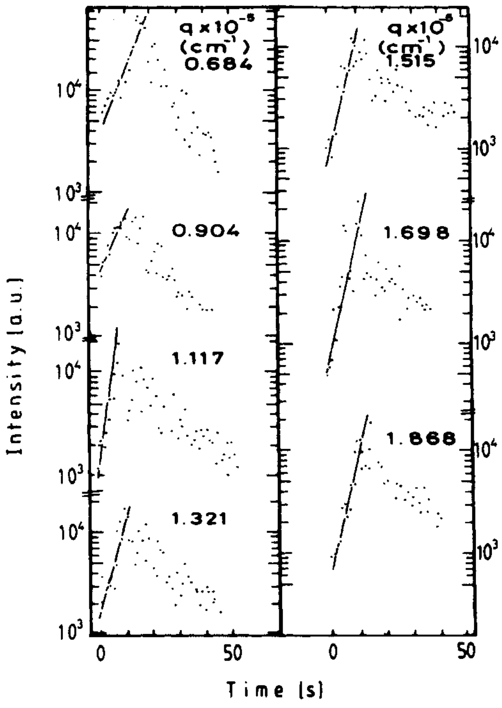

Figure 1. Time dependence of the scattered light intensity from *N*-*n*-propylacrylamide hydrogel at 26 °C at various wave numbers.

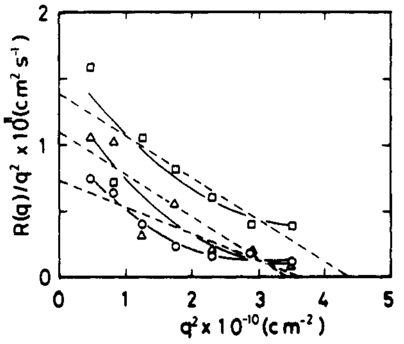

Figure 2. Plots of R/q^2 versus q^2 at various temperatures: (○) 25 °C, (△) 25.5 °C, (□) 26.0 °C.

where

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

and $I(q,t)$ is the scattered light intensity at scattering vector and q and time t, θ the scattering angle of the light, and λ its wave length in the medium. The growth rate of fluctuation, $R(q)$, is defined by

$$R(q)/q^2 = D_{\rm app}[1 - (1/2q_{\rm m}^{\,2})q^2] \qquad (3)$$

where $D_{\rm app}$ is the apparent diffusion coefficient, and $q_{\rm m}$, the peak scattering vector.

According to eq 1, the scattered light intensities measured at each temperature were plotted against the scattering vector q is a semilogarithmic scale. Figure 1 shows the example of such a plot at 26 °C. As predicted by eq 1, the data reveal a linear relation, which was also observed at the other temperatures. Thus we determined $R(q)$ at each temperature.

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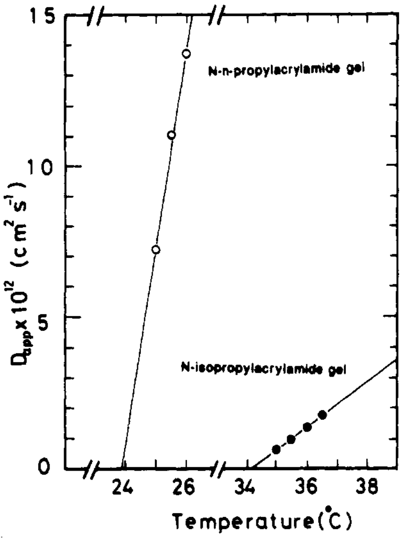

Figure 3. Temperature dependence of the apparent diffusion coefficient.

In Figure 2, the determined values of $R(q)$ are plotted according to eq 3. The $R(q)/q^2 \sim q^2$ plots at each temperature in the figure are slightly concave toward the q^2 axis. A similar tendency is observed in most cases of experimental work in the literature conducted in the spinodal decomposition for polymer mixture systems. As pointed out by Nose[10] and Hashimoto,[11] the discrepancy from Cahn's linearized theory may result from the lack of the consideration of thermal noise in the theory. However, eq 3 has often been applied to make a rough estimation of D_{app} values.[12] Accordingly, we approximated the solid curves in Figure 2 by the dashed lines to determined the D_{app} values. These values of *N*-*n*-propylacrylamide gel are shown in Figure 3 together with those of *N*-isopropylacrylamide gel, which were determined in the previous paper.[6] It can been seen from Figure 3 that there is an obvious difference in the D_{app} values and their temperature dependences between the *N*-*n*-propylacrylamide and *N*-isopropylacrylamide gels.

Our previous work[9] suggested that the phase transition of thermoresponsible hydrogels, which get ordered upon heating, was a hydrophobic interaction driven phenomenon and that the hydrophobic interaction of *N*-*n*-propylacrylamide gel was larger than that of *N*-isopropylacrylamide gel, owing to the difference in the hydration number of their N-substituted groups. This means that the free energies of the gel systems are strongly dependent on the hydrophobic interaction. Therefore, it can be considered that the phase separation speed of *N*-*n*-propylacrylamide gel is faster than that of *N*-isopropylacrylamide gel.

The spinodal temperature at which the apparent diffusion coefficient equals zero was determined by extrapolating the measured diffusion coefficient to the temperature axis, as shown in Figure 3. The spinodal temperature determined was about 24 °C, and almost the same as the transition temperature.

Thus the present work has shown that the temperature dependence of the apparent diffusion coefficient of *N*-*n*-propylacrylamide gel is much stronger than that of *N*-isopropylacrylamide gel. In other words, the *N*-*n*-propylacrylamide gel has a greater susceptibility for thermal stimulus than the *N*-isopropylacrylamide gel.

References and Notes

(1) Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1984**, *81*, 6379.
(2) Hirotsu, S.; Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1987**, *87*, 1392.
(3) Otake, K.; Inomata, H.; Konno, M.; Saito, S. *J. Chem. Phys.* **1989**, *91*, 1345.
(4) Otake, K.; Inomata, H.; Konno, M.; Saito, S. *Macromolecules* **1990**, *23*, 283.
(5) Tanaka, T.; Sato, E.; Hirokawa, Y.; Hirotsu, S.; Peeterman, V. *Phys. Rev. Lett.* **1985**, *55*, 2455.
(6) Otake, K.; Inomata, H.; Yagi, Y.; Konno, M.; Saito, S. *Polym. Commun.* **1989**, *30*, 203.
(7) Cahn, J. W. *J. Chem. Phys.* **1965**, *42*, 93.
(8) Itoh, S. *Jpn. J. Polym. Sci. Technol.* **1989**, *46*, 437.
(9) Inomata, H.; Goto, S.; Saito, S. *Macromolecules* **1990**, *23*, 4887.
(10) Nose, T. *Phase Transitions* **1987**, *8*, 245.
(11) Hashimoto, T. *Phase Transitions* **1988**, *12*, 47.
(12) Nojima, S.; Tsutsumi, K.; Nose, T. *Polym. J.* **1982**, *14*, 225.