Structure of the network and the mechanism of phase transition in gels

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Present status of research on the volume phase transition in gels is reviewed briefly in relation to their network structure. It is pointed out that experimental studies on the shrunken phase have been scarce in contrast to those in the swollen phase. This unbalanced situation preclude us from proper understanding of the mechanism of the transition. Here, some new experimental results on the shrunken phase and on the spinodal decomposition are given.

1. INTRODUCTION

Gels can be classified in several ways. We can divide them into chemical and physical gels. Alternatively, they are classified into neutral and ionic (polyelectrolyte), or into synthetic and biological gels.

Among various types of gels, the one made of neutral homopolymer chains crosslinked by covalent bonds constitutes the simplest gel system. Thus, the basic understanding of gel properties have mostly been obtained on these neutral, homopolymer, chemical gels. Our present knowledge on volume phase transitions and structural inhomogeneities have been obtained from extensive studies on these gels.

As far as the phase transition is concerned, poly-N-isopropylacrylamide (NIPA) gels cross-linked by N,N'-methylenebisacrilamide(BIS) is the most extensively studied. Also, the structural inhomogeneity inherent to polymer network has been studied in poly-acrylic acid and NIPA-based gels.

In this article, we will be concerned with these topics by reviewing some recent progress and by pointing out unsolved issues.

2. PHASE TRANSITION

Polymer chains swell in a good solvent and shrink in a poor solvent. This is the basis of all the "phase-transition-like" behavior taking place in polymer-solvent systems. These include coil-globule transition in a single chain, macroscopic phase separation of polymer solutions, network collapse or volume phase transition of gels, and other related phenomena. I used above the term "phase-transition-like" because many of these changes are not phase transitions in a strict

sense. In this article, however, I will follow the common usage of this term in polymer science by regarding steep, but not discontinuous change of polymer size as a function of some external parameter as phase transitions.

As stated in Introduction, volume phase transition has mostly been studied on NIPA-based gels.[1,2] The transition can be observed on crossing the coexistence curve along the equilibrium swelling curve as shown in Fig.1. This is a very slow process because it takes a long time to attain equilibrium. If, on the other hand, the temperature increases fast enough to jump over the two phase region, the gel enters the unstable region. In such a case, phase change proceeds via spinodal decomposition in which the new phase appears everywhere throughout the gel. This is manifested by the instantaneous development of granular structure all through the
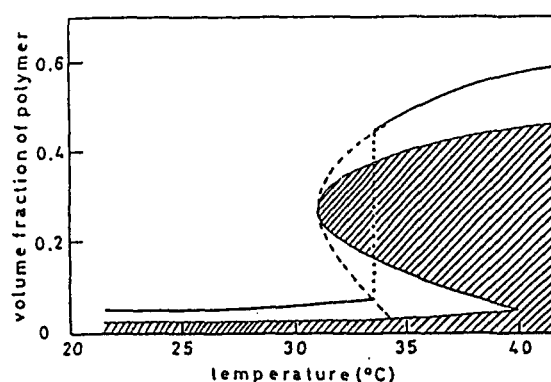
Fig.1 Phase diagram of neutral NIPA gel calculated from the Flory-type free energy. Hatched region is unstable. Bold and dashed lines represent equilibrium and coexistence curves, respectively.

gel. We will discuss below the equilibrium phase transition first, and next the spinodal decomposition.

Historically, the possibility of discontinuous gel-gel transitions was first investigated theoretically,[3] but the conclusion was negative for freely swollen gels. Later, however, the discontinuous transitions were found on freely swollen acrylamide-family gels,[4] and these transitions have been interpreted as the realization of gel-gel transitions. Here, gel is meant by a network containing free water. Experimentally, however, there seems to be no evidence indicating the presence of free water in the shrunken phase of NIPA gel. On the contrary, evidences obtained so far indicate that there is no free water in the shrunken phase.

Figure 2 shows the equilibrium swelling curves of NIPA-acrylic acid (AAC) gels, according to which the volume of gel in the shurunken phase is independent of the amount of acrylic acid. This shows that the carboxyl groups do not dissociate in this phase, which may be inconsistent with the presence of free water.

From the curves of Fig.2, we can calculate the number of water molecules per NIPA monomer as a function of temperature. This is shown in Fig.3. Around 20°C,there are nearly 150 water molecules per monomer, whereas only about 4.0 of which remain at 35°C. This small number of walter molecules may not constitute bulk water but may be hydrogen-bonded to hydrophilic groups of the network.
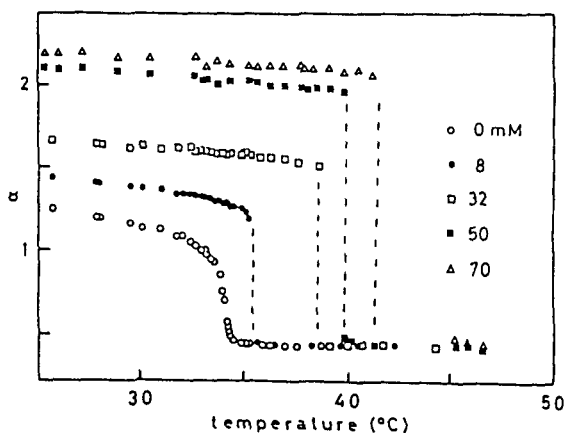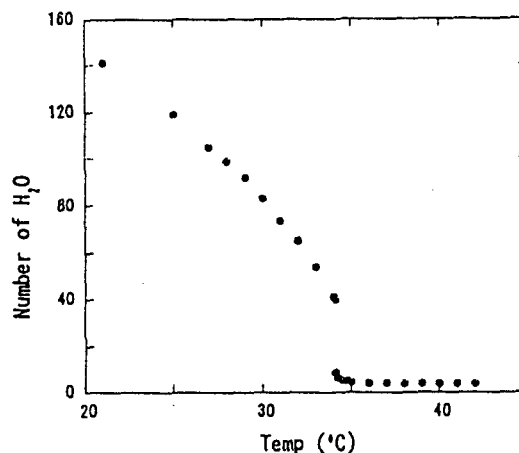

Fig. 3 Number of water molecules per monomer in neutral NIPA gels as a function of temperature.

Thus, it seems to be more appropriate to regard the shrunken phase as containing only bound water. In other words, the volume phase transition, at least that in NIPA gels, is not a gel-gel transition but a precipitation of the solid network from saturated swollen gel. The term "solid" does not exclude the presence of bound water molecules. Remember that protein crystals need bound water molecules for their stability, but swelling equilibrium is irrelevant for them.

The "network-precipitation model" for the volume phase transition proposed above has not been argued before. Unfortunately, experimental studies on the shrunken phase are extremely scarce, and thus, our knolwedge about the structure of this phase is quite limited. It is true that experiments on the shrunken phase are much more difficult than those on the swollen phase, but they are inevitable to understand the mechanism of the volume phase transition.

The spinodal decomposition is quite distinct from the equilibrium phase transition because in the initial stage of the decomposition, the volume hardly changes. In fact, the gel shrinks extremely slowly and it takes weeks to months to complete the transition process even for gels as small as a few mm in size. Thus, we can say that the decomposition is pinned in a very early stage, resulting in the development of mesoscipically phase-separated structure. This transient state, sometimes called"milky gel phase" from its appearence, has scarecely been investigated besides some small-angle light scattering studies.[5,6]

Recently, we have observed[7] an interesting

Fig. 2 Linear swelling ratio α of NIPA-AAC gels as a function of temperature. Numerals denote the initial concentration of AAC.

elastic response associated with the spinodal de-composition. A thin rod of NIPA gel was stretched in the swollen phase, and its length was fixed. Then the restoring force of the gel was monitored with an electronic balance as the temperature of the gel was increased steadily at a rate of 1 - 3°C/min. The result is shown in Fig. 4. As soon as the gel becomes opaque, a clear peak appears in the tension vs. time curve. Inversely, cooling the gel from the milky phase, the peak reappears as soon as the gel regains transparency.

Although detailed analysis of this result has not been completed yet, these peaks may reflect discontinuous change of the entropy of the network associated with freezing and melting of chain degrees of freedom. We expect this result, together with other eleastic properties which is now under study, will be of help to disclose the structure and properties of the milky gel phase.
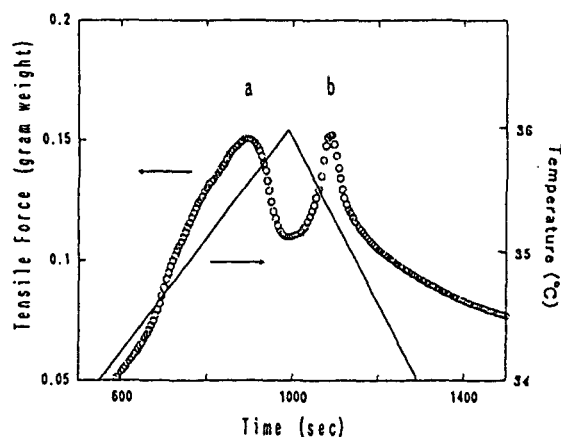

Fig.4 Tensile stress developed in a neutral NIPA gel rod kept at constant length under a constant rate of heating and cooling as a function of time. Straight lines depict temperature of the sample. The peaks a and b occurred when the sample becomes milky and regains transparency, respectively.

3. Structure and Dynamics

Structure and dynamics of gel networks has been studied actively by small-angle neutron scattering as well as by dynmic light scattering. Owing to these studies, details of large-scale inhomogenuities and mesoscopic structures inhrent to gel neworks have been clarified. Here, the term "inhomogenuity " refers to random, static fluctuation of the network density, while "mesoscopic structure" to more or less periodic density distribution.

Connection between inhomogeneity and the

density of cross-links has been noted[8] for a long time. It has been known that inhomogeneity is large both in high- and low-cross-link-density regions. In other words, there is an optimum value of the ratio between the number of cross-linker and monomer for the gel network to attain the most homogeneous structure. In NIPA and acrylamide, the so-called standard composition nearly satisfies the optimum condition.

Even gels with the "standard composition", however, inhomogeneity is serious which results mainly from non-uniform distribution of cross-links. This is termed a large-scale inhomogeneity because the characteristic length of the non-uniformity is on the scale of the wavelength of visible light. Thus light scattering is best suited for studying this structural characteristics.

Inhomogeneity manifests itself in the extremely large fluctuation of the scattered intensity with respect to position.[9] This leads to non-ergodic behavior of the scattering intensity. A sophisticated technique has been developed[10] to extract the ensemble-averaged quantity from light scattering experiments on non-ergodic media.

Formation of mesoscopic structure in ionic gels is distinct from the inhomogeneity discussed above. Originally, structure formation has been known for semidilute solution of polyelectrolytes, which has been ascribed to interplay between long-range Coulomb force and van der Waals interaction. Later, Schosseler et al,[11] and Shibayama et al[12] found a similar phenomenon in swollen gels by small-angle neutron scattering. The structure has been interpreted as induced by a charge separation between fixed and counter ions.

In spite of the mesoscopic structure, ionic gels seem to be homogeneous on the scale of the wavelength of light, as found by Mossaid et al[13] on AAC gels. It is considered that long-range Coulomb interaction masks the inhomogeneity inherent to neutral gels. Thus, it should be noted that the inhomogeneity is a relative concept which depends on the length scale characteristic to the experimental technique employed.

4. PHENOMENA CHARACTERISTIC   TO IONIC GELS

It is known that polyelectrolyte solution is one of the most formidable systems in material science. Thus, it is not unreasonable to find that structure and properties of polyelectrolyte gels are more difficult to understand than those of neutral gels. Among the characteristics of ionic

gels, two curious phenomena which have attracted present author's interest will be mentioned below.

1) Stable coexistence of swollen and shrunken phases at the volume phase transition:[2,14]

The volume phase transition is a discontinuous change of the network volume. It is not always easy, however, to discriminate between a truly discontinuous change from a very steep continuous one. The most reliable way to confirm the discontinuity will be to observe coexistence of the two phases at the transition.

Coexistence of the swollen and shrunken phases around the transition temperature is observed easily on NIPA-AAC copolymer gels. The process of the volume phase transition in NIPA-AAC gel rod on heating is shown schematically in Fig.5. A peculiar point of this result is that the coexistence of the two phases is very stable as long as the temperature is kept constant within the two-phase region. Furthermore, the rate of the shrunken to the swollen portion depends on temperature. Thus, the transition of the whole gel stops at an intermediate stage keeping the two-phase (or three-phase including pure water) structure as it stands. Increasing the temperature a little, the shrunken portion increases in proportion to the magnitude of the temperature change and the transition stops again. The transition proceeds step by step until the whole gel transforms to the shrunken phase. Such a behavior is not at all in accord with the van-der Waals-tyle theory of first-order transition, in which the coexistence can occur at a single temperature only.

Although the two-phase coexistence around the transition temperature is usually observed in NIPA-AAC gels, and rarely in neutral NIPA gels,
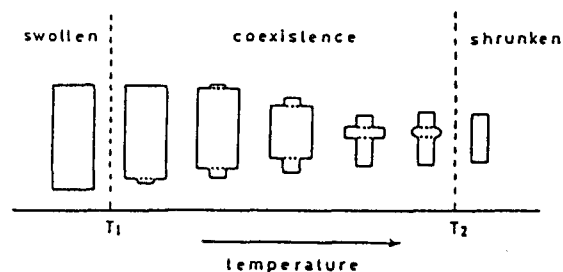
it is not yet clear whether ions play essential roles in stabilizing the coexistence. Rather, difference in the temperature width of the two-phase region may interpret the above fact. Actually, the width is less than 0.1°C in neutral NIPA gels, while it amounts to several degrees in high-ionic content gels.

The behavior depicted in Fig.5 is reminiscent of a phase separation in binary liquids at least in the two-phase region. The important point is that the phase separation occurs within a gel, between concentrated and dilute portions of a single network, and not between a swollen gel and outer solvent. This viewpoint of the volume phase transition may be in accord with the network-precipitation model discussed in the second chapter. It is expected that a new formulation of the volume phase transition in terms of the precipitation model will solve some peculiar features of the volume phase transition.

2) Shape-dependent properties:[14,15] Another puzzling feature of ionic gels is the shape-dependent swelling (and phase transition). This is quite simply observed as follows.

Suppose preparing gels by radical co-polymerization in aqueous solution of neutral monomer (e.g.,NIPA), ionizable monomer (e.g.,AAC) and crosslinker (BIS). Using glass capillaries of different sizes as molds, we can obtain gel rods with various diameters from the same pre-gel solution. Put them into a large amount of water and wait until the thermal equilibrium is reached. It can easily be confirmed that the degree of swelling depends significantly on the thickness of gels, i.e., the larger the diameter at preparation, so is the swelling degree. In NIPA-AAC copolymer gels, the transition temperature also increases as the diameter of the rod increases. Typical results are shown in Figs.5 (a) and (b).

It is natural to regard this property as arising from the surface of the ionized network i.e., the surface of these gels has different structure from the bulk. It has once been argued[16] that surface of ionized network has differnet swelling prpperty from the bulk because the density of counter ions should be much smaller near the surface than that of the bulk. Therefore, it is naturally supposed that a surface layer has smaller degrees of swelling and lower transition temperature. This situation is equivalent to having a surface with large surface tension. Inward pressure due to surface tension is inversely proportional to the diameter of the rod, which interprets qualitatively the observed thickness dependence of the swelling ratio and the transition
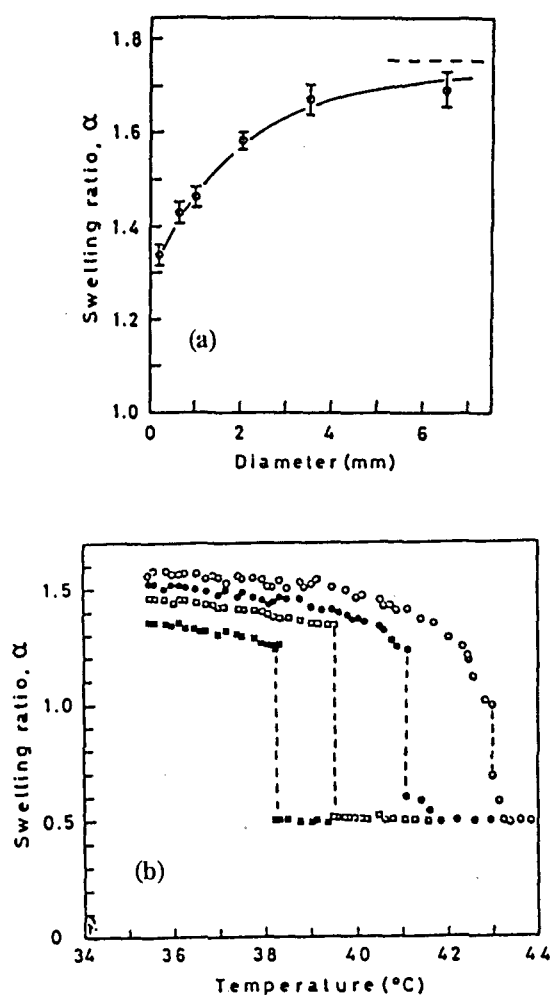

Fig.5 Process of the discontinuous transition observed on a NIPA-AAC gel rod (1.0 - 3.0 mmφ) immersed in water. Between T_1 and T_2, two phases coexist and the coexisence structure is stable as long as the temperature is kept constant.

Fig.6 (a) Linear swelling ratio of NIPA (680mM) - AAC (20mM) gels at 20°C as a function of diameter at preparation. A solid line is a guide for the eye. A dashed horizontal line denotes the value measured on cubes and plates, which is independent of the sample size. (b) The same quantity as in (a) as a function of temperature. Diameters are 0.6(■), 1.0(□), 2.0(●), and 3.5mm(○).

temperature.

5. Relaxation

Volume relaxation of gels has been studied both theoretically and experimentally.[17] The theory is based on the classical equation of motion of a solid network, and the resulting relaxation function is expressed as a series of exponential terms. Although it is a common practice to fit experimental volume relaxation data to a single exponential formula, it is only a crude approximation. A large deviation is always observed in a short-time region.

Recently we have measured stress relaxation on various NIPA based gels under various con-

ditions.[18] A sample gel is kept in a temperature-controlled water bath, and the stress generated in the sample is led to an electronic balance with a thin glass capillary. What is measured is a stress-relaxation curve at constant deformation. The results on the swollen and the shrunken phase of neutral NIPA gel is shown in Figs. 6(a) and (b).

As in volume relaxation, the stress relaxation in the swollen phase can be fitted fairly well with a single exponential function except for an initial stage. In the shrunken phase, however, the fit to a single exponential is definitely wrong
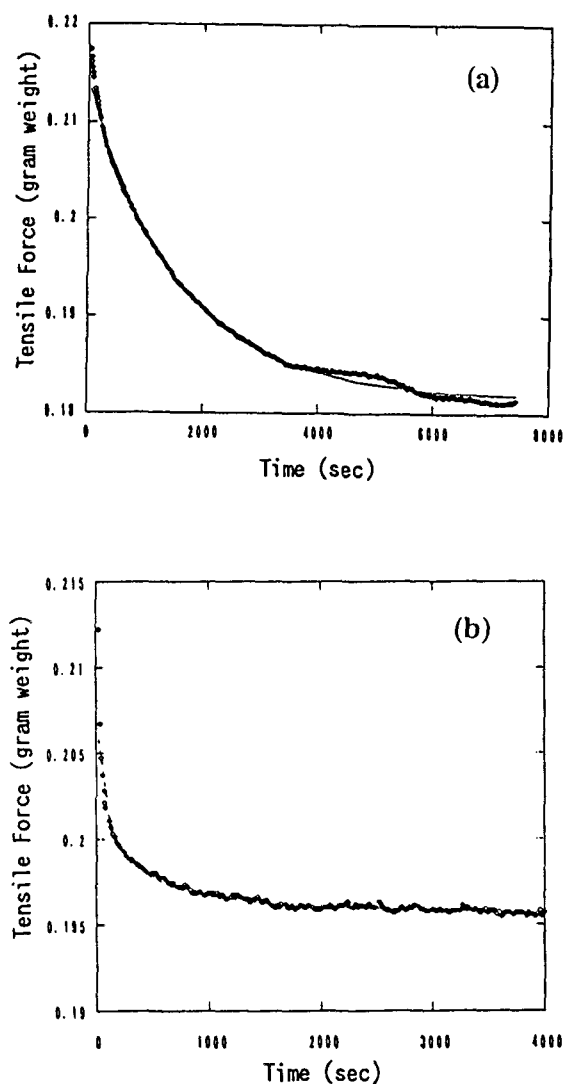

Fig.7 Relaxation of the tensile restoring force developei in a NIPA gel rod after elongated and kept at constna length. (a) In the swollen phase at 30.0°C. A solid lim is a fit to a single-exponential formula. (b) In the shrunke phase at 35.0°C. A dashed line is a fit to a stretched exponential formula.

and the use of the Kholraush-Williams-Watt (KWW) function is needed for a satisfactory fit.

It is known that the KWW (stretched exponential) function can be derived naturally on several models of amorphous materials.[19] The fact that the stress relaxation in the shrunken phase follows the KWW function is consistent with the view that the shrunken gel will better be described as a glassy solid than a gel, as was stated in Sec.2. The molecular process underlying this relaxation law is not clear at present.

6. SUMMARY

In view of the growing diversity of gel family, it becomes more and more difficult to grasp the whole image of gel studies. However, the hope of us gel researchers is to understand the structure and properties of these diverse family of gels from a unified viewpoint of a system composed of network and solvemt. Although we are far short of this ultimate goal, our understanding of gels is steadily advancing.

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