

Shrinking Behavior Induced by Temperature Jump of N-isopropylacrylamide Gels - Pattern Formation and Turbidity

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NIPAgels are well-known to make the volume phase transition independently of electric charge. There are a number of many reports concerning the volume change of the gels. In NIPAgel/water, by the temperature jump near the volume phase transition temperature, the turbidity and the surface pattern have been observed. The mechanisms of these phenomenons have been not entirely understood yet. The purpose of the present study is the illumination of these mechanisms. In both the discontinuous and continuous transition gels, the observation of the turbidity and the surface pattern induced by temperature jumps was performed. In result, it was found that the region where the turbidity occurs dose not coincide with the region where the surface pattern appears. The characteristic patterns were observed not only in the discontinuous transition gel but the continuous transition gel.

Key words: gels, shrinking, temperature jump, pattern formation, turbidity

1. INTRODUCTION

In NIPAgel/water, the turbidity and the surface pattern of the gel are observed by the temperature jump near the volume phase transition temperature T_v and many studies concerning these phenomena have been performed experimentally[1, 2, 3, 4] and theoretically[5, 6, 7]. The turbidity has been generally described due to the phase separation[8, 9]. By the quick heating, the gel becomes unstable and is separated into the collapse phase and the swollen phase. The surface pattern has been usually described as follows. Since the surface of the gel shrinks faster than the bulk, the osmotic pressure inside the gel is enhanced and then the shrunken surface re-swells heterogeneously[1]. Recently it is supposed that a so-called skin layer of dense, collapsed polymer network (the skin layer) is formed on the gel surface and causes the surface pattern[10]. The origin of the skin layer has been explained by the kinetic theory of the shrinking gel[10, 11], the thermodynamic instability of the volume phase transition[7, 12], and so on.

The studies of the turbidity and the surface pattern have been performed only in respect to the discontinuous transition gel. It seemed to be described that these are induced by the discontinuous volume change. On the approach to the turbidity, the experiments have been always performed in the spinodal region calculated on the basis of the classical Flory-Renher theory[13, 14, 15]. In order to understand the mechanisms of the turbidity and the surface pattern, at the first, the observation of these phenomena is performed in the present study. The continuous transition gel is considered as well as the discontinuous gel in the present study.

2. EXPERIMENTAL

2.1 Preparation of gels

Gels used in the present study were cylindrical and disklike NIPA gels prepared from N-isopropylacrylamide (NIPA) monomer and N,N'-methylenebisacrylamide (BIS) cross-linker by radical polymerization. Initiator and accelerator for polymerization reaction were N,N,N',N'-tetramethylethylenediamine (TEMED) and ammonium persulfate (AP).

The monomer and the cross-linker were dissolved in distilled water to final volume of 50ml. The monomer concentration was $C_{NIPA}=700\text{mM}$. The cross-linker concentrations were $C_{NIPA}=8.60\text{mM}$ and 25.8mM . The solution was bubbled with N_2 gas to get rid of oxygen and filtered to remove dust particles. To initiate the polymerization reaction, 80mg of AP and $480\mu\text{l}$ of TEMED were added to the solution. To make thin cylindrical and disklike gels, the solution was transferred into microcapillary tubes (inner diameter 0.85mm) and parallel glass plates (spacer thickness 0.2mm). Gelation reaction was completed in a few hours at 6°C . After about 24 hours gels were took out, and then the gels were immersed in a large amount of distilled water and kept in a week to wash out unreacted reagents.

2.2 Measurement of equilibrium swelling-ratio

The cylindrical gels were used in this measurement. The gels were entered in optical cells of rectangular shape (inner size $8\times 8\text{mm}^2$, length 20mm) which were filled with distilled water. The cells were then set in a temperature-controlled water-bath and the diameters of gels were measured with cathetometer (accuracy 0.01mm). In order to make the gels to be in equilibrium, after heating procedure the gels were kept in six fours and then the measurement was performed.

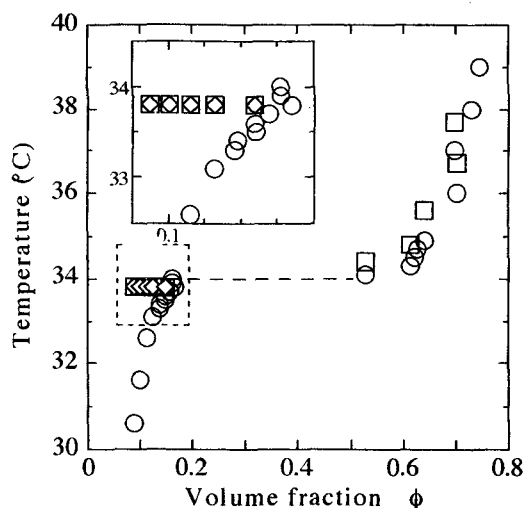


Fig.1: The results of temperature jump experiments of the discontinuous transition gel. \circ : The equilibrium swelling points, \square : the temperatures above which the gel becomes opaque, \diamond : the temperatures above which the surface pattern appears on the gel. The inset is the magnification of the region indicated by the square of dotted line.

2.3 Measurement of temperature jump

Observation of turbidity: The disklike gels (thickness 0.2mm, diameter 1mm) were used in this measurement. Each of the gels was entered in the shallow hole (diameter 18mm) of glass slide which was filled with distilled water. The slide was covered with cover glass and set in a hot stage. It was kept in 30 minutes at the initial temperature T_i to allow the gels to come to be in equilibrium. The observation was started by temperature jump to the final temperature T_f , which was made by the quick heating from T_i to T_f with the heating ratio 3 °C/min. The turbidity of the gels was observed with the unaided eye. In this measurement both T_i and T_f were varied ($30.0\text{ }^\circ\text{C} \leq T_i, T_f \leq 40.0\text{ }^\circ\text{C}$). The lowest T_f that the appearance of the turbidity was observed was determined as the lowest turbidity-appearance temperature T_t .

Observation of surface patterns: The observation was carried out in the same way as the turbidity. The surface patterns of the gels were observed by an inverted microscope coupled with an CCD camera and recorded on videotapes. The lowest T_f that the appearance of the surface patterns was observed was determined as the lowest surface patterns-appearance temperature T_p .

3. RESULTS

3.1 Phase diagram

The discontinuous transition gel: The phase diagram of τ gel (C_{NIPAA}) is shown in Fig.1. As it is clear from Fig.1, this gel is a discontinuous transition gel. In the temperature jumps of $T_i \leq T_v$, both the turbidity and the surface pattern in the gel could be observed. Fur-

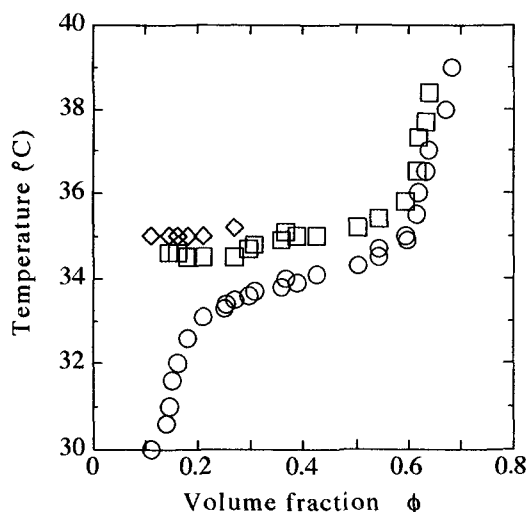


Fig.2: The results of temperature jump experiments of the continuous transition gel. The meaning of symbols is the same as Fig.1

thermore in these temperature jumps, both T_t and T_p were constants independently of the volume fraction ϕ and corresponded to T_v . On the other hand in the temperature jumps of $T_i \geq T_v$, the turbidity could be only observed, but the surface pattern could not. As T_i increased, T_t increased parallel to the equilibrium swelling curve. The phase diagram of the gel is distinctly divided with two regions. One of the regions where both the turbidity and the surface pattern could be observed and the other region where the turbidity could be only observed and the surface pattern could not.

The continuous transition gel: The phase diagram of a gel (C_{NIPAA}) is shown in Fig.2. As it is clear from Fig.2, this is a continuous transition gel. Under $\phi_x=0.28$, both the turbidity and the surface patterns could be observed. Furthermore in the region, both T_t and T_p were invariable independently of ϕ . The T_t was not corresponded to T_p . The T_t was about 34.5 °C and T_p was about 35.1 °C. Over $\phi_x=0.28$, the turbidity could be only observed and the surface pattern could not. As T_i increased, T_t increased parallel to the equilibrium swelling curve. The phase diagram of the gel distinctly divided with two regions as well as the discontinuous transition gel. One of the regions where both the turbidity and surface pattern could be observed and the other region where the turbidity could be only observed and the surface pattern could not. At $\phi_x=0.28$, several experiments were done. In some cases, the surface pattern could be observed, and in the other cases it could not. Hence on the consideration of the experimental accuracy in the present study, ϕ_x is fairly close to the discontinuous boundary between the two regions.

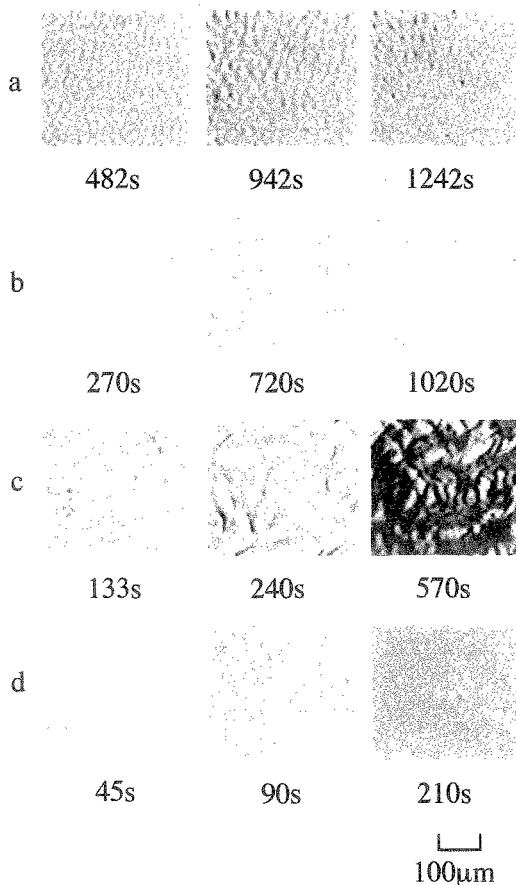


Fig.3: The photomicrographs of the surface patterns appeared in the discontinuous transition gel by the temperature jumps a: $30.6\text{ }^{\circ}\text{C} \rightarrow 33.8\text{ }^{\circ}\text{C}$, b: $33.6\text{ }^{\circ}\text{C} \rightarrow 33.8\text{ }^{\circ}\text{C}$, c: $30.6\text{ }^{\circ}\text{C} \rightarrow 34.5\text{ }^{\circ}\text{C}$, d: $33.6\text{ }^{\circ}\text{C} \rightarrow 34.5\text{ }^{\circ}\text{C}$.

3.2 Surface pattern formation

The discontinuous transition gel: The pattern observations of the discontinuous transition gel is shown in Fig.3. In the temperature jump of a ($30.6\text{ }^{\circ}\text{C} \rightarrow 33.8\text{ }^{\circ}\text{C}$), an ordered network-like pattern started to form at about 480sec. The pattern was transformed to an ordered droplet pattern at about 940sec. At about 1240sec, the drops became small and afterward the surface of the gel became flat. In the temperature jump of b ($33.6\text{ }^{\circ}\text{C} \rightarrow 33.8\text{ }^{\circ}\text{C}$), the behavior of the pattern formation corresponded to that in a, but the time-development of b was faster than that of a. In the temperature jump of c ($30.6\text{ }^{\circ}\text{C} \rightarrow 34.5\text{ }^{\circ}\text{C}$), although the observation was not well performed, an ordered pattern started to form at about 130sec. As time passed, the pattern distorted grew and the contrast became sharp. Afterward the observation could not be performed after about 570sec because of the strong scattering from the turbidity. In the temperature jump of d ($33.6\text{ }^{\circ}\text{C} \rightarrow 34.5\text{ }^{\circ}\text{C}$), an ordered network-like pattern started to form at about 45sec. As time passed, the pattern grew distorted. Afterward the observation could not be performed after about 210sec because of the strong scattering from the turbidity. All the patterns observed

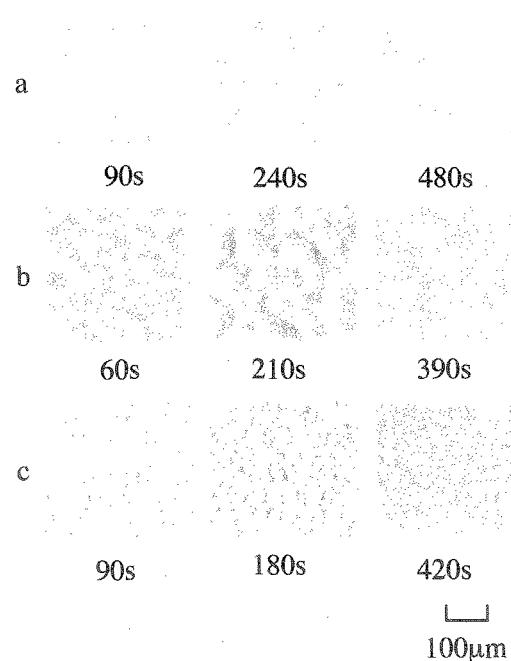


Fig.4: The photomicrographs of the surface patterns appeared in the continuous transition gel by the temperature jumps a: $32.0\text{ }^{\circ}\text{C} \rightarrow 35.5\text{ }^{\circ}\text{C}$, b: $33.0\text{ }^{\circ}\text{C} \rightarrow 35.5\text{ }^{\circ}\text{C}$, c: $32.0\text{ }^{\circ}\text{C} \rightarrow 38.0\text{ }^{\circ}\text{C}$.

in the initial stage were ordered. Furthermore the characteristic lengths of their patterns were seemed to be equal. All the patterns observed in the final stage, however, were strongly dependent on T_f . When $T_f \cong T_v$ (a and b), the pattern disappeared within the observation-time (1 hour). When $T_f \geq T_v$ (c and d), the patterns grew distorted and could not be observed because of the strong scattering from the turbidity.

The continuous transition gel: The pattern observations of the continuous transition gel is shown in Fig.4. In the temperature jump a ($32.0\text{ }^{\circ}\text{C} \rightarrow 35.5\text{ }^{\circ}\text{C}$), an ordered hexagonal pattern started to form at about 60sec. As time passed, the pattern grew rough. Afterward the surface of the gel became flat at about 480sec. In the temperature jump b ($33.0\text{ }^{\circ}\text{C} \rightarrow 35.5\text{ }^{\circ}\text{C}$), the behavior of the pattern formation corresponded to that in a, but the characteristic length of the pattern of b was shorter than that of a. In the temperature jump c ($32.0\text{ }^{\circ}\text{C} \rightarrow 38.0\text{ }^{\circ}\text{C}$), an ordered hexagonal pattern started to form at about 90sec. As time passed, the pattern grew rough. Afterward the observation could not be performed after about 420sec because of the strong scattering from the turbidity. All the patterns observed in any stage were ordered hexagonal patterns. When T_f was constant, the characteristic length of the surface pattern decreased as T_i increased. When T_i was constant, the characteristic length of the surface pattern decreased as T_f increased.

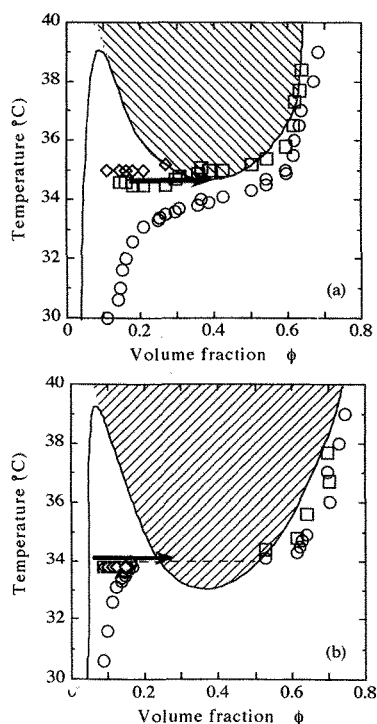


Fig.5: The phase diagram of (a): the continuous transition gel and (b): the discontinuous transition gel. The meaning of symbols is the same as Fig.1. The curves are the expected spinodal curves. The hatched areas indicate unstable regions.

4. DISCUSSION

In the present study, we determined the region where the turbidity was observed and the region where the surface pattern was observed. It was found that the turbidity and the surface pattern of the continuous transition gel are observed as well as the discontinuous transition gel. The discontinuous boundary (ϕ_x) exists in the phase diagram of the continuous transition gel. It became evident that these two regions are similar but are not same. The region of the turbidity did not agree with the spinodal region calculated on basis of the classical Flory-Rehner theory.

The region of the turbidity in the continuous transition gel may be explained by the spinodal region and the shrinking behavior of the gel (Fig.5(a)). The unstable region has lowest critical temperature T_c . Under $\phi_x=0.28$, if $T_f \geq T_c$, by temperature jumps the gel shrinks and goes into the unstable region and then the turbidity is observed. On the contrary if $T_f < T_c$, by temperature jumps the shrinking gel does not enter the unstable region and the turbidity is not observed. Thus it is clear that T_t is constant independently of ϕ . On the other hand, the region of the turbidity in the discontinuous transition gel was observed may be explained in the same way as the continuous transition gel (Fig.5(b)). Since T_c is lower than T_v , by the

temperature jump of $T_f \geq T_v$, the gel becomes unstable. Thus both T_t and T_p correspond to T_v .

In the present investigation, the characteristic patterns were observed not only in the discontinuous transition gel but the continuous transition gel. Some tendencies of these pattern formations were found. It is generally described that the surface pattern is caused by the difference of the excluding velocity of solvent between on the surface and in the bulk[1, 10, 11]. The kinetic effect on the surface pattern formation should be considered.

These studies are in progress and the detail report with quantitative discussion is to be published elsewhere.

5. CONCLUSION

It was found that there is difference between the region where the turbidity occurs and the region where the surface pattern appears in both the discontinuous and continuous transition gels. The characteristic patterns were observed not only in the discontinuous transition gel but the continuous transition gel. Some tendencies of these pattern formations were found. But the mechanism of these phenomenon have been not illuminated yet. More studies of the turbidity and the surface pattern of gels should be performed.

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