Phase Transitions in Ionic Gels

Toyoichi Tanaka, David Fillmore, Shao-Tang Sun, Izumi Nishio,
Gerald Swislow, and Arati Shah
Department of Physics and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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The polymer network of a gel, under certain conditions, undergoes a discrete transition in equilibrium volume with changes in solvent composition or temperature. This Letter demonstrates that ionization of the gel network plays an essential role in the phase transition. The volume collapse is also observed when the pH within the gel is varied.

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The polymer network of certain acrylamide gels immersed in acetone-water mixtures has been reported to undergo a collapse when the acetone concentration is increased or when the temperature is lowered.[1] In some gels a continuous transition is observed, rather than a discrete collapse. In either case, the transition is reversible. For the discrete transition, an almost infinitesimal change in solvent composition or temperature brings about a finite change in gel volume.[2]

In this Letter we demonstrate that ionization of the polymer network plays an essential role in the phase transition. A nonionized acrylamide gel immersed in acetone-water mixtures shows a continuous change in equilibrium volume when the acetone concentration or temperature is changed. If a small portion of acrylamide groups in the network is hydrolized into ionizable acrylic acid groups, a reversible volume collapse as large as 350-fold occurs when the acetone concentration is increased. With the aid of the Flory-Huggins theory, we show that this dramatic volume collapse is accounted for by the osmotic pressure of hydrogen ions dissociated from the ionizable groups. We also observe that the volume collapse can be induced by varying the pH of the gel fluid. This is strong evidence that ionization of the polymer network plays a key role in the phase properties of the gel.

The samples were prepared by the standard method.[1,3] Acrylamide (5 g), the linear constituent; N, N′-methylene-*bis*-acrylamide (0.133 g), the tetra-functional crosslinking constituent; ammonium persulfate (40 mg), the initiator; and N, N, N, N-tetramethylethylenediamine (TEMED) (240 μl), the accelerator were dissolved in distilled, degassed, and nitrogen-saturated water at 0 °C to a final volume of 100 ml. The solution was then transferred to small glass tubes, where gelation occurred within five minutes. The gels were left in the tubes for an hour, then removed and immersed in nitrogen-saturated water for 24 h in order to wash away residual acrylamide, bisacrylamide, ammonium persulfate, and TEMED.

We then placed these gels in a basic solution (pH 12) of 0.4% (volume) TEMED in water to hydrolyze a portion of the acrylamide groups into acrylic acid groups ($-\mathrm{CONH}_2 \rightarrow -\mathrm{COOH}$). The chemistry of the hydrolysis of acrylamide groups in a basic solution is well established.[3] The gels were then washed in water and placed in acetone-water mixtures of various compositions. After the gels had reached equilibrium, the diameter of each was measured using a dissecting microscope with calibrated eye piece to determine its equilibrium volume. Figure 1 shows the relationship of acetone concentration to the swelling ratio φ/φ^*. The quantity φ/φ^* represents the ratio of final network concentration to initial network concentration for gels hydrolyzed in the TEMED solution for various lengths of time. The ratio is given by $(d^*/d)^3$ where d^* and d are the initial and final equilibrium diameters of the gel, respectively. For swollen gels $\varphi/\varphi^* < 1$, whereas for shrunken gels $\varphi/\varphi^* > 1$.

For short hydrolysis times of 0 to 1 d, the final equilibrium network concentration changes continuously with the acetone concentration. If the gels are hydrolyzed in the TEMED solution for 2 d, the curve has a zero slope inflection point. For longer hydrolysis times, discrete transitions are observed. Volume change at the transition becomes larger, and the acetone concentration required at the transition becomes higher. The last plot of the series in Fig. 1 is for gels hydrolyzed in a 4% (volume) TEMED solution for 60 d. This gel exhibits a volume collapse of 350-fold.

We now present a theory of phase transitions in ionic gels. We start with the Flory-Huggins formula for the osmotic pressure, Π, of an ionic gel,[4]

$$\Pi = -\frac{NkT}{v}\left[\varphi + \ln(1-\varphi) + \frac{1}{2}\frac{\Delta F}{kT}\varphi^2\right] + \nu kT\left[\frac{1}{2}\frac{\varphi}{\varphi_0} - \left(\frac{\varphi}{\varphi_0}\right)^{1/3}\right] + \nu f kT\left(\frac{\varphi}{\varphi_0}\right), \tag{1}$$

where N is Avagadro's number, k is the Boltzman constant, T is the temperature, v is the molar volume of the 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 consituent polymer chains have random-walk configurations, ν is the number of constituent chains per unit volume at $\varphi = \varphi_0$, and f is the number of dissociated hydrogen ions per effective chain.

The osmotic pressure of a gel must be zero for the gel to be in equilibrium with the surrounding solvent. Zero osmotic pressure is also necessary for the free energy of the gel, F, to be minimized, since $\Pi = -\partial F/\partial V$, where V is the volume of the gel and $V \propto \varphi_0/\varphi$. From Eq. (1), this condition may be expressed as

$$\tau \equiv 1 - \frac{\Delta F}{kT} = \frac{\nu v}{N\varphi^2}\left[(2f+1)\left(\frac{\varphi}{\varphi_0}\right) - 2\left(\frac{\varphi}{\varphi_0}\right)^{1/3}\right] + 1 + \frac{2}{\varphi} + \frac{2\ln(1-\varphi)}{\varphi^2}, \tag{2}$$

where the parameter τ may be called the reduced temperature. The left side of Eq. (2) corresponds to the reduced temperature, which changes with temperature and solvent composition. The equation then

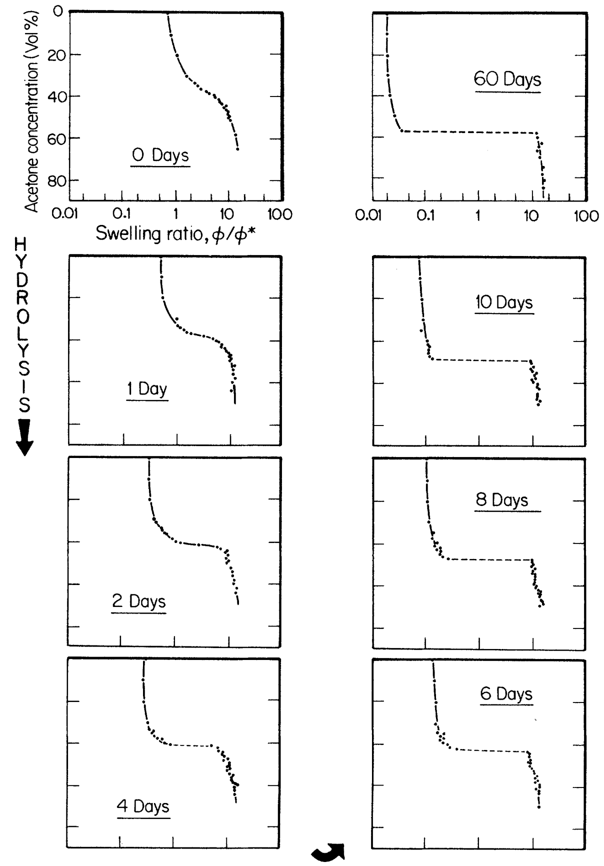

FIG. 1. The acetone concentration dependence of the swelling ratio, φ/φ^*, for increasing hydrolyzation of the gel network. All curves are for gels immersed in 0.4% (volume) TEMED solutions for the times indicated, except for the upper right-hand plot, which is for gels immersed in a 4% (volume) TEMED solution for 60 d.

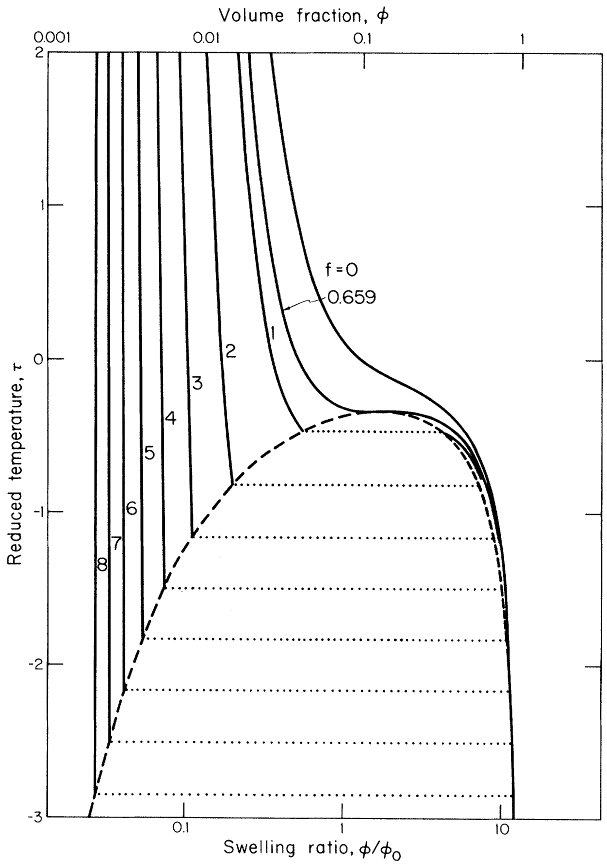

FIG. 2. The states at which the osmotic pressure of the gel network is zero, for various values of f, the degree of ionization of the network, calculated with use of Eq. (2), with the parameters $S_0 \equiv \nu v/N\varphi_0^3 = 10$ and $\varphi_0 = 0.05$.

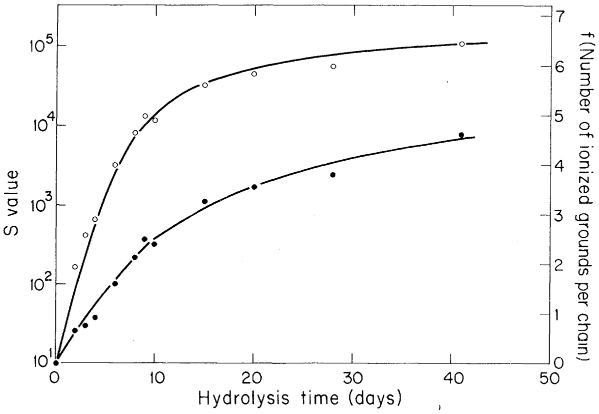

FIG. 3. The value of f (open circles), the degree of ionization of the network, and $S = S_0(2f+1)^4$ (solid circles), the collapse parameter, as a function of hydrolysis time in 0.4% (volume) TEMED solutions. The values for f are determined with use of the experimental swelling curves and the theoretical curves of Fig. 2. The solid curves are to guide the eye.

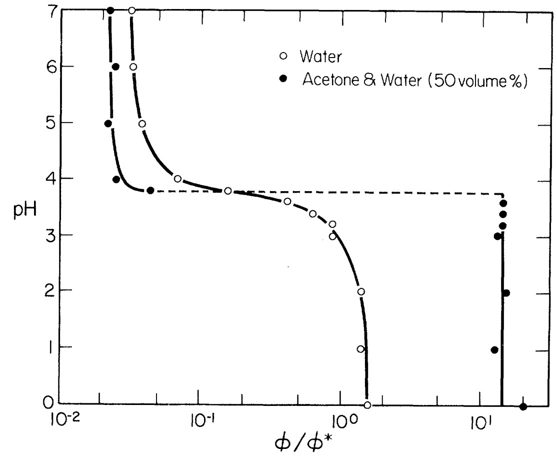

FIG. 4. The pH dependence of the swelling ratio for gels hydrolyzed in a 4% (volume) TEMED solution for 60 d. The smooth curve is for gels immersed in water. The discontinuous curve is for gels in a 50% acetone-water mixture.

determines the equilibrium network concentration as a function of the reduced temperature. For certain values of the reduced temperature, however, Eq. (2) is satisfied by three values of φ, corresponding to two minima and one maximum of the free energy. 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.

In Fig. 2 we plot the calculated equilibrium value of the swelling ratio,[5] φ/φ_0, as a function of the reduced temperature for various degrees of hydrolysis, f. The theoretical curves are qualitatively in agreement with the experimental results shown in Fig. 1. As the graph shows, the hydrolysis of a small amount of acrylamide groups (for a change of f from 0 to 6) causes a drastic change in the collapse size at the transition. The situation may be understood if the term ln $(1-\varphi)$ in Eq. (2) is expanded, retaining terms to order φ^3. This yields

$$t = S(\rho^{-5/3} - \tfrac{1}{2}\rho^{-1}) - \tfrac{1}{3}\rho, \tag{3}$$

where

$$t \equiv (1 - \Delta F/kT)(2f+1)^{3/2}/2\varphi_0, \tag{4}$$

$$S \equiv (v\nu/N\varphi_0^{\,3})(2f+1)^4 \equiv S_0(2f+1)^4, \tag{5}$$

and

$$\rho \equiv (\varphi/\varphi_0)(2f+1)^{3/2}. \tag{6}$$

In this approximation, the relationship between the renormalized reduced temperature, t, and the renormalized concentration, ρ, is determined by a single parameter S. In other words, the ratio of the two concentrations at the transition, which represents the size of the collapse, is a function only of S. Equation (5) shows that the S value changes very rapidly with f, the number of ionized groups per constituent chain. As f changes from 0 to 6, S changes by a factor of 3×10^4. The strong dependence of S on ionization accounts for the drastic change in the collapse with hydrolysis. In Fig. 3, both S and f are plotted as functions of hydrolysis time.

The role of ionization in the phase transitions of the gels is most conspicuous when the pH of the solvent is lowered. When the pH is changed—with the temperature and solvent composition fixed—the degree of ionization of the network is modified, altering the S value. Both continuous and discrete transitions may be induced by changing the pH. As Fig. 2 shows, if the reduced temperature is greater than -0.338, the equilibrium value of φ/φ_0 increases continuously with f. However, below -0.338 the value of φ/φ_0 changes discretely. Both types of transitions were observed. Water was used as a solvent in the case of the continuous transitions, a 50% acetone-water mixture was used in the discrete transition. The results are shown in Fig. 4.

In conclusion, the ionization of the polymer network plays an essential role in the phase transitions of gels. It is now important to study the effects of salts on the transition.

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[5] In calculations of the equilibrium swelling ratio, the value $\varphi_0 \sim 0.5$ was used with the assumption that on gelation acrylamide and *bis*-acrylamide monomers polymerized in a random walk fashion to form a network. Then φ_0 is equal to the original volume concentration of the network, φ^*, at gelation. The value $\nu v/N\varphi_0{}^3 = 10$ was chosen so that the theoretical curves agree with the experimental data.

Observation of a Two-Step Melting in the Submonolayer Region of Tetramethyltin $Sn(CH_3)_4$ Adsorbed on (0001) Graphite, by Mössbauer Spectroscopy

H. Shechter and R. Brener
Physics and Solid State Institute, Technion–Israel Institute of Technology, Haifa, Israel

and

J. Suzanne
Départment de Physique, Faculté des Sciences de Luminy, Université d'Aix-Marseille II, F-13288 Marseille, France

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Mössbauer cross section isotherms of $Sn(CH_3)_4$ adsorbed on graphite show a two-step melting process which suggest the formation of two-dimensional moving islands in the intermediate phase. Above 0.65 of a monolayer and $T \lesssim 85$ K, the cross section increases sharply which we tentatively interpret as a coalescence of the islands into a large, still "continent." At $\simeq 100$ K, the islands melt into an isotropic fluid.

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During the last few years, there has been an increasing interest in the problems of melting of two-dimensional (2D) matter. Many experimental methods were used to investigate the phenomenon such as heat capacity,[1] neutrons,[2,3] Mössbauer effect,[4,5] etc. The results do not indicate any conclusive behavior. In some cases, the 2D melting transition appears to be first order,[6] where in some other cases higher-order transitions (continuous) were observed.[7]

A detailed 2D-melting theory was suggested recently by Halperin and Nelson (NH).[8] With use of the Kosterlitz-Thouless model which describes a dislocation mediated melting, they show that the transition from a 2D solid to a 2D liquid can occur, when on smooth substrate, in two *second*-order transitions. Frenkel and McTague (FM) pointed out[9] that an experimental verification of the NH theory can be complicated because of subtle changes in the physical quantities at the transition. They applied molecular-dynamics (md) calculation for supporting the NH theory. Abraham's thermodynamical computer experiments,[10] however, suggest that only one first-order melting transition can be expected in those systems. His view is supported by Toxvaerd[11]; using md calculations, he showed that the behavior of 2D Lennard-Jones systems is quite similar to the corresponding 3D case, with liquid-gas critical point, and *first*-order phase transition. In Toxvaerd's calculations, however, no evidence is found for the NH two-stage process in the melting of such a 2D system. It is evidently interesting to see if it is possible for a 2D system on a "smooth" substrate to transform into mobile phase in more than one stage, in practical sys-