Phase Transition, Spinodal Decomposition, and Pattern Formation in Polymer Gels

Shunsuke Hirotsu

*Department of Biological Sciences, Faculty of Bioscience
and Biotechnology, Tokyo Institute of Technology,
Nagatsuta, Midoriku, Yokohama 227, Japan*

Abstract. Heterogeneous structures can easily be developed in polymer gels during their state change, which includes continuous swelling, discontinuous phase transition, and spinodal decomposition. The heterogeneity manifests itself as variety of surface and bulk patterns. Recent experimental findings on pattern formation and phase transition in acrylamide-derived polymer gels are presented. A unique role played by the surface of gels in the course of state change is stressed. In addition, very peculiar phenomena of shape-dependent swelling and phase transition properties in ionized gels are reported. A possible mechanism underlying these phenomena is proposed in terms of a large surface tension inherent to ionized gels.

1. Continuous Versus Discontinuous Swelling of Gels

Gel is a solution in a thermodynamical sense, but it is a solid from a mechanical point of view. This dual character is the origin of some characteristic behaviors of gels. The most conspicuous feature of gel is swelling, i.e. gel exhibits a large volume change by absorbing or expelling solvent according to external conditions. In most cases the volume change is continuous with respect to the change of external conditions, but in some cases it is discontinuous. The discontinuous volume change is induced by the presence of an unstable region in the phase diagram, and is called a volume phase transition.

For example, the swelling curve of poly-N-isopropylacrylamide gel (abbre-

viated as NIPA gel) is shown in Fig. 1. Here, ϕ is the polymer concentration, which is inversely proportional to the volume V of gel, i.e. $\phi = V_0\phi_0/V$, where the subscript 0 means the value at the time of gelation. The curve of Fig. 1 represents the concentration of gel which is in equilibrium with excess solvent. On changing temperature, volume changes discontinuously at the transition temperature T_0 of ~33.6°C.
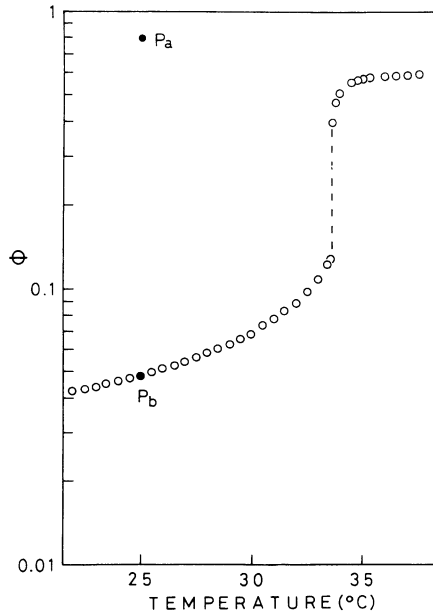

Fig. 1. Equilibrium polymer concentration ϕ of neutral NIPA gel as a function of temperature (open circles). State change $P_a \rightarrow P_b$ represents a continuous swelling under nonzero osmotic pressure, see text.

A gel is in equilibrium with outer solvent when its osmotic pressure π vanishes. According to the phenomenological theory of gels developed by Flory (1966), π can be expressed as

$$\pi / RT = -v_1^{-1}\left[\phi + \ln(1 - \phi) + \chi\phi^2\right] - N_c(NV_0)^{-1}\left[(\phi / \phi_0)^{1/3} - 0.5(\phi / \phi_0)\right]$$

Here, χ is the phenomenological parameter representing the free-energy change per solvent molecule (divided by $k_B T$) induced by the contact between polymer seg-

ments and solvent molecules, v_1 is the molar volume of solvent, N_c is the number of chains contained in a gel, and N is Avogadro's number. Physical properties of gel change drastically when χ traverses 0.5. In the region of $\chi < 0.5$, gel absorbs a large amount of solvent so that it swells extensively, while for $\chi > 0.5$, it expels most of solvent and shrinks to a smaller volume. The temperature and concentration dependence of χ is the origin of the phase transition of gel. The transition point corresponds to $\chi \approx 0.5$. For the transition to be discontinuous, rather strong concentration dependence of χ is necessary (Erman and Flory, 1986).

Gels can be put into a stable state with non-zero π. In Fig. 1, the region above the swelling curve corresponds to a state with positive π, while the region below the curve corresponds to a state with negative π. On changing π, gels swell or deswell continuously towards the new equilibrium states. The continuous swelling or deswelling occurs in any gel whenever some external conditions change.

Gels are unstable when the network bulk modulus is negative. Figure 2 shows a phase diagram of neutral NIPA gel calculated on the basis of modified Flory's theory (Hirotsu and Kaneki, 1988; Hirotsu, 1991). The unstable regions are shown hatched. When gels are brought into these regions, a phase separation occurs through spinodal decomposition.
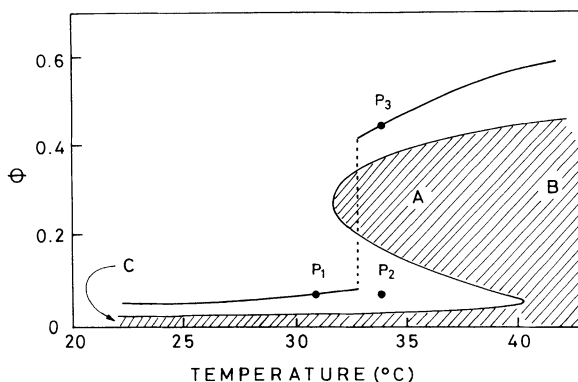

Fig. 2. Phase diagram of neutral NIPA gel calculated on the basis of the modified Flory's theory. Thick lines represent equilibrium swelling curves, a dashed line a first-order transition, and hatched regions unstable regions. For the meaning of A ~ C, and P_1 ~ P_3 see text.

Change of state of gels always involves transfer of solvent between inside and outside of gels. This is a slow diffusion process, and thus the inhomogeneity of concentration develops during state change. The inhomogeneity manifests itself as various patterns, which is interesting from the viewpoint of nonequilibrium statistical thermodynamics. In the present article I will report some recent experi-

mental results obtained by the author's group on volume phase transition and pattern formation in gels.

2. Surface Pattern Formed During Bulk Continuous Swelling

Tanaka *et al.* (1987) reported that honeycomb like polygonal patterns appear on a gel plate which undergoes an extensive and rapid swelling at a fixed temperature.

We have studied the evolution law of this pattern (Hirotsu *et al.*, 1989). Samples used were acrylamide-acrylic acid copolymer gels and NIPA-acrylic acid copolymer gels. As-prepared gels had initial concentration of $\phi_0 = 0.05 \sim 0.08$. They were dried at room temperature to $\phi \sim 0.8$. As soon as they are put into water, fine polygonal patterns appeared and they coarsened with time. The change of state in the case of NIPA gel is represented by $P_a \rightarrow P_b$ of Fig. 1. The average edge length of polygons R was measured as a function of time t. The result is shown in Fig. 3. It is seen that R fits the power law $R \sim t^\alpha$ with $\alpha = 0.46 \pm 0.1$ very well. The value of α was essentially the same for acrylamide and NIPA gels.

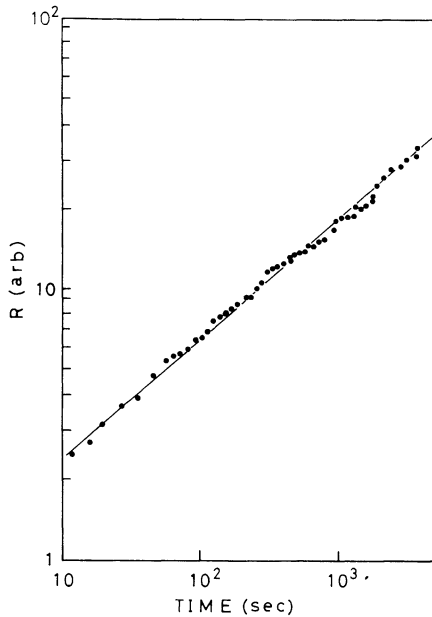The above result can be understood considering the three-dimensional struc-

Fig. 3. Evolution of the characteristic length of the pattern observed on the surface of acrylamide-acrylic acid copolymer gels during bulk continuous swelling. The line represents $R \sim t^{0.46}$.

ture of the pattern and the mechanism of their formation. The cross-sectional view of the pattern is depicted in Fig. 4. Edges of polygons are cusps formed in the surface layer. They are formed because the swelling occurs first at the surface layer and then extends gradually into the bulk.
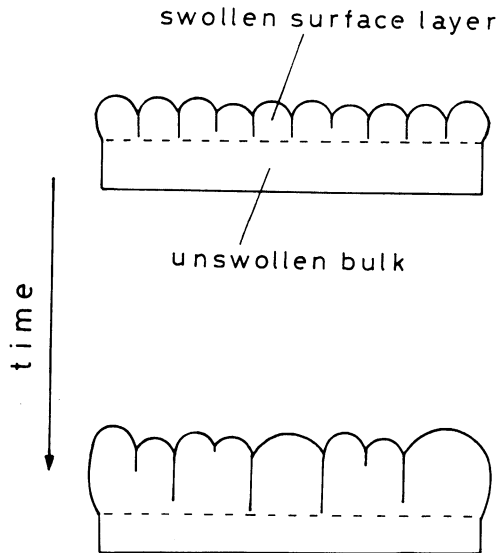

Fig. 4. Schematics of cross-sectional view of the surface pattern appearing during bulk continuous swelling.

Thus gel during swelling is divided into the swollen surface layer and the unswollen bulk. In this situation, the surface layer which has already been fully swollen must accommodate its area to that of the unswollen bulk. Cusps are formed to compensate for this mismatch of area. Then during rapid and continuous swelling, the surface becomes elastically unstable even though the bulk of gel shows no instability. In other words, the cusp formation is the result of surface spinodal decomposition (Onuki, 1989; Sekimoto and Kawasaki, 1989).

As long as the depth D of the surface layer is small, many cusps are needed to compensate for the large difference of area. As D gets larger, the neighbouring cusps exert elastic forces with each other such as to eliminate the neighbours, and as a result, the number of cusps decreases with time. The evolution of D is governed by diffusion of the network which leads to the power law with $\alpha = 1/2$.

In some cases, however, surface patterns that do not fit the above simple explanation have been observed. For example, near the transition point, patterns

with ridges rather than cusps can be observed (Hirotsu, to be published) which has been predicted to occur theoretically (Onuki, 1989). Also, the exponent α substantially different from 1/2 has been observed in some cases (Hirotsu *et al.*, 1989). More experimental work is necessary to understand the nature and evolution of various patterns appearing on gel surface.

3. Deformation of Bulk Sample Associated with the Strongly First-Order Transition

Near the first-order transition of gels, three phases coexist, i.e. swollen gel, shrunken gel, and pure solvent phases. An example is shown in Fig. 5, which was observed on ionized NIPA gel rod. A nucleus of new phase appears almost always at the ends of rod and a clear phase boundary separating swollen and shrunken phases is formed perpendicular to the rod axis. The temperature interval where the clear phase boundary can be observed is much wider near the strongly first-order transition in ionized gels than near the weakly first-order one in neutral gels. Hence the results presented below were all obtained on ionized NIPA gels. A number of peculiar features have been noted on the behavior of this phase boundary (Hirotsu, to be published), of which I will mention a few below.

Unlike the coexistence of stable and metastable phases at conventional first-order phase transitions, the coexistence shown in Fig. 5 is quite stable, so that the phase boundary does not move as long as the temperature is kept constant. When
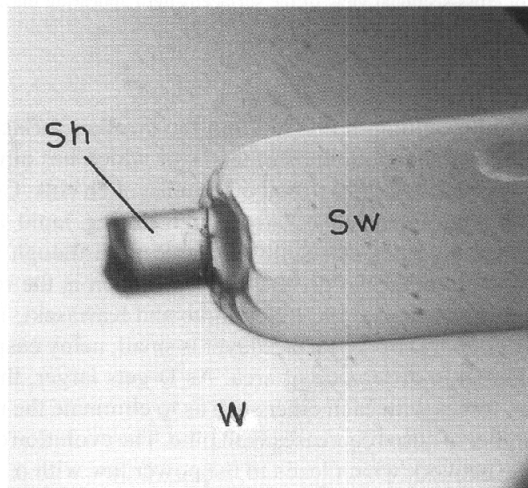

Fig. 5. Coexistence of the swollen (Sw) and shrunken (Sh) phases observed on a rod-shaped ionized NIPA gel in pure water (W).

the temperature is changed slightly, the boundary shifts along the rod axis and stops at the new position. Thus, the volume ratio between the swollen and shrunken phases in the sample is a function of temperature. This results in a peculiar situation that the total volume of sample changes continuously through the transition, whereas the discontinuity of volume is obvious on a local scale.

Moreover, the formation of macroscopic phase boundary such as shown in Fig. 5 depends on the shape of sample. In samples other than rod-shaped one, no clear phase boundary is formed. If we bring plate or cube gel into the transition region, the whole sample distorts irregularly, indicating that nuclei of the new phase are formed randomly so that the phase coexistence takes place locally over the whole sample. In this case, the total volume of the sample does not show any discontinuity throughout the transition in spite of the fact that the transition occurs discontinuously on a local scale. This is consistent with the observation on a rod sample.

The nature of the macroscopic phase boundary, as well as the condition of its formation have not yet been investigated in detail. It should be mentioned, however, that the uniaxial elastic anisotropy seems to be inevitable for the stabilization of the macroscopic phase boundary. In fact, if we apply a uniaxial tension to a gel plate in the transition region, an irregular deformation of the whole sample disappears and instead a clear phase boundary perpendicular to the tension appears. In this connection, it is inferred that a rod-shaped ionized gel has automatically a uniaxial elastic anisotropy because of a large surface tension, which will be discussed in Section 5.

4. Spinodal Decomposition Observed Near the Weakly First-Order Transition

The unstable regions shown in Fig. 2 are divided into three parts designated as A, B, and C. If a gel is put into region A, it decomposes into swollen and shrunken phases. Similarly, a gel brought into region B decomposes into shrunken gel and pure water, and a gel brought into region C decomposes into swollen gel and pure water. Practically, however, the distinction between regions A and B may not be important because a pure water phase cannot exist in bulk gel. Thus a gel put into region B will, as in region A, decomposes into highly swollen and shrunken gels.

If the bulk spinodal decomposition actually occurs, gel turns strongly opaque almost instantly while keeping its volume unchanged. Although the microscopic structure of this heterogeneous gel is interesting, we will not be concerned with this problem here because no macroscopic pattern was observed during this state change.

To study the initial stage of spinodal decomposition, we put a neutral NIPA gel into a metastable region slightly beyond the transition temperature and allows it to undergo a weakly first-order transition. The change of state induced by this procedure is indicated in Fig. 2, i.e. from the equilibrium state P_1 to the metastable state P_2 and then slowly to the new equilibrium P_3. Gel crosses the unstable region during $P_2 \rightarrow P_3$.

By means of light scattering measurement and microscopic observation, we investigated the evolution of inhomogeneity induced during the state change $P_1 \rightarrow P_2 \rightarrow P_3$. Samples were thin discs of neutral NIPA gel with 0.2 mm in thickness and 10 mm in diameter. The samples was first in equilibrium at 31.5°C (P_1 in Fig. 2) and then its temperature was jumped to 33.8 ~ 34.8°C (P_2).
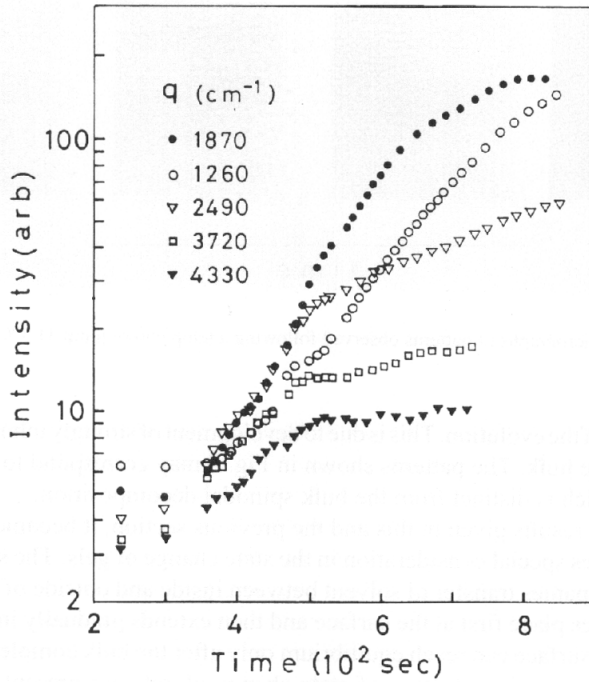
The evolution of light-scattering intensity observed for $T(P_2)$ = 33.8°C are shown in Fig. 6. As is seen in Fig. 6(b), the initial rise of the scattered intensity can well be represented by an exponential function of time. Patterns observed during this state change are shown in Fig. 7. The slow decomposition process revealed by these results may plausibly be associated with a surface instability induced by rapid shrinking of surface layer. In the course of this evolution, gel becomes only slightly opaque so that the experiments were possible throughout the process.

The process becomes faster as $T(P_2)$ increases, and at the same time, a qualitatively different patterns appears when $T(P_2)$ exceeds 34.0°C. The patterns observed for $T(P_2)$ = 34.8°C are shown in Fig. 8. In the course of development of these patterns, gel became strongly opaque so that the measurements became impossible
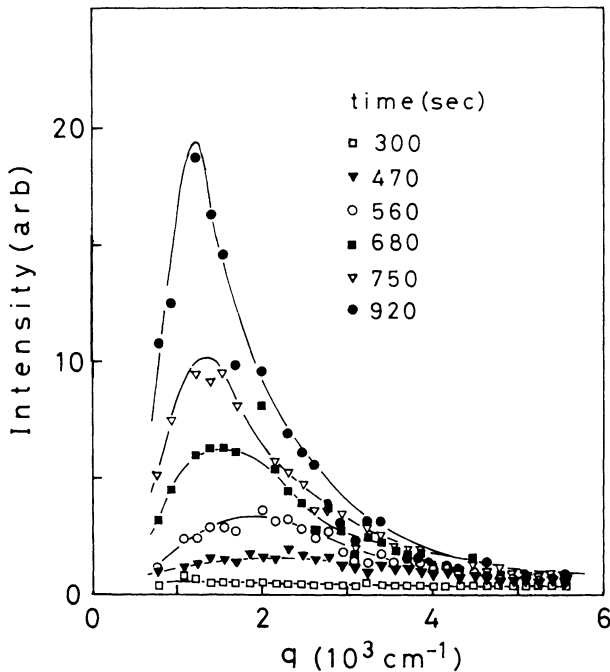
(a)

Fig. 6

(b)

Fig. 6. Evolution of intensity of light scattered from neutral NIPA gels following a temperature jump 31.5 → 33.8°C. (a) The intensity at various times as a function of wave number. (b) The logarithm of intensity at various wave numbers as a function of time.
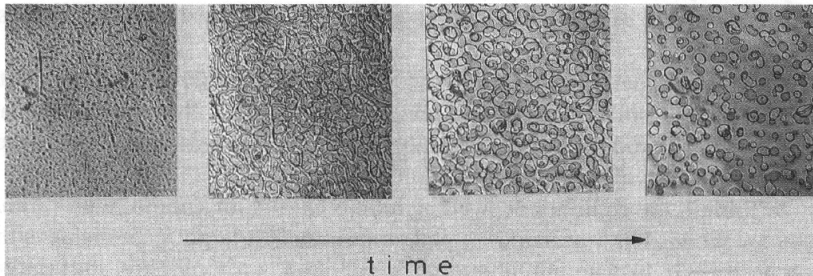

Fig. 7. Photomicrographs of patterns observed during the same experiment as in Fig. 6.
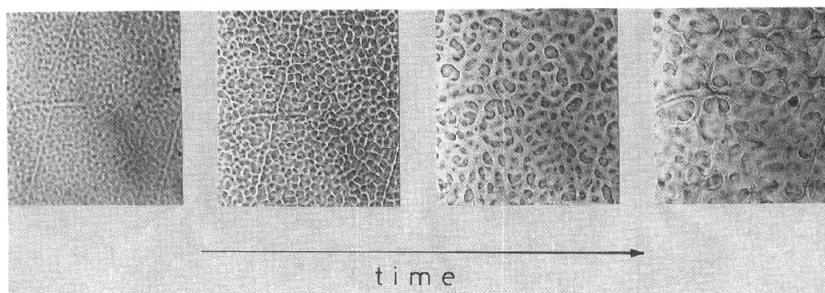
Fig. 8. Photomicrographs of patterns observed following a temperature jump 31.5°C → 34.8°C.

in the middle of the evolution. This is due to development of strongly inhomogeneous structure in the bulk. The patterns shown in Fig. 8 may correspond to the surface instability which is distinct from the bulk spinodal decomposition.

From the results given in this and the previous section, it becomes clear that surface requires special consideration in the state change of gels. The state change always accompanies transfer of solvent between inside and outside of gels, which inevitably takes place first at the surface and then extends gradually into the bulk. However, the surface can reach equilibrium only after the bulk completes the state change. This is a unique feature of state change of gels not present in polymer solution.

5. Shape Dependent Swelling and Phase Transition in Ionized Gels

Recently it has been found (Hirotsu, 1992) that the swelling and phase transition properties of ionized gels depend strongly on the shape of a macroscopic sample. To the author's knowledge, such a peculiar behavior has not been reported in any other systems so far. Here, I will mention briefly the experimental result demonstrating this behavior and outline a possible mechanism leading to these phenomena.

We prepared ionized NIPA (680 mM NIPA-20 mM acrylic acid) gel rods with various thickness, and also plates and cubes of various sizes. It is essential that all of them were prepared from the same pre-gel solution at the same time. This ensures that all samples have the identical bulk properties.

In Table 1, the equilibrium swelling ratio α at 20°C of samples with various shapes are shown. It is seen in rod-shaped samples that the larger is the diameter the larger becomes α. In plate and cube gels α is independent of their sizes, and is larger than that of any rod. This result shows that α depends strongly on the curvature of the surface, i.e. it is an increasing function of the radius of curvature of the surface.

In Fig. 9, α of ionized NIPA gel rods with various thickness are plotted as a function of temperature. It is seen that the thicker is the rod the higher becomes the

Table 1.   Equilibrium swelling ratio α measured at 20°C on 680 mM NIPA-20 mM acrylic acid copolymer gels of various shapes. D_0 is the diameter of rod and L_0 is the edge length of plate, both at the time of gelation.

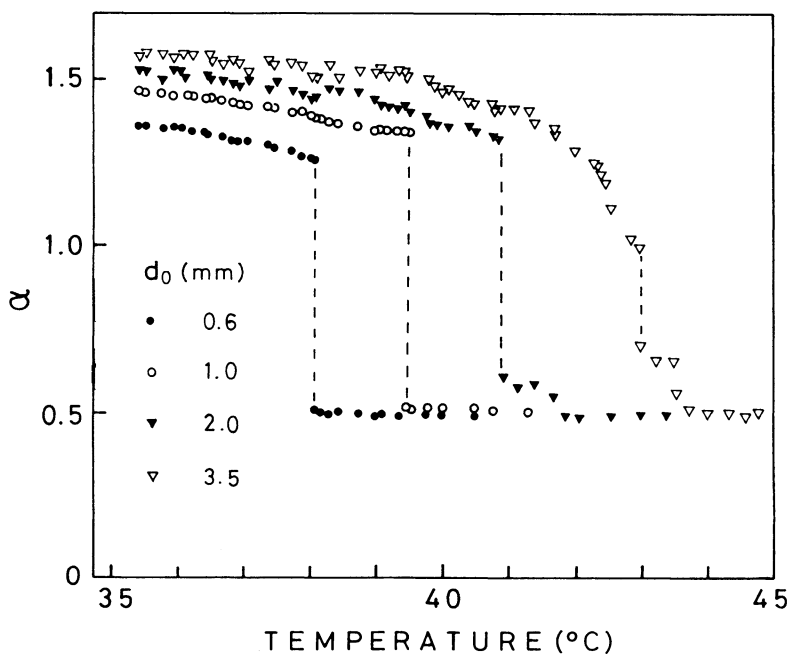| Rods	
D_0 (mm)	α
0.2	1.43 ± 0.02
0.6	1.43 ± 0.02
1.0	1.46 ± 0.02
2.0	1.58 ± 0.01
3.5	1.67 ± 0.03
6.5	1.69 ± 0.03
Plate	
L_0 (mm)	α
26.45	1.76 ± 0.03
30.70	1.76 ± 0.03

Fig. 9. Swelling ratio of NIPA (680 mM)-acrylic acid (20 mM) copolymer gel rods with various thickness as a function of temperature.

transition temperature T_0. Plate and cube gels have T_0 higher than any rod.

For comparison, I made the same measurements as above on neutral NIPA gels. The result was in sharp contrast with that of ionic gels, i.e. both α and T_0 are independent of the size and shape of the sample within an experimental error.

To understand the mechanism underlying the above phenomena, it is necessary to check the equilibrium condition of gels given in Section 1 carefully. The expression for π given in Section 1 is valid only when the surface of gel is flat. If it is curved, the surface tension should make an additional contribution to π which can be written as $\pi = \gamma/\rho$, where γ is the surface tension and ρ is the radius of curvature of the surface. As long as γ is small, this effect is negligible. However, if γ is unusually large, the dependence of the bulk properties on the surface curvature will become detectable.

It has been argued previously (Flory, 1966) that in ionized gels, a surface layer should be present where counter ion density is smaller than that of the bulk. The depletion of counter ion will result in large surface tension. At least two such mechanisms are conceivable. One is of elastic origin. Because of the smaller density of counter ions, the surface layer should have smaller swelling ratio and a lower transition temperature as compared with the bulk. Thus the surface layer will exert a surface force on the bulk to squeeze the latter. This force is equivalent to the surface tension. However, rough numerical estimate of this force using the known elastic moduli (Hirotsu, 1990) and the stress dependence of the transition temperature (Hirotsu and Onuki, 1989) indicates that the effect will be too small to explain the observed shape-dependent properties.

An alternative mechanism is of electrostatic origin. At the gel-solvent interface, a discontinuity of the electrostatic potential due to charge separation (formation of an electrical double layer) will be induced. It is well known in electrochemistry that an electrostatic interaciton at such an interface yields large surface tension. Details will be published elsewhere.

6. Concluding Remarks

There are many unsolved problems in the physics of gels. This is because physicists have turned their attention to gels only relatively recently. The importance to obtain physical understanding of gels will be obvious if we note the existence of a variety of gel or gel-like states in nature, especially in biological bodies.

Almost all biogels are ionized hydrogels. Unfortunately, though, theoretical understanding of ionized gels remains at a primitive stage. As has been stressed in this article, surface will play an especially important role in ionized gels.

REFERENCES

Erman, B. and Flory, P. J. (1986), Critical phenomena and transition in swollen polymer networks and

in linear macromolecules, Macromolecules, **19**, 2342–2353.

Flory, P. J. (1966), Principles of polymer chemistry, Cornell Univ. press, chaps., 12–14.

Hirotsu, S. and Kaneki, A. (1988), Dynamics of phase transition in polymer gels, Dynamics of ordering processes in condensed matter, edited by Komura, S. and Furukawa, H., p. 481–486, Plenum Pub. Co.

Hirotsu, S. (1991), Softening of bulk modulus and negative poisson's ratio near the volume phase transition of polymer gels, J. Chem. Phys., **94**, 3949–3957.

Hirotsu, S., Kaneki, A., Iwasaki, K., and Yamamoto, I. (1989), Dynamical aspects of volume phase transition and pattern formation in polymer gels, Cooperative dynamics in complex physical systems, edited by Takayama, H., p. 68–69, Springer-Verlag.

Hirotsu, S. and Onuki, A. (1989), Volume phase transition of gels under uniaxial tension, J. Phys. Soc. Jpn., **58**, 1508–1511.

Hirotsu, S. (1990), Elastic anomaly near the critical point of volume phase transition in polymer gels, Macromolecules, **23**, 903–905.

Hirotsu, S. (1992), Shape-dependent swelling and first-order phase transition in polymer gels with an ionized network, Macro-molecules, **25**, 4445–4447.

Onuki, A. (1989), Theory of pattern formation in gels, Phys. Rev., **A39**, 5932–5948.

Sekimoto, K. and Kawasaki, K. (1989), Elastic instability and phase coexistence of gels, Physica, **A154**, 384–420.

Tanaka, T., Sun, S. T., Hirokawa, Y., Katayama, S., Kucera, J., and Hirose, Y. (1987), Mechanical instability of gels at the phase transition, Nature, **325**, 796–798.