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Reentrant Phase Transition in Acrylamide-Derivative Copolymer Gels

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ABSTRACT: *N,N*-Diethylacrylamide and *N*-isopropylacrylamide gels having ionizable groups were found to undergo a reentrant volume transition between swollen and collapsed states when the ratio of water to dimethyl sulfoxide in the solvent was monotonically varied. The behavior of the gels was interpreted by assuming the free energy of contact between polymer segments was not a linear function of the solvent composition.

I. Introduction

A number of acrylamide-derivative gels having ionizable groups undergo a reversible, discontinuous volume change when external conditions such as solvent composition,[1,2] ionic composition,[3] pH,[2] and temperature[1,2,4] are varied. A small change in the electric potential applied across a gel also induces a discontinuous volume change.[5] The volume change of the gel is a phase transition and has been analyzed by using the mean field formula for the osmotic pressure of an ionic gel, originally derived by Flory and Huggins.[6]

This paper presents the results of observations on two acrylamide-derivative copolymer gels. An unusual feature of the swelling behavior of these gels is a reentrant phenomenon where the gels collapse once and reswell as a particular external condition is varied monotonically. The gels consist of a copolymer network of either *N,N*-diethylacrylamide or *N*-isopropylacrylamide and sodium acrylate and a mixture of dimethyl sulfoxide (Me_2SO) and water. Sodium acrylate is incorporated into the polymer network because its ionizable group makes the phase transition first order. The gels are swollen in pure water. When Me_2SO is added to the water, the gels gradually shrink. When the Me_2SO concentration reaches a critical value, the gel discontinuously collapses into a very compact state. Upon further increase in the Me_2SO concentration, the gels undergo a discontinuous reswelling into the expanded state. The behavior is similar to the reentrant phenomenon of a binary fluid system.[7] In this paper we also give a qualitative interpretation of the reentrant phenomenon in terms of the interactions between the network and the Me_2SO and water molecules.

II. Experimental Section

Preparation of Gels. The monomers, *N,N*-diethylacrylamide and *N*-isopropylacrylamide, were synthesized from acryloyl chloride with diethylamine and isopropylamine, respectively.[8] Monomer (5.00–8.95 g), *N,N'*-methylenebis[acrylamide] (cross-linking monomer, 0.133 g), sodium acrylate (ionizable monomer, 0–1.28 g), and *N,N,N',N'*-tetramethylethylenediamine (TEMED, reaction accelerator, 240 μL) were dissolved in distilled, degassed, and nitrogen-saturated water to a final volume of 100 mL and cooled to 4 °C. After addition of a 4% aqueous solution of ammonium persulfate (initiator, 1 mL) the solution was immediately transferred into a test tube into which cylindrical micropipets (1.35-mm i.d.) were then placed. The solution filled the micropipets and gelled within 30 min. After 20 h at 4 °C, the gels were removed from the micropipets and immersed in pure water for 3 days of washing to remove unreacted molecules.

Measurements of Gel Size. The washed cylindrical gels were cut into pieces 1 cm long and immersed in Me_2SO–water mixtures of various compositions, measured by volume percent prior to mixing. The mixtures were kept at room temperature for 2 weeks to allow the gels to reach equilibrium. The final equilibrium diameter of each gel was measured under a calibrated microscope. The initial diameter (d_0) of each gel was 1.35 mm. From these diameters we calculated the degree of swelling, $V/V_0 = (d/d_0)^3$, where V and V_0 are the initial and final equilibrium volumes of the gel.

III. Results

Figure 1 shows the degree of swelling of the *N,N*-diethylacrylamide gel as a function of Me_2SO concentration. The gel containing 1.28 g of sodium acrylate (filled circles) is swollen at Me_2SO concentrations from 0 to 40%. At 40% Me_2SO the gel undergoes a discontinuous volume collapse of more than 100 times and remains collapsed for increased Me_2SO concentrations up to approximately 80%. At this Me_2SO concentration, the gel reswells discontinuously by more than 50 times in volume. In Figure 2, the same effect is seen for the *N*-isopropylacrylamide gel, except the first transition occurs at 45% Me_2SO.

The proportion of ionizable groups incorporated into the network affects the transition. The volume change at the transition was smaller for gels made with 0.64 g of sodium acrylate (open circles in Figures 1 and 2). In addition, with a decrease in the proportion of ionizable groups, the Me_2SO concentration required for the upper transition is raised while that for the lower transition is lowered. For the *N*-isopropylacrylamide gel made with 0.64 g of sodium acrylate, the volume change at 80% Me_2SO is continuous.

The dependence of the proportion of the ionizable groups on the phase transition of *N,N*-diethylacrylamide gels is shown in Figure 3. The gels were made by using 8.95 g of *N,N*-diethylacrylamide, with 0.133 g of *N,N'*-methylenebis[acrylamide] and 0–1.13 g of sodium acrylate. We have indicated in Figure 3 a closed-loop phase boundary, representing a domain of instability. Inside this domain the gel must separate into two phases, each having a different degree of swelling. These two phases are given by two points on the phase boundary at a particular solvent composition. The upper and the lower consolute points correspond to the upper and the lower critical points, respectively.

IV. Theoretical Consideration

In order qualitatively to interpret the reentrant phenomena we use the mean field theory of phase transition of ionic gels.[2] In the framework of mean field theory, the osmotic pressure Π of a gel is described by the Flory–Huggins formula[6]

$$\Pi = -\frac{NkT}{v}\left[\phi + \ln(1-\phi) + \frac{\Delta F}{2kT}\phi^2\right] + \nu kT\left[\frac{\phi}{2\phi_0} - \left(\frac{\phi}{\phi_0}\right)^{1/3}\right] + \nu fkT\left(\frac{\phi}{\phi_0}\right) \quad (1)$$

where N is Avogadro's number, k is the Boltzmann constant, T is the temperature, v is the molar volume of the

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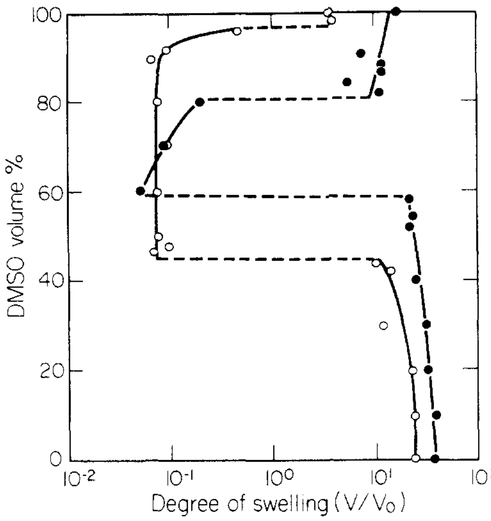

Figure 1. Swelling ratio (final to initial equilibrium volume) of *N,N*-diethylacrylamide–sodium acrylate copolymer gels in mixtures of dimethyl sulfoxide (Me_2SO) and water. Open circles indicate the swelling ratio for gels made using 0.64 g of sodium acrylate. Filled circles are for gels made using 1.28 g of sodium acrylate.

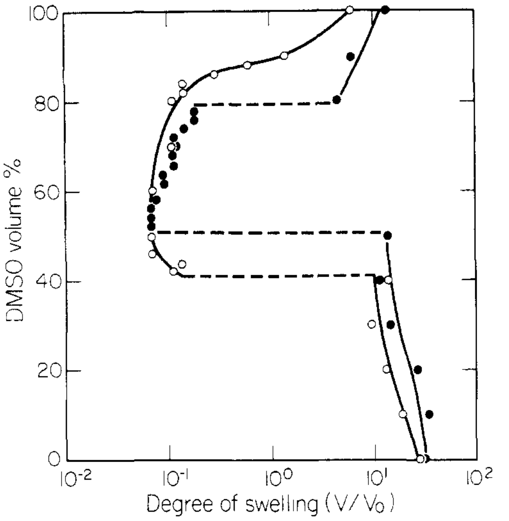

Figure 2. Swelling ratio of *N*-isopropylacrylamide–sodium acrylate copolymer gels. Open circles represent gels made from 0.64 g of sodium acrylate. Filled circles are for gels made using 1.28 g of sodium acrylate.

solvent, ϕ is the volume fraction of the network, ΔF is the free-energy decrease associated with the formation of a contact between polymer segments, ϕ_0 is the volume fraction of the network at the condition the constituent polymer chains have random-walk configurations, ν is the number of constituent chains per unit volume at $\phi = \phi_0$, and f is the number of dissociated counterions per effective chain.

The osmotic pressure difference between the inside and outside of the gel must be zero for the gel to be in equilibrium with the surrounding solvent. The requirement of zero osmotic pressure difference is equivalent to minimizing the free energy of the gel, F, since $\Pi = \partial F/\partial V$, where V is the volume of the gel. From eq 1, this condition is expressed as

$$\tau = 1 - \frac{\Delta F}{kT} = -\frac{\nu v}{N\phi^2}\left[(2f+1)\left(\frac{\phi}{\phi_0}\right) - 2\left(\frac{\phi}{\phi_0}\right)^{1/3}\right] + 1 + \frac{2}{\phi} + \frac{2\ln(1-\phi)}{\phi^2} \qquad (2)$$

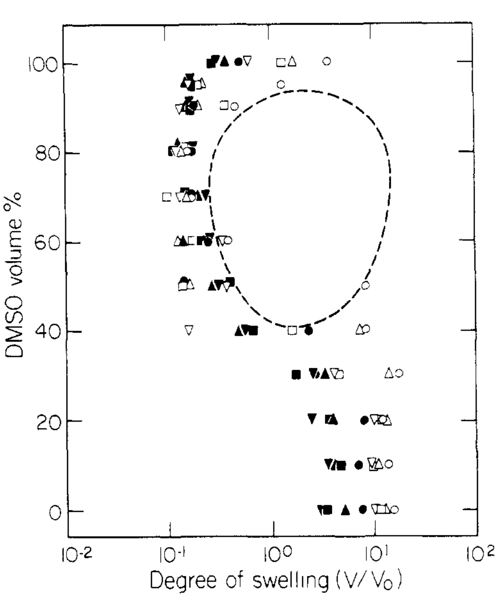

Figure 3. Swelling ratio for gels consisting of *N,N*-diethylacrylamide and various amounts of sodium acrylate: 1.13 (○), 0.85 (△), 0.66 (□), 0.47 (▽), 0.28 (●), 0.09 (▲), 0.05 (■), and 0 g (▼).

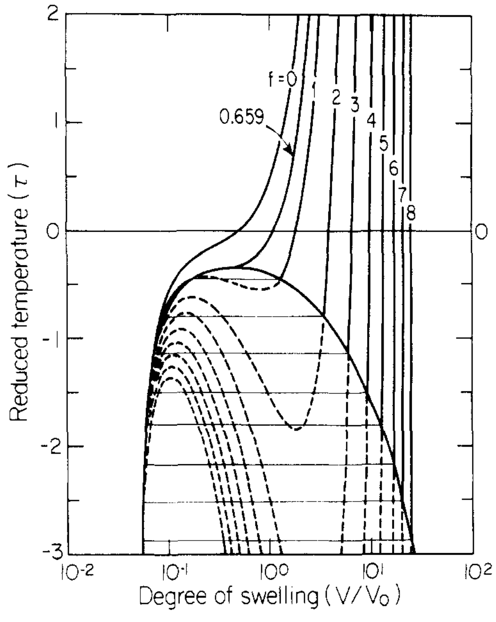

Figure 4. Swelling curves calculated from eq 2 using the parameters $\nu v/N\phi_0^3 = 10$ and $\phi_0 = 0.05$ for various values of f. This figure is adopted from Figure 2 of ref 2.

where τ is the reduced temperature that depends both on temperature and on solvent composition. Equation 2 then determines the equilibrium network concentration as a function of the reduced temperature. For certain values of τ, however, eq 2 is satisfied by three values of ϕ, corresponding to two minima and one maximum of the free energy as first noted by Dusek and Patterson.[9] The value of ϕ corresponding to the lower minimum represents the equilibrium value. A discrete volume transition occurs when the two free-energy minima have the same value. Since the equilibrium volume of the gel is inversely proportional to its equilibrium concentration, $V/V_0 = \phi_0/\phi$, where V_0 is the volume of the gel at $\phi = \phi_0$.

In Figure 4 the reduced temperature, τ, is plotted as a function of the degree of swelling (V/V_0) for a series of values of f, the parameter proportional to the amount of ionizable group incorporated into the network. With larger values of f, the magnitude of the collapse becomes larger, and the value of the reduced temperature at the volume transition is smaller.

On the basis of Figure 4, the phenomena observed in this study can be qualitatively understood by assuming that the reduced temperature (or the free energy, ΔF, of contact between polymer segments) is not a monotonic function of the percent Me_2SO. The reduced temperature must be high in both pure Me_2SO and pure water and has a minimum of negative value at approximately 70% Me_2SO. In this case the phase diagram is formed by replacing the lower half of Figure 4 with a mirror image of the upper half. The swelling curves then become a set of reentrant curves. The two transitions for larger amounts of ionizable group show larger volume changes and occur at closer values of percent Me_2SO.

The nonmonotonic dependence of the reduced temperature (or the free energy of contact ΔF) on percent Me_2SO may be interpreted in the following way. The copolymer gels (*N*,*N*-diethylacrylamide–sodium acrylate and *N*-isopropylacrylamide–sodium acrylate) are swollen in both pure Me_2SO and pure water. This behavior indicates that attractive interactions between polymer chain and solvent molecule dominate over the attraction between polymer chains. When Me_2SO and water are mixed, the two solvents have an attractive interaction resulting in an increase of free energy, ΔF, for polymer–polymer contact and in a decrease in reduced temperature. The increase in the affinity among polymer segments would induce the collapse of the polymer network. Therefore, the gels are collapsed in the intermediate range of mixtures of Me_2SO and water.

The volume change should be the same for the upper and the lower transitions if ΔF depends only on percent Me_2SO, but the volume changes observed experimentally at the two transitions are not identical. The volume change occurring at the lower Me_2SO concentration is usually larger than the one at the higher Me_2SO concentration. This difference can be explained by the dependence of the degree of ionization of sodium acrylate groups on the Me_2SO concentration, and probably due to the difference between the molar volumes of two solvent. In solutions with a higher Me_2SO concentration, ionization may be depressed because of the lower polarizability of Me_2SO than of water; thus the volume change at the upper transition is smaller.

V. Conclusion

The reentrant phenomenon has been observed for the first time in polymer gels. It will be of particular interest to study the behavior of a polymer network as the area of the closed-loop instability diminishes. Our preliminary experiments have shown that the size of closed-loop area can be changed by varying the network structure of the gel. Also to be studied is the situation where the reduced temperatures at which the two discontinuous transitions occur are brought to coincide. The kinetics of the reentrant phase transition at this special situation is of particular interest when temperature or solvent change involves two phase transitions simultaneously.

The phase transition in gels, marked by a discrete volume collapse, appears to be a universal phenomenon which can be observed by choosing appropriate combinations of polymers and solvents. Theoretical considerations also support this view. In addition to the scientific merit, it is important to study and understand the specific roles played by the chemical constituents in order to develop technology that employs polymer gels. The reentrant phenomenon seems to widen the possible application of the phase transition in gels to switches, memories, sensors, and mechanochemical transducers.

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Preparation of Deuterated Poly(2,6-dimethyl-1,4-phenylene oxide)

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ABSTRACT: Phenol has been deuterated in the ortho and para positions with deuterium oxide using sodium deuterioxide catalysis and then has been methylated with perdeuteriomethanol over a magnesium oxide catalyst at 450 °C. A sample of 99.9% 2,6-dimethylphenol has been isolated from the reaction mixture and then oxidatively coupled to form poly(2,6-dimethyl-1,4-phenylene oxide). The deuterium content of the 2,6-dimethylphenol was 5.54 methyl and 1.33 aryl deuteriums per molecule and that of the polymer was 5.53 methyl and 0.36 aryl deuteriums per repeating unit.

Introduction

Neutron scattering studies on blends containing poly(2,6-dimethyl-1,4-phenylene oxide) required samples of the polymer with approximately 75% of the hydrogen replaced with deuterium.[1] The preparation of the monomer, deuterated 2,6-dimethylphenol, and such a polymer by reac-