Phase transitions in gels and a single polymer

Toyoichi Tanaka
Department of Physics and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
(Received 8 July 1979)

We describe phase transitions and critical behaviour of covalently crosslinked polyacrylamide gels, and a single polyacrylamide chain. In both samples, we observed discrete changes in size when the solvent underwent continuous transition from poor to good solvent. Critical divergence and slowing-down of network concentration fluctuations in the gels were observed using laser light scattering spectroscopy. These phenomena are analysed in terms of the Flory-type mean field theory, and the mode coupling theory.

INTRODUCTION

One of the central problems in polymer physics is the effect of intramolecular and intermolecular interactions on the equilibrium and viscoelastic properties of polymer systems such as a single polymer in solution and in gels. We can expect that at sufficiently high temperatures or in good sol vents, a polymer system would have an expanded state, whereas at sufficiently low temperatures or in poor solvents, the system would have a compact state[1]. It is of great interest to study the equilibrium and viscoelastic properties of polymer systems when their solvents undergo continuous transition from good to poor solvent. Recently, we found that polyacrylamide gels and a single polyacrylamide chain show phase transitions upon changing temperature or solvent composition. It is the purpose of this article to describe these phase transitions and to explain the physics underlying the phenomena.

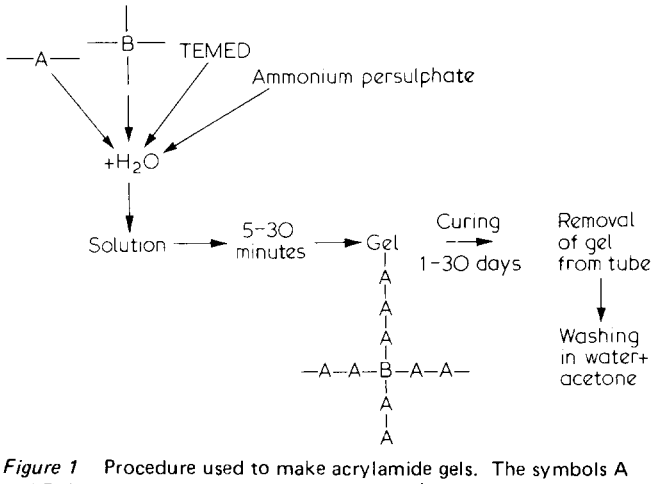


Figure 1 Procedure used to make acrylamide gels. The symbols A and B denote acrylamide momomer and *N,N'*-methylene-bisacrylamide monomer, respectively

POLYACRYLAMIDE GEL

We first describe the chemical structure of the acrylamide gel. The network sturcture plays an essential role in determining the collapsing and other equilibrium aspects of the gels. Acrylamide gel consists of linear polymer chains of acrylamide molecules crosslinked by bisacrylamide molecules, which consist of two acrylamide molecules connected together. The interstitial spaces in the polymer network are filled with water. The gel is very easily made as shown in *Figure 1*. 100 ml of water is placed in a beaker. Acrylamide monomers (5 g) and bisacrylamide monomers (0.133 g) are dissolved in water. Then ammonium persulphate (40 mg) and TEMED (tetramethyl ethylenediamine) are added to the solution. These are the initiators which start the polymerization chain reaction. First, ammonium persulphate attacks a TEMED molecule and breaks it into two molecules, each of which carries a free radical. These half molecules of TEMED with free radicals nucleate the polymerization. This free radical in a half-part of a TEMED molecule attacks and opens one of the doubly bonded carbon atoms of the acrylamide and bisacrylamide monomers. One electron of the double bond in acrylamide or bisacrylamide molecule pairs with the odd electron of the free radical to form a bond between the free radical and this carbon atom; the remaining electron of the double bond shifts to the other carbon atom, which then becomes a free radical. In this way, the active centre shifts uniquely to the newly added monomer, which is thereby rendered capable of adding another monomer. This continues until a network consisting of an almost infinite number of bonded monomers is formed. Both polymerization and crosslinking take place almost instantaneously when the first free radical appears, which is normally about 30 min after mixing the solution at room temperature. The infinite polymer network is thus formed at this instant. The polymer network at this moment is expected to have many free branches whose ends are not connected to the main network. The ends of these free branches can still have the active free radicals. Such free radicals would eventually encounter uncrosslinked bisacrylamide molecules or another free radical. This process is very slow because it involves the motion of large molecules and because of the small probability of encounters due to the small concentration of the free branches. The polymer network becomes more and more perfect with time, but does so slowly. We may call the fast polymerization gelation, and the slow disappearance of the free branches, the curing of the gel. We shall see immediately that this curing plays an essential role in the phase equilibria of the gel.

0032–3861/79/111404–09$02.00

SWELLING EQUILIBRIA

We now describe the swelling experiments and the observations of the collapse of the gels[2-4]. Gels of 5% acrylamide were prepared using various amounts of the TEMED initiator (15–100 μl in 25 ml gel) in small tubes. The gels were left in the tubes for a set period of time, which we call a curing time. In our experiments, the curing time ranged from 1 to 29 days. After curing, we took the gels out of the tubes. Separation of the gel from the tube wall was effected with syringe and needle by forcing water between the gel and the wall. Each gel sample was then immersed in a large volume of acetone–water mixtures of various compositions. The water inside the network and the acetone–water mixture outside were exchanged within 30 min by diffusion. However, equilibrium was not yet achieved. Depending on the acetone concentration, some gels swelled and some gels shrank. In *Figure 2*, we plot the degree of swelling as a function of acetone concentration for various curing times and TEMED amounts. The degree of swelling, ϕ/ϕ^*, is defined as the ratio of the final concentration ϕ to the original concentration ϕ^* of the polymer network. $\phi/\phi^* > 1$ means that the network shrinks and the network concentration increases, and $\phi/\phi^* < 1$ means that the network swells. Let us, for example, examine the swelling curve of a gel made using 40 μl TEMED and cured for 1 day (F–I). At low acetone concentration, the gel swells. As the acetone concentration is increased the gel gradually shrinks. The degree of swelling changes continuously with the acetone concentration. For a gel made with the same amount of TEMED, but cured for 8 days (F–II), the swelling curve shows an inflection point at which the swelling curve has a zero slope. For a gel cured for 15 days (F–III) the swelling curve has a discrete transition. At low concentrations of acetone the gel swells. As the acetone concentration increases, the gel shrinks a little but at 39% acetone concentration, the network suddenly collapses, and remains collapsed at higher concentrations. This phenomenon is entirely reversible. If a collapsed gel is transferred into a mixture having an acetone concentration lower than 39%, the gel swells until it reaches the network concentration indicated by the swelling curve. *Figure 2* shows that the size of the collapse becomes larger for longer curing times and larger amounts of TEMED. The maximum concentration change of the gel at the transition was approximately one hundred-fold.

So far, the collapse of the gels has been caused by changing the acetone concentration in the mixture at room temperature. What would happen if the acetone concentration of the mixture were fixed and its temperature changed. A similar collapse of the gels is observed, and its dependence on curing time and amount of TEMED initiator. *Figure 3* shows the swelling ratio curves of the gels (gel I was cured for 30 days and gel II for 3 days with 100 μl/ml TEMED) immersed in mixtures of fixed acetone and water composition. At temperatures higher than room temperature the network swells and below, it shrinks. There is a discontinuous change in gel I at room temperature whereas the curve for gel II is continuous.

EQUATION OF STATE

In order to understand these phenomena, let us examine the equation of state which relates the osmotic pressure, π, of a gel to its volume concentration, ϕ, and temperature, T. Flory's equation[1,2] gives:

$$\pi = -N_A/kT \left\{ \ln(1-\phi) + \phi + \frac{\Delta F}{2kT}\phi^2 + \frac{v_0}{Nv}\left[\left(\frac{\phi}{\phi_0}\right)^{1/3} - \frac{\phi}{2\phi_0}\right]\right\} \quad (1)$$

where N_A is Avogadro's number, k is the Boltzmann constant, $\Delta F = \Delta H - T\Delta S$ is the free energy decrease associated with formation of a contact between the polymer segments, v_0 is the specific volume of the solvent molecule, v is that of a polymer segment, N is the number of segments in one polymer chain whose ends both terminate at the neighbouring crosslinks. It is important to notice that N does not include the segments of free branches whose one end is free. ϕ_0 is the volume concentration of the network in the absence of interaction among polymer segments. The first three terms in equation (1) represent the interactions among polymer segments and solvent molecules. The last term is the rubber elasticity. Equation (1) can be expanded in the following way:

$$\pi = N_A kT\phi_0^3[S(\rho/2 - \rho^{1/3}) + (A/2\phi_0)(1 - \theta/T)\rho^2 + \rho^3/3 + \ldots] \quad (2)$$

where $\rho \equiv \phi/\phi_0$; $S \equiv v_0/(vN\phi_0^3)$, $A \equiv (1 + \Delta S/k)$, and $\theta = \Delta H/(\Delta S + k)$

From equation (2) we can see the equivalence of changing temperature and solvent composition: in the parentheses of equation (1) only the third term coefficient changes with these parameters. The parameter S determines the relative contribution of the rubber elasticity and the polymer–solvent interaction. As shall be shown later, S plays an essential role in determining the size of the collapse of a gel. A microscopic interpretation of the parameter S can be seen by the following simple argument. Let the linear chain connecting neighbouring crosslinks consist of N free-jointed segments of radius a and length b ($v \sim a^2 b$). Then, the r.m.s. end-to-end distance of the single polymer is $R \sim N^{1/2}b$. Since R is also the r.m.s. distance between neighbouring crosslinks, we see that $\phi_0 \sim (Nba^2/R^3)(1 + \phi_f/\phi_e) \sim (a/b)^2(1 + \phi_f/\phi_e)/(N)^{1/2}$ where ϕ_f and ϕ_e are the volume concentrations of the free branches and effective polymers whose ends are both incorporated in the network, respectively. From these relations we have

$$S \sim v_0(N)^{1/2}(a^4/b^7)/(1 + \phi_f/\phi_e)^3 \quad (3)$$

PHASE DIAGRAM

Using the equation of state, the phase diagram and the swelling curve of the gel may now be calculated[2]. The osmotic pressure is plotted as a function of the volume concentration of a gel for a fixed temperature (and solvent composition). Such a curve is called an isotherm. *Figure 4a* shows the isotherms at various temperatures calculated for $S = 600$, $\phi_0 = 0.01$, $A = 1$, and $\theta = 400$K. From these isotherms we can obtain the relation between ϕ and T at phase boundaries. Two conditions are required for stable phases. First, the osmotic pressure must be positive or zero. If it is negative, the gel shrinks and separates into two phases for which $\pi = 0$. These correspond to pure fluid and a gel with a volume fraction for which $\pi = 0$. These conditions provide the points

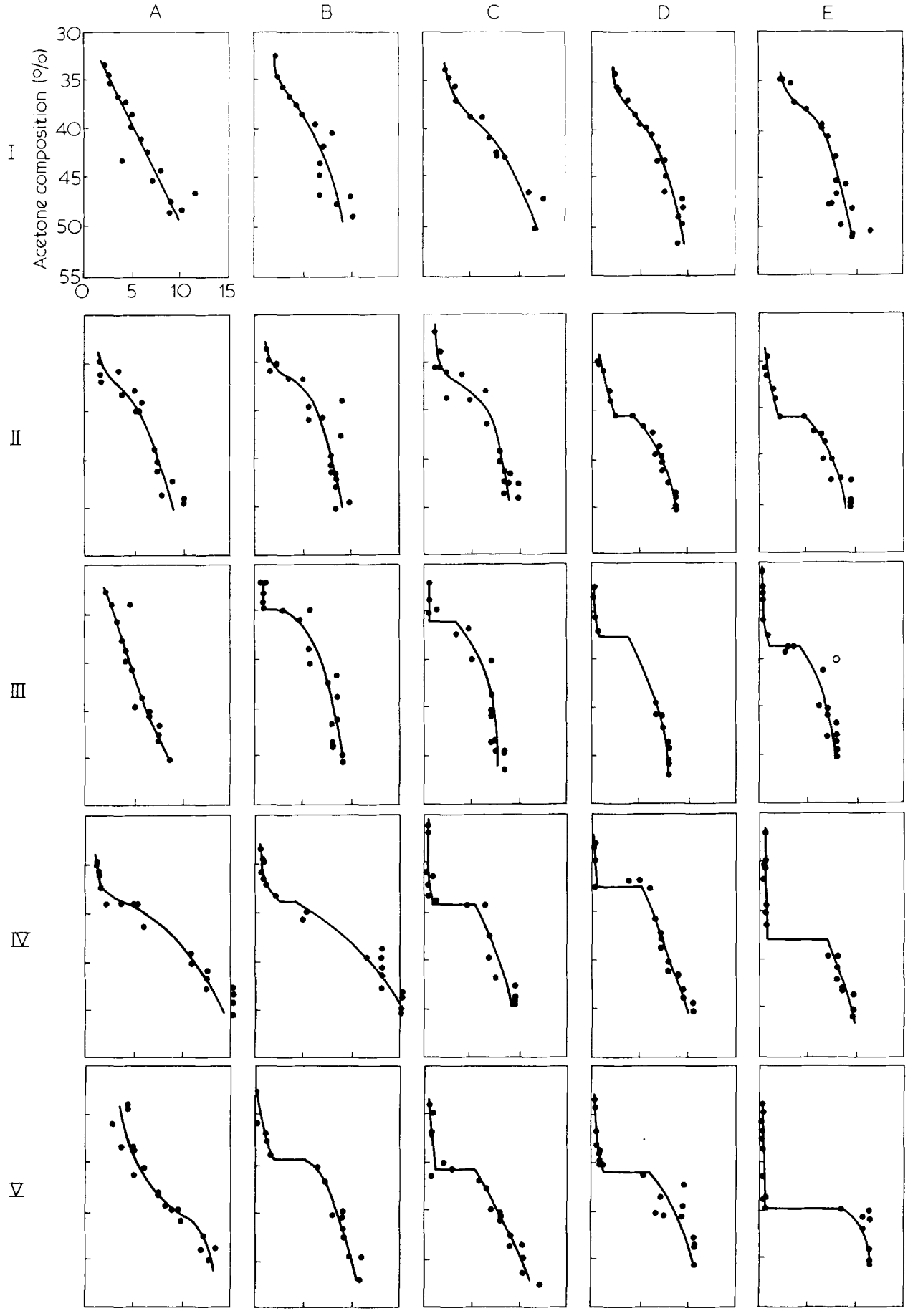
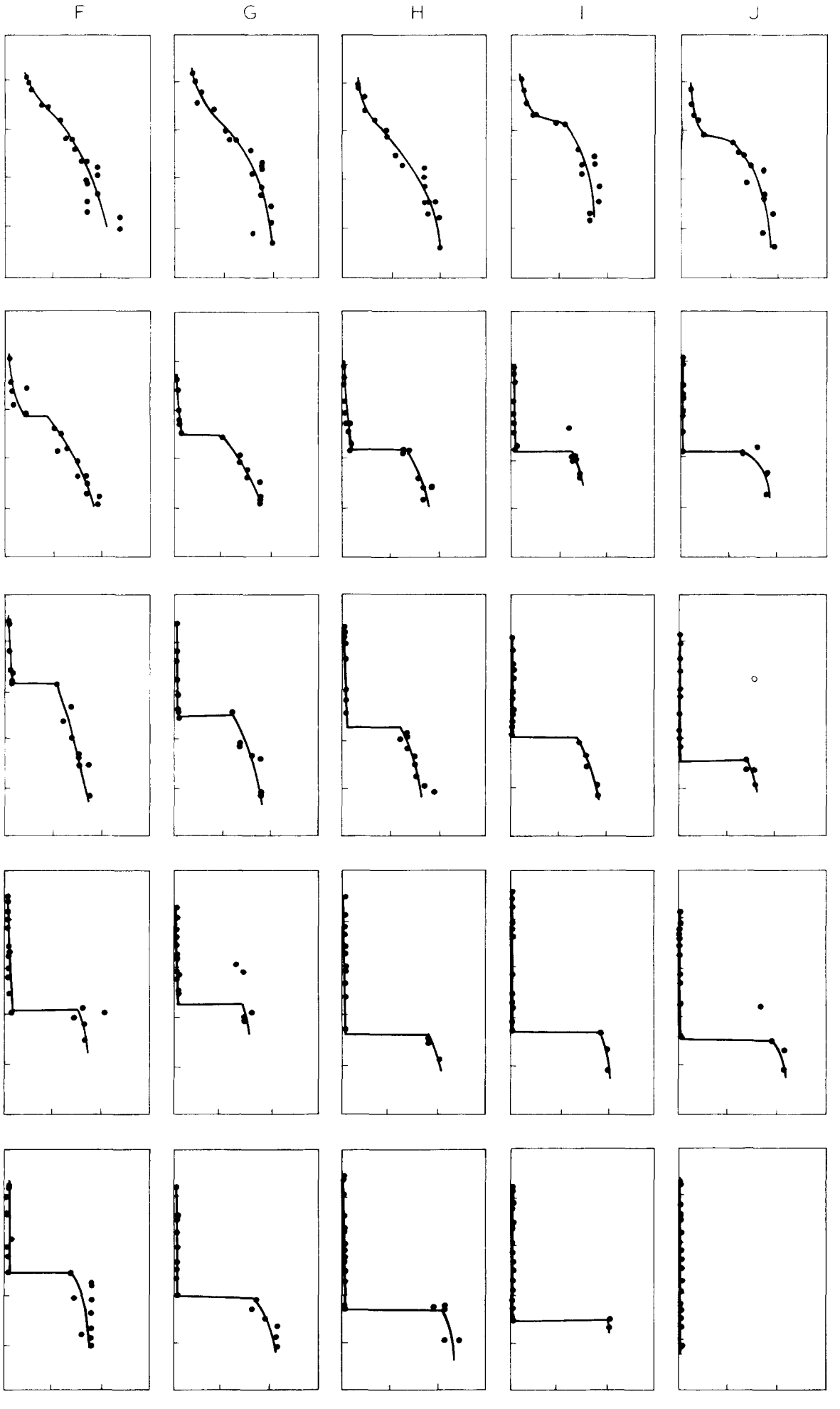


Figure 2 Ratio of the final equilibrium concentration, ϕ, of the acrylamide network to the original network concentration, ϕ^*, as a function of acetone concentration. The letters A, B, C, D, E, F, G, H, I and J indicate the amount of TEMED used in the gelation. They were 15, 20, 25, 30, 35, 40, 45, 60, 80 and 100 μl per 25 ml of gel, respectively. The Roman numerals I, II, III, IV and V denote curing times of 1, 8, 15, 22 and 29 days, respectively


F
G
H
I
J

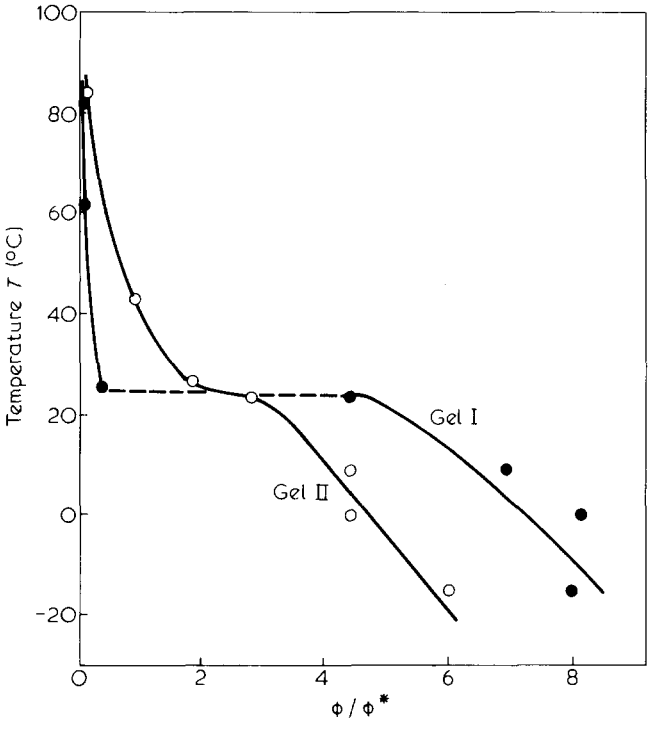


Figure 3 Temperature dependence of the swelling ratio of the polyacrylamide gels made with 40 μl TEMED in 25 ml gel. ●, Data for gel I (curing time 30 days) immersed in the acetone–water mixture (42% acetone concentration). ○, data for gel II (curing time 3 days) immersed in 40% acetone–water mixture

in the descending curve of *Figure 4b*, for example, A, B, D and I. Second, even if $\pi \geqq 0$, along each isotherm the gel must satisfy the condition of thermodynamic stability. When the isotherm contains van der Waals loops, the stability conditions are obtained using the Maxwell construction. Values of ϕ along the horizontal Maxwell line correspond to unstable states. The end-points of the Maxwell line (e.g. points E and F in *Figure 4a*) represents volume fractions along the coexistence curve. The values of the volume fractions between these points and the maximum and the minimum of the van der Waals loops are those of metastable states. The maximum and the minimum of the loops fix the volume fractions along the spinodal curve, within which no metastability is allowed. Along the spinodal curve the amplitude and relaxation time of the concentration fluctuations diverge. Using these considerations it is possible to construct the coexistence curve and spinodal curve shown in *Figure 4b*.

The swelling ratio curve, which represents the equilibrium concentrations for different temperatures, can be also derived from these isotherms. It is defined by the condition, $\pi = 0$, which assures the equilibrium between the gel and the surrounding fluid. π is zero at the intersection of each isotherm with the ϕ axis (e.g. A for $T > T_c$, and B for $T = T_c$ in *Figure 4a*. The curve obtained in this way is shown in *Figure 4b*, and shows a discrete transition at a temperature T_t at which the Maxwell line is the isotherm touches the axis.

All the elements required for a complete phase diagram for a gel is contained in *Figure 4b*. At any temperature and at a volume fraction in the region between the coexistence curve and the swelling ratio curve, the gel will separate into two different gels having volume fractions determined by the intersects of the T = constant line with the coexistence curve. For values of ϕ and T beneath the swelling ratio curve, the gel will also separate into those phases determined by the intersection of the T = constant line with the swelling ratio curve and the T-axis (pure fluid).

The experimentally observed collapse of gel I obtained by lowering the temperature (shown in *Figure 3*) corresponds precisely to the swelling ratio curve (*Figure 4b*). Also, the experimentally observed collapse of the gel upon increasing the acetone concentration (*Figure 2*) corresponds to the swelling ratio curve, with the understanding that the temperature dependence of the osmotic pressure (equation 2) enters as θ/T. Experiments involving changes in acetone concentration involve changes in θ; in the temperature experiments T changes. S characterizes the network structure and is independent of acetone concentration.

Having understood the discrete collapse of the gel, let us now consider how the curing affects the size of the collapse of the gels. On curing, the number of free branches decreases and the S value increases. Careful examination of equation (2) shows that for $S < S_e \equiv (3/5)(40/9)^4$ there is no collapse. Collapses can be seen for $S > S_e$ and its size increases with the value of S. *Figure 5* shows how the phase diagram varies with S. The critical point can exist only for $S > S_e$ and terminates at $S = S_e$ at which $\phi = \phi_e \equiv (40/9)^{3/2}\phi_0$, and $A(1 - \theta/T) = (34/15)\phi_e$. This may be called the critical end-point.

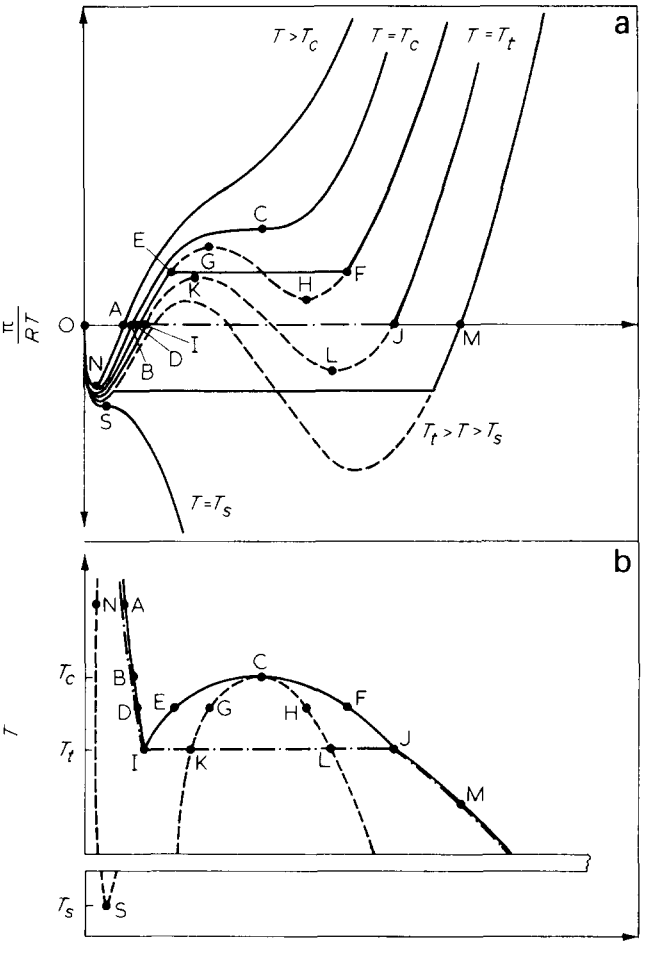


Figure 4 (a) Osmotic pressure of a gel as a function of the volume fraction of the network at various temperatures. The value S = 600, ϕ_0 = 0.01, and θ = 400K were used. T_c denotes the critical temperature (310K); T_t is the temperature at which collapse occurs (303K), and T_s is the minimum in the spinodal curve (210K). (b) Coexistence curve (———), the spinodal curve (— · — · —) and the swelling ratio curve (— — —)

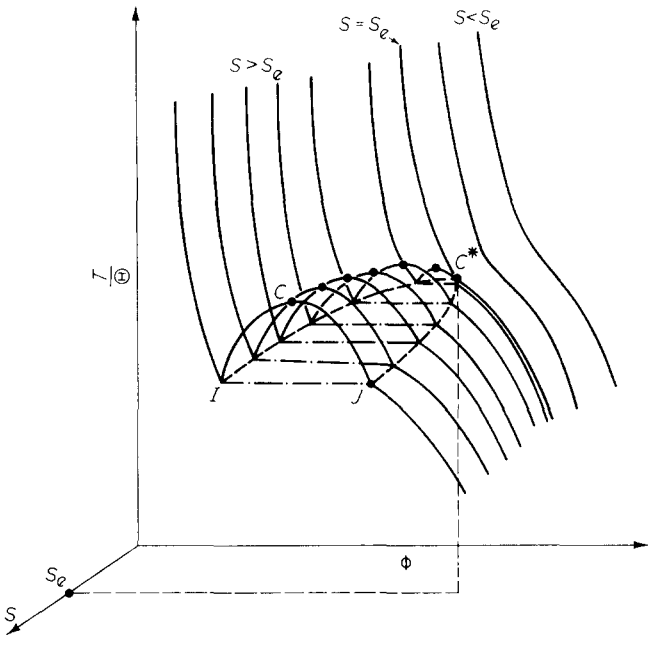


Figure 5 Dependence of the phase diagram on the parameter S. At $S = S_e$, the critical point disappears (point C^*). This corresponds to the critical end point. The parameter S decreases with the number of free branches in the network

CRITICAL BEHAVIOUR OF GELS

The critical divergence and slowing-down of concentration fluctuations in the polyacrylamide gels[4] are now described.

Tanaka, Hocker and Benedek[5] and de Gennes[6] presented a theory which describes the concentration fluctuations in a gel polymer network and showed that the elastic modulus of the network can be determined from the intensity of light scattered from the fluctuations. They also showed that the ratio of the elastic modulus and the frictional coefficient of the network in the fluid medium can be determined from the correlation time of the scattered light[5]. The normal modes of the concentration fluctuations in the gel network can be described as overdamped phonons[5]. The phonons in the network are overdamped because of the large frictional drag of the fluid medium which is proportional to the velocity of the network relative to the fluid medium. The light incident on the gel is scattered by such overdamped phonons and the correlation function of the scattered light field is expressed in the following way:

$$\langle E(\vec{q},t)E(\vec{q},0)\rangle = C(\phi\partial n^2/\partial\phi)^2 \cdot \frac{kT}{K}\exp(-Kq^2t/f) \equiv I\exp(-\Gamma t) \tag{4}$$

Here E is the amplitude of the scattered light field, $\vec{q}$ is the scattering vector, n is the refractive index of the whole gel, K is the elastic modulus of the network in the fluid medium, and C is a constant depending only on the optical geometry. The frictional coefficient, f, multiplied by the velocity of the network relative to the fluid medium gives the frictional force per unit volume of the network. Equation (4) has been confirmed experimentally by Tanaka, Hocker and Benedek[5], and Munch *et al.*[6]. In *Figure 6*, we show the temperature dependence of the intensity and the correlation time of laser light scattered by the 2.5% polyacrylamide gel. Both the intensity and the correlation time of the scattered light increase by a factor of more than 200 as temperature decreases and appear to diverge at a certain temperature. This temperature corresponds to the spinodal temperature at which the elastic modulus of the network becomes zero. In other words, the network has infinite compressibility[4]. The elastic modulus K can be calculated using the equation of state (equation 1):

$$K = \phi\partial\pi/\partial\phi \tag{5}$$

$$= N_A kT\left\{\frac{\phi^2}{1-\phi} - \frac{\Delta F\phi^2}{kT} + \frac{\nu_0}{N\nu}\left[\frac{\phi}{2\phi_0} - \left(\frac{\phi}{\phi_0}\right)^{1/3}\right]\right\} \tag{6}$$

$$= A(T - T_s) \tag{7}$$

where

$$A \equiv N_A k\left\{\frac{\phi^2}{1-\phi} + \frac{\nu_0}{N\nu}\left[\frac{\phi}{2\phi_0} - \frac{1}{3}\left(\frac{\phi}{\phi_0}\right)^{1/3}\right]\right\} \tag{8}$$

$$T_s \equiv N_A\Delta F\phi^2/A \tag{9}$$

T_s corresponds to the spinodal temperature. Equations (4) and (7) show that the scattered light intensity, I, varies with temperature as:

$$1/I \propto 1/T_s - 1/T \tag{10}$$

This relation is confirmed in *Figure 7*. Having understood the critical behaviour of the elastic modulus, let us examine the friction coefficient, f, between the polymer network and water. Since it is not easy to calculate f directly, we calculated the decay rate, Γ, of concentration fluctuations using mode coupling theory[7]. The result in the hydrodynamic régime ($q\xi < 1$) is given by:

$$\Gamma = (kT/6\pi\eta\xi)q^2 \tag{11}$$

$$K = N_0(b/\xi)^2kT \propto 1/\xi^2 \tag{12}$$

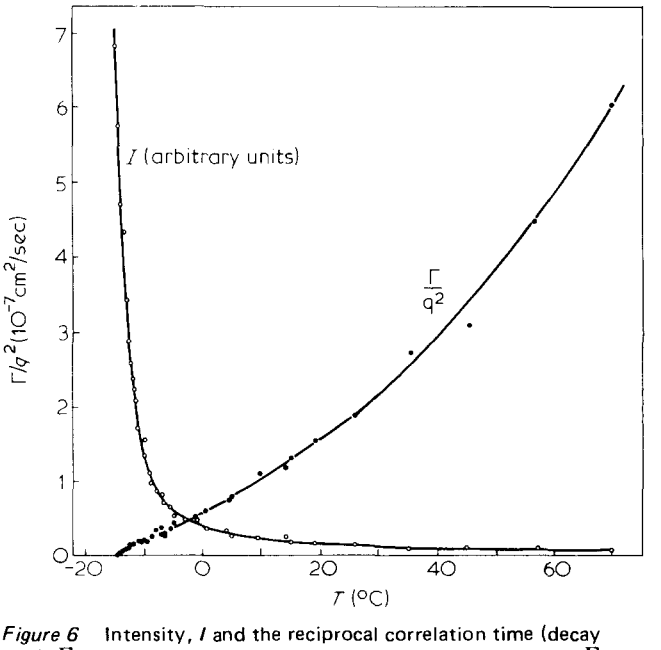


Figure 6 Intensity, I and the reciprocal correlation time (decay rate), Γ, of laser light scattered by a 2.5% polyacrylamide gel. Γ is divided by the square of the scattering vector, $|\vec{q}|^2$

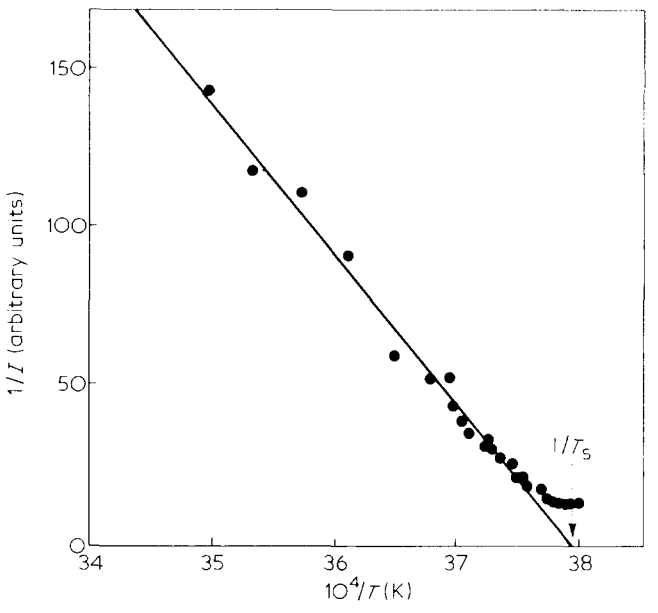


Figure 7 Inverse of the laser light intensity scattered by a 2.5% polyacrylamide gel as a function of reciprocal absolute temperature

$$f = N_0(b/\xi)^2 6\pi\eta\xi \propto 1/\xi \tag{13}$$

where N_0 is a constant, b represents the length of segments constituting the network polymers, η is the viscosity of water and

$$\xi = b[T/(T - T_s)]^{1/2} \tag{14}$$

represents the correlation length over which the movements of the polymer segments are correlated. This correlation length diverges as the temperature approaches the spinodal temperature, T_s. In *Figure 8*, we compare the calculated curve of the decay rate, Γ, and the data. They show excellent agreement.

These results indicated that as we approach the spinodal temperature the network becomes increasingly compressible ($K \to 0$) and porous ($f \to 0$). How can the permanently cross-linked gel change its pore size with temperature? When the network becomes more compressible large concentration fluctuations appear in the network which lead to the formation of large regions of swollen and compressed regions in the network. The large regions of swollen network determine the effective pore size of network, which becomes increasingly larger as the spinodal temperature is approached.

We have determined the entire spinodal line using intensity measurements[8]. Gels made with 100 μl TEMED in 25 ml gel were cured for 12 days. They were cut into pieces 1 cm long, and dried at 30°C. Each dried gel was then put into an acetone–water mixture having a composition ratio of 44.56 by volume. After a certain amount of the mixture had soaked into the network, the gel was removed and placed in an ampoule. The ampoule was immediately sealed to prevent any loss of the solvent. Gels of different concentrations were prepared in this way. The network concentration of each gel was determined by measuring the weights of dry and swollen gel.

The scattered light intensity at a 90° angle was determined for each sample as a function of temperature. It has been shown above that $1/I$ vs. $1/T$ is linear. The experimental points are fitted to a straight line and the spinodal temperature is obtained from the intercept of the straight line with the $1/T$ axis which corresponds to infinite scattered light intensity. The deviation of the data points from the straight line as the spinodal temperature is approached probably results from multiple scattering of the light. The spinodal temperature is plotted as a function of gel concentration in *Figure 9a* (○). We also determined the swelling equilibrium concentration of the gel which was immersed in a large volume of the acetone–water mixture at various temperatures. They are also plotted in the *Figure 9a* (●). In *Figure 9b*, we show the spinodal line calculated from $\partial\pi/\partial\phi = 0$, and the swelling ratio curve at which $\pi = 0$ as calculated from equation (1). The parameters used are $\Delta S = 5.5 \times 10^{-16}$ erg/°C, $\Delta H = 2.1 \times 10^{-13}$ erg, $\phi_0 = 0.0045$ and $v_0(vN) = 0.0026$. We have a qualitative agreement between the theory and the experimental results.

COIL–GLOBULE TRANSITION

The conformations of a single polymer chain in solution have been studied extensively since the 1940s. Theories and experiments established that at high temperatures and in good solvents, a polymer has an extended configuration, whereas at low temperatures, and in poor solvents, it is in a compact state. The transition between the extended and compact states as the temperature or solvent compositions was varied was thought to be smooth and continuous[1]. Experiments supported this idea[1]. However, in 1968 Lifshitz suggested the possibility that this transition was discrete[9]. He labelled this discrete change in polymer extension the coil–globule transition. The mechanism of the transition as described by Lifshitz is quite similar to that of the gas–liquid transition: the extended polymer corresponds to the gas state, whereas the collapsed polymer corresponds to the liquid state. Since Lifshitz's work, there have been numerous theoretical works on this possible coil–globule transition[10–12]. For example, deGennes[13], using the analogy of the magnetic transition, pointed out that the coil–globule transition of an infinitely long polymer may correspond to a tricritical point. On the experimental side, there have been reports on the temperature dependence of the radius of gyration of polystyrene in cyclohexane[14–16], and on poly(acrylic acid) in dioxane[16]. In these experiments, however, the existence of the coil–globule transition was not confirmed.

In the previous sections, we have seen that the polyacrylamide gels can undergo reversible collapse upon changing

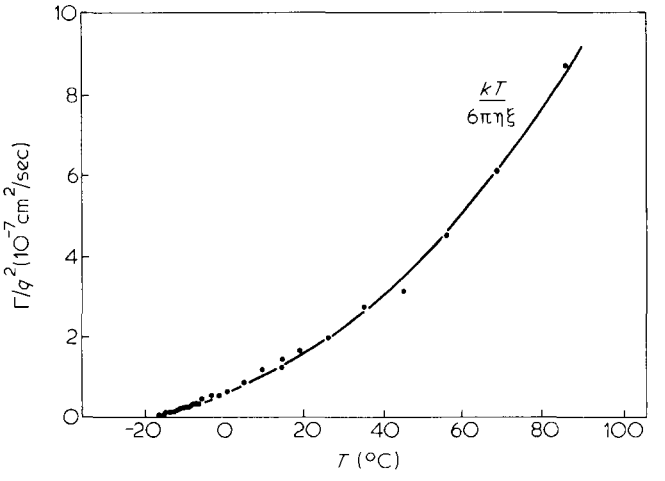


Figure 8 Decay rate calculated using a mode coupling theory (———). ●, measured data

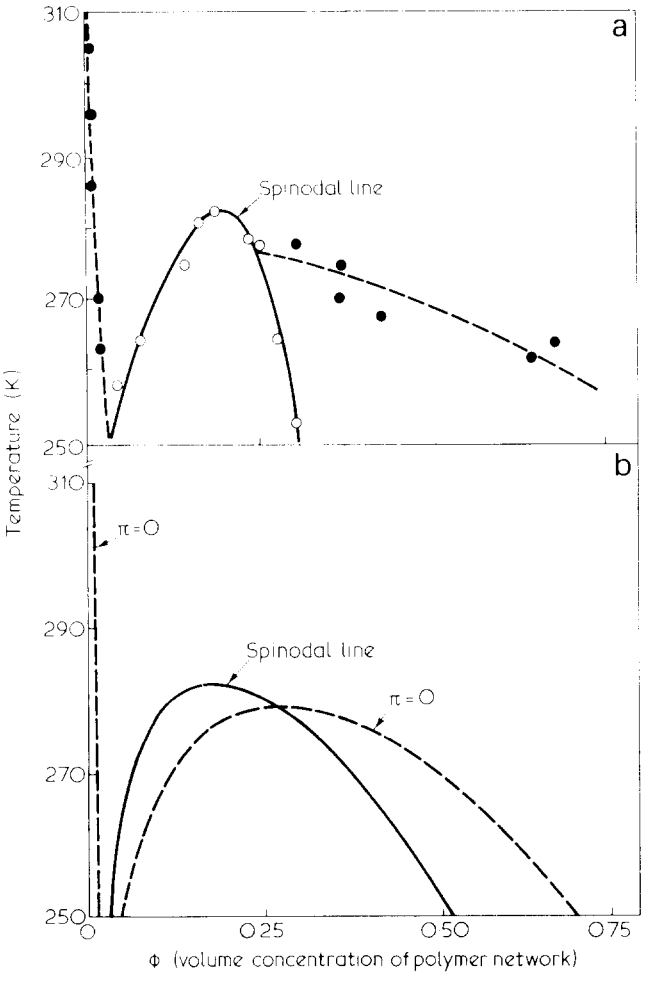


Figure 9 (a) Spinodal line (○) determined by light scattering measurements. ●, denote the equilibrium concentrations of the acrylamide gel which is immersed in a 44% acetone–water mixture at different temperatures. (b) Spinodal line (——) and the zero osmotic pressure line (– · – ·) calculated from equation (1) in the text. The latter represents the equilibrium concentration of a gel which is immersed in a large amount of fluid

temperature or the acetone concentration of the solvent. This suggests that a single polyacrylamide chain may undergo a coil–globule transition in acetone–water mixtures. In this section, we describe the first observation of the coil–globule transition in a single polyacrylamide chain in an acetone–water mixture by Nishio, Sun, Swislow and Tanaka, using laser light scattering spectroscopy.

Monodisperse polyacrylamide polymers of molecular weight 5–6 x 10^6 daltons purchased from Polysciences Inc. were used. A single chain of the polymer consists of approximately 8 x 10^4 acrylamide monomers and has a length of about 24 μm. Mixtures of distilled water and acetone of various compositions were used as solvents. The concentration of polymer in solution was less than 10 μg/ml, at which the mean distance between the nearest adjacent polymers was 1 μm. This turns out to be much larger than the extended hydrodynamic diameter of 1000 Å, and thus interpolymer aggregations were avoided.

The hydrodynamic radius of the polymer was determined using the technique of laser light scattering spectroscopy[17]. An argon ion laser (Spectra Physics, Model 165) at 5145 Å wavelength was used as a light source. The power of the laser was approximately 1.2 W. The correlation function of light scattered from the sample at a 90° angle was measured using a photomultiplier tube and photon correlation equipment (Nicoli Instrum). All measurements were made at 25°C.

From the decay rate of the correlation function of the scattered light intensity, we determine the diffusion coefficient, D, of the polymer, which is related to the hydrodynamic radius, ξ, of the polymer through the Stokes–Einstein relation[17]:

$$D = kT/(6\pi\eta\xi) \qquad (15)$$

where k is the Boltzmann constant, T is the absolute temperature and η is the viscosity of the solvent.

In *Figure 10* (○), we plot the measured hydrodynamic radius ξ of the polyacrylamide chain as a function of acetone concentration. At low acetone concentrations, the radius is 500 Å. Around an acetone concentration of 39% the polymer shows a drastic decrease in its hydrodynamic radius, down to 200 Å. The radius remains constant when the acetone concentration is further increased. The radius of gyration of the chain was also determined from measurements of the angular dependence of scattered light intensity[18]. The data are plotted in *Figure 10* (●), and show results consistent with those for hydrodynamic radius.

The coil–globule transition observed in this paper is very sharp, but not exactly discrete. This may be due to the finite number of monomer units composing the polymer chain. An infinite number of monomers would be required to observe a discrete transition. It is important to investigate further the effect of the finite size of the system on the coil–globule transition.

CONCLUSIONS

The sharp volume changes in gels and a single polymer on changing temperature or solvent composition can provide

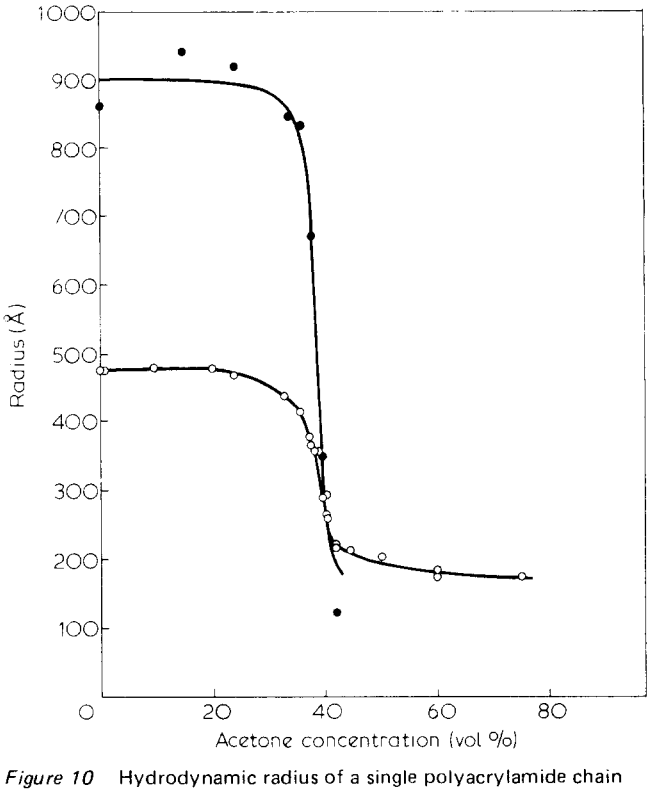


Figure 10 Hydrodynamic radius of a single polyacrylamide chain in acetone–water mixtures determined by laser light scattering spectroscopy (○). ● show the radius of gyration of the polyacrylamide chain determined from the measurements of the angular dependence of scattered light intensity

amplification, switching and memory. This would meet wide applications in biology, medicine and chemical engineering. It is also hoped that the studies presented here can provide an improved perspective on the interdisciplinary field where polymer science and the physics of critical phenomena merge.

ACKNOWLEDGEMENTS

The work described here has been carried out in collaboration with C. Ishimoto, S. Ishiwata, I. Nishio, S. -T. Sun, A. Hochberg, D. Nicoli, G. Swislow and D. J. Fillmore. The work has been supported by NSF, CHE77-26924, NIH, EY-01696, Health Sciences Fund, MIT, and a Biomedical Research Support Grant, MIT.

REFERENCES

1 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953
2 Tanaka, T. *Phys. Rev. Lett.* 1978, **40**, 820
3 Fillmore, D. J. and Tanaka, T. to be published
4 Tanaka, T., Ishiwata, S. and Ishimoto, C. *Phys. Rev. Lett.* 1977, **38**, 771
5 Tanaka, T., Hocker, L. O. and Benedek, G. B. *J. Chem. Phys.* 1973, **59**, 5151
6 See the discussions on the theory of de Gennes, P. G. in Munch, J. P. *et al. J. Polym. Sci.* 1976, **14**, 1097 and *J. Phys. (Paris)* 1974, **35**, 239
7 Tanaka, T. *Phys. Rev. (A)* 1978, **17**, 763
8 Hochberg, A., Tanaka, T. and Nicoli, D. to be published
9 Lifshitz, I. M. *Zh. Eksp. Theor. Fiz.* 1968, **55**, 2408
10 Edwards, S. F. in 'Critical Phenomena' (Eds. M. S. Green and J. V. Sengers) *US NBS Miscell. Publication No. 273, Washington DC*: 1966
11 Domb, C. *Polymer* 1974, **15**, 259
12 Lifshitz, I. M., Grosberg, A. -Yu and Khokhlov, *Rev. Mod. Phys.* 1978, **50**, 683
13 de Gennes, P. G. *J. Phys. (Paris) Lett.* 1975, **L36**, 55
14 Mazur, J. and McIntyre, D. *Macromolecules* 1975, **8**, 464
15 Mashimo *et al. J. Phys. Soc. Jpn* 1975, **39**, 1529
16 Cuniberti, C. and Bianchi, U. *Polymer* 1974, **15**, 346
17 Benedek, G. B. in 'Polarization, Matter, and Radiation', Presses Universitaire de France, 1969, pp. 49–84
18 Doty, P. and Edsall, J. T. 'Advances in Protein Chemistry', Vol VI, Academic Press, New York, 1951, pp. 35–121