

# Shrinking pattern and phase transition velocity of poly(*N*-isopropylacrylamide) gel

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We have studied the shrinking phase transition of cylindrical poly(*N*-isopropylacrylamide) gels with submillimeter diameter. The macroscopic conformation change and the phase transition velocity were obtained during the heating process by two different methods. One is a continuous heating process with a constant temperature drift rate, and the other is an isothermal process after a steplike temperature increase beyond the transition point. In the former measurement, the phase transition can be controlled by the nucleation mechanism in the smaller temperature drift rates; at the transition point, after the fine pattern appears and disappears on the surface, for instance, the gel gradually and uniformly shrinks while keeping a smooth surface. On the other hand, at the larger temperature drift rates, the phase transition comes into the unstable region before being completed; after the fine pattern disappears, a coarse pattern appears on the surface, and the entire gel becomes opaque. The gel gradually becomes transparent with time from the surface layer to the core portion. These two processes, characterized by two types of surface pattern as well as the growth of a collapsed surface skin layer, can be clearly observed in the latter measurements, which depend on the degree of super-heating (how far the final temperature is from the transition point). The results are discussed qualitatively on the basis of the classical phase separation model of nucleation and spinodal decomposition, as well as the phase diagram of the present gel system. © 1999 American Institute of Physics. [S0021-9606(99)70125-X]

## I. INTRODUCTION

Polymer gel is a dilute solid with a complex network structure swollen in a liquid, and one can view it as a soft condensed material of a random two-phase system: polymer (solid) and solvent (liquid).<sup>1</sup> It is well known that a polymer gel, made of slightly cross-linked networks of homopolymers, displays both solidlike and liquidlike behavior due to its elastic and osmotic nature. Such a gel can exist in two distinct phases, swollen and collapsed, in a liquid. A number of studies on slightly cross-linked polymer gels have shown a very sharp volume change, which has been considered a discontinuous volume phase transition.<sup>2,3</sup> Hirokawa and Tanaka reported,<sup>4</sup> for the first time, that among the phase transition gels, neutral poly(*N*-isopropylacrylamide) (NIPA) gel, which is weakly cross-linked by *N,N'*-methylenebis(acrylamide) (BIS), can exhibit the volume phase transition in water only if the temperature is changed. The transition mechanism has been attributed to the change in the balance of hydrophilic and hydrophobic interactions. The swelling curve is easily reproduced. In the case of this neutral NIPA gel with submillimeter diameter,<sup>5,6</sup> for example, the phase transition can be induced at exact temperatures when the temperature is regulated at an accuracy of  $\pm 0.05$  °C (increased or decreased with a minimum temperature step of 0.1 °C) in the vicinity of the transition temperature. The effects of the composition of NIPA, BIS, and total monomer concentration on the transition behavior have been well investigated.<sup>7</sup> The static properties of mechanically con-

strained NIPA gels through the phase transition behavior<sup>8–10</sup> have also been experimentally established. In our reports,<sup>9,10</sup> the diameter and the force of cylindrical NIPA gels of submillimeter diameter have been measured with slight elongation in the uniaxial direction. The qualitative swelling behavior under mechanical constraint has been described by the equation of state on the basis of Flory-type free energy.<sup>8,11</sup> Almost all the swelling properties of this material<sup>4,6,12,13</sup> have been quite successfully described by the equation of states of gels. Although the static swelling behavior as well as the kinetic properties of NIPA gels have been extensively studied, the phase transition velocity and its fundamentals are not yet fully understood. As for the kinetic properties of polymer gels, most studies<sup>14–18</sup> have been based on the collective diffusion of polymer networks; the Tanaka-Fillmore model<sup>19</sup> has often been used to understand the time course of the volume change. In this model, the diameter change to approach an equilibrium state is expressed by a simple function of time after the change in the environment. For the general situations, such as bulk gels with all sorts of shapes, the basic kinetic mechanism is still not well understood, and no theory can explain completely the initial to final size change of the phase transition. We believe that the reason for the deficient model results from not taking into consideration the network imperfections and that this problem is also related to the network structures. The NIPA polymer has the lower critical solution temperature (LCST), and the cloud point is around 31 °C.<sup>20</sup> Therefore, one can expect the network inhomogeneity<sup>21–23</sup> to depend strongly on the gelation temperature below or above the cloud point. Recently, Hi-

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rokawa *et al.* studied the internal structure of NIPA gels by means of confocal microscopy, laser light scattering, and small angle neutron scattering.<sup>24</sup> They found that the mesoscopic level network structure could be constructed by highly cross-linked microgels connected by the loose network.

This paper focuses on the kinetic properties of the neutral NIPA gel and the velocity of the shrinking phase transition during the heating process. The purpose of the work is to establish an underlying foundation of the phase separation processes by the shrinking phase transition. We discuss the macroscopic conformation change during the phase transition in terms of the conventional nucleation model and spinodal decomposition, and we present the mechanism of the process of making up the collapsed network.

## II. EXPERIMENTAL METHOD

Gels were synthesized by a free radical polymerization reaction in glass microcapillary tubes with an inner diameter of 141.5  $\mu\text{m}$ . In this synthesis, the base solution was the standard mixture of NIPA gel;<sup>4,6</sup> 7.8 g of purified NIPA (main constituent, Kohjin), 133 mg of BIS (cross-linker, Wako), and 240  $\mu\text{l}$  of *N,N,N',N'*-tetramethylethylenediamine (TEMED, accelerator, Wako) were dissolved in 100 g water. The solution was stored at 0  $^{\circ}\text{C}$ . After the solution was fully saturated with nitrogen, 40 mg of ammonium persulfate (APS, initiator, Wako) was added to this mixture to initiate the reaction. The microcapillaries were then inserted into the pregel solution. Gelation was carried out overnight at 0  $^{\circ}\text{C}$ . After gelation was completed, cylindrical gels were removed from microcapillaries and washed in distilled deionized water to remove residual chemicals and unreacted monomers from the polymer networks.

The experimental setup was similar to that used in Ref. 6. Water that was temperature-controlled to an accuracy of  $\pm 0.05$   $^{\circ}\text{C}$  was circulated in the cell. After reaching equilibrium at each temperature, the gel was imaged by an optical microscope apparatus with a calibrated charge coupled device (CCD) camera and a video processor. For the measurement of phase transition velocity, the temperature was continuously increased with a constant heating rate using a computer controlled water-bath, and the circulating initial water temperature (33.6  $^{\circ}\text{C}$ ) was abruptly increased to the final temperatures by switching the water flow from one water-bath to another. Note that the same gel was used for all measurements. Nevertheless, one can believe that it did not disturb the general pictures since the gels synthesized from the same solution at the same time exhibit quantitatively the same shrinking behavior within the present macroscopic measurements, such as the absolute diameter and the transition temperature.

## III. RESULTS

### A. Swelling curve

We first measured the diameter change of the neutral NIPA gel as a function of temperature. Figure 1 shows the equilibrium diameter during the heating and cooling pro-

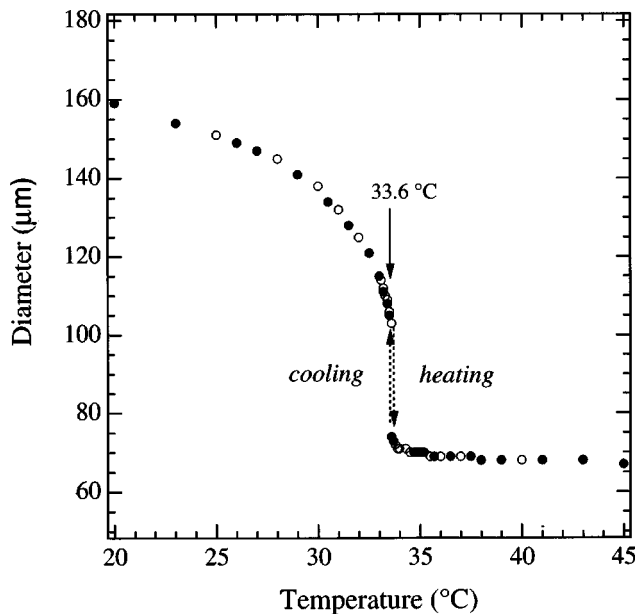


FIG. 1. Equilibrium diameter change of the neutral NIPA gel as a function of temperature during the heating process (open circles) and on the cooling process (closed circles). The hysteresis less than 0.2  $^{\circ}\text{C}$  is observed.

cesses. As is reported in the literature,<sup>4</sup> the gel exhibited a slight discontinuous phase change with a small hysteresis as a function of temperature. On the gradual heating process, the gel was transformed from the swollen to collapsed phase by raising the temperature only 0.1  $^{\circ}\text{C}$ ; the gel used in the present study started to shrink when the temperature was increased from 33.6 to 33.7  $^{\circ}\text{C}$  (minimum step, 0.1  $^{\circ}\text{C}$ ). With the temperature at a constant 33.7  $^{\circ}\text{C}$ , the gel finally reached its collapsed state after a long time (more than an hour). On the cooling process, the collapsed to swollen phase transition occurred when the temperature was decreased from 33.6 to 33.5  $^{\circ}\text{C}$ . It should be noted that the collapsed diameter just after the transition (about 73  $\mu\text{m}$ ) was larger than the completely collapsed diameter (about 68  $\mu\text{m}$ ); the gel gradually shrank with increasing temperature after the phase transition (higher than the transition point). Little attention has been paid to this fact until now, and it is related to the fact that the gel synthesized by the present recipe was near the critical point.<sup>4,7</sup>

### B. Shrinking pattern and conformation change

The conformation change and the phase transition velocity were studied in the vicinity of the volume phase transition temperature during the heating process by two different methods. The first was a continuous heating process with a constant temperature drift rate, and the other was an isothermal temperature process after a steplike temperature increase beyond the transition point. In a continuous heating process, when the temperature drift rate,  $v_T$ , is high enough, we obtained the characteristic pictures, shown in Fig. 2, with an optical microscope. We observed two types of surface patterns. At the transition point, a fine pattern appeared on the surface and then quickly disappeared. Later, the gel became opaque, with a larger, coarse surface pattern. After that, the gel again became transparent starting with the surface layer,

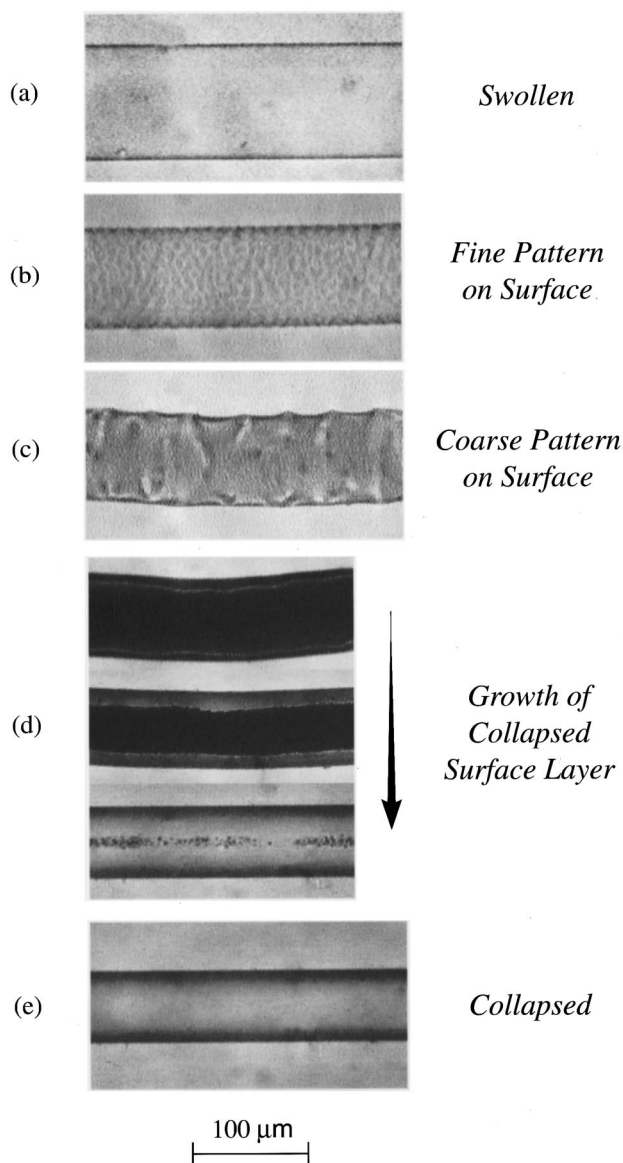


FIG. 2. Pictures of the neutral NIPA gel on a continuous heating process (during the swollen to collapsed phase transition). The temperature was increased with a temperature drift rate,  $v_T$ , higher than approximately  $0.05^\circ\text{C min}^{-1}$ . Shown are the (a) swollen state, (b) fine surface pattern, (c) coarse surface pattern, (d) growth of collapsed skin layer, and (e) completely collapsed state.

and the surface skin (collapsed phase) developed with time. The dark core portion became smaller and smaller, finally disappearing in a completely collapsed phase. When  $v_T$  was decreased (less than approximately  $0.05^\circ\text{C min}^{-1}$ ), the coarse pattern could not be observed, but the collapsed surface skin layer grew after the appearance of the fine pattern. When  $v_T$  was low enough, the coarse pattern as well as the collapsed skin growth could not be observed, but the gel, which had a smooth surface, continuously and uniformly shrank after the fine pattern disappeared. In this case the phase transition ended at a temperature lower than  $34.5^\circ\text{C}$ . These characteristic conformation changes can be clearly observed in the latter measurements, which depend on the degree of "super-heating,"  $\Delta T$  (the difference between the final temperature and  $33.6^\circ\text{C}$ ); the shrinking patterns in the

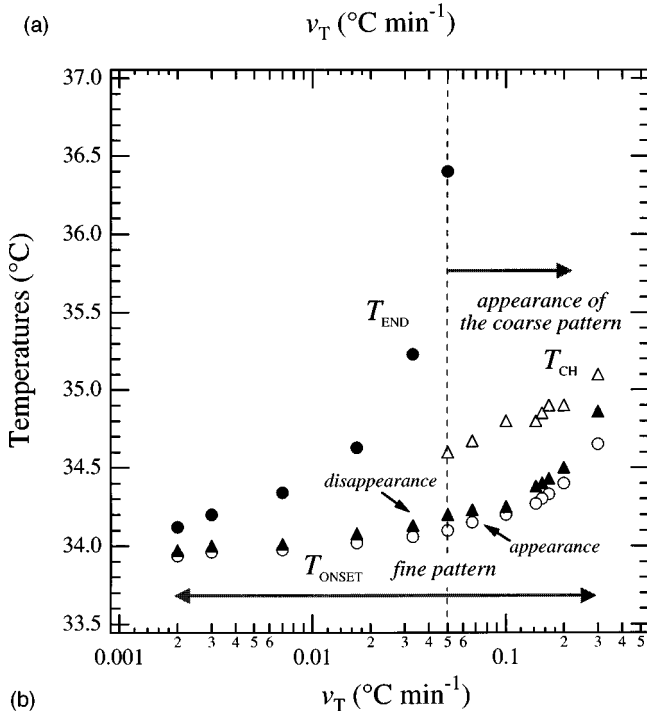
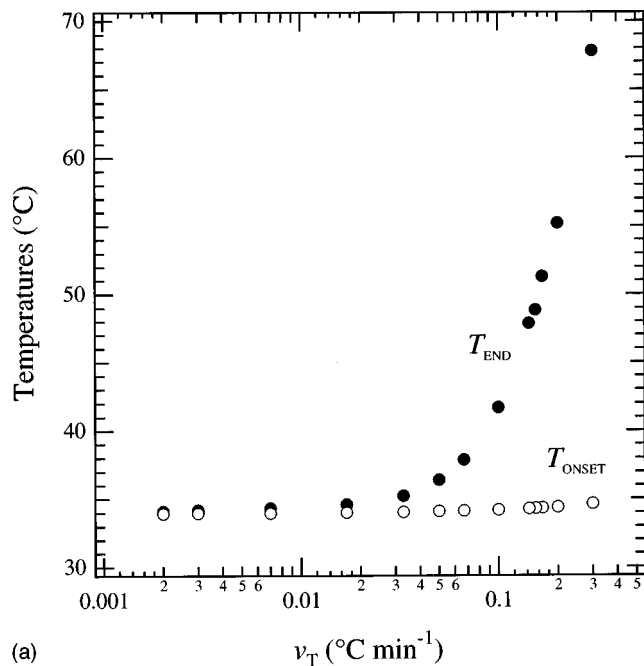


FIG. 3. Characteristic temperatures on continuous heating processes with constant temperature drift rates,  $v_T$ . (a)  $T_{\text{ONSET}}$  and  $T_{\text{END}}$  in the whole range of  $v_T$  between  $0.001$  and  $0.3^\circ\text{C min}^{-1}$ , and (b)  $T_{\text{ONSET}}$ ,  $T_{\text{END}}$ , and  $T_{\text{CH}}$ , together with the disappearance temperature of the fine pattern in the smaller temperature range.

cases of smaller and larger  $\Delta T$  correspond to those of smaller and larger  $v_T$ , respectively. The critical difference of macroscopic observations in low or high  $v_T$  or  $\Delta T$  could be related to different shrinking mechanisms. Note that the fine pattern can be observed on both processes under all conditions of  $v_T$  ( $0.002^\circ\text{C min}^{-1} < v_T < 0.3^\circ\text{C min}^{-1}$ ) or  $\Delta T$  at the first stage of phase transition, although it is too fast to identify when  $\Delta T$  exceeds  $5.0^\circ\text{C min}^{-1}$  on the isothermal process.

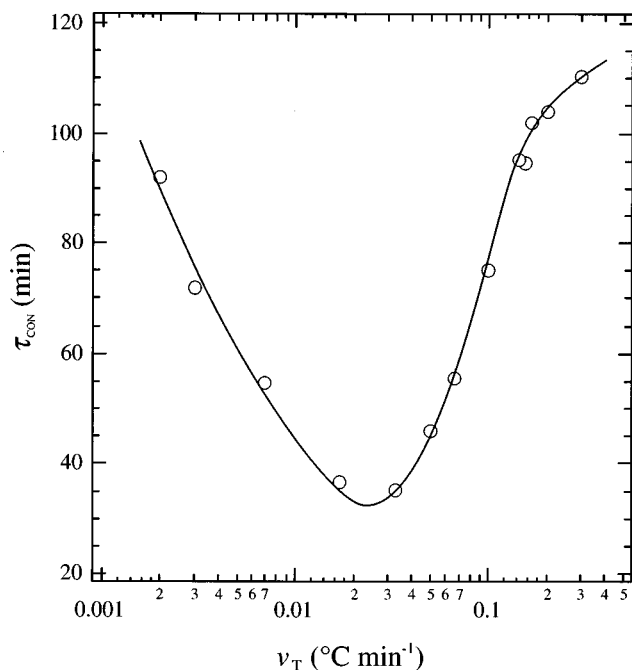


FIG. 4. Time,  $\tau_{\text{CON}}$ , from onset to end of the swollen to collapsed phase transition as a function of the temperature drift rate,  $v_T$ , on continuous heating process. Lines added are to guide the eye.

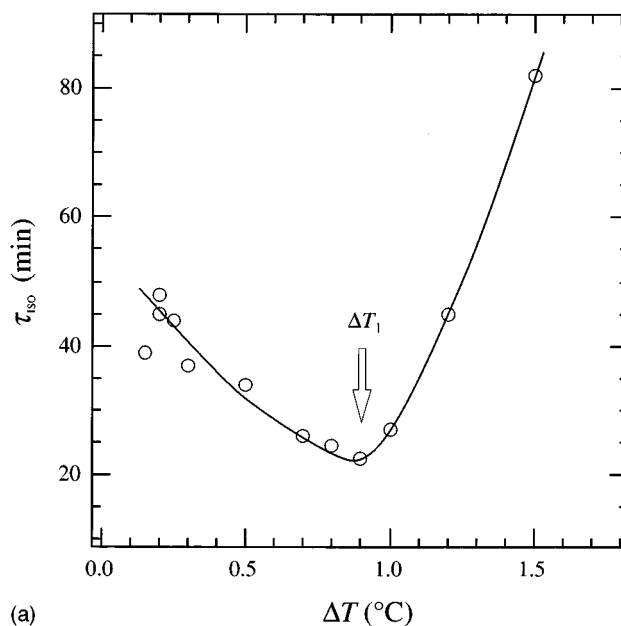
### C. Transition temperature during the heating process with constant drift rates

Figure 3(a) shows the onset and end temperature of the phase transition on the continuous heating processes. The onset temperature,  $T_{\text{ONSET}}$ , is defined as the temperature of the appearance of the fine surface pattern. The end temperature,  $T_{\text{END}}$ , is defined as the temperature where the length change stops. One can see that  $T_{\text{ONSET}}$  is almost constant with increasing  $v_T$  (or shows a slight increase), while  $T_{\text{END}}$  greatly increases. When  $v_T$  decreases,  $T_{\text{END}}$  approaches  $T_{\text{ONSET}}$ , and  $T_{\text{END}}=T_{\text{ONSET}}$  at the limit of  $v_T \rightarrow 0$ . In Fig. 3(b),  $T_{\text{ONSET}}$ ,  $T_{\text{END}}$ , and the characteristic temperature,  $T_{\text{CH}}$ , in the smaller region of  $v_T$  are plotted, together with the disappearance temperature of the fine pattern, where  $T_{\text{CH}}$  is defined as the temperature of the appearance of the coarse surface pattern. This kind of pattern does not appear when  $v_T$  is lower than  $0.05 \text{ }^\circ\text{C min}^{-1}$ . Note that  $T_{\text{CH}}$  is not lower than  $34.5 \text{ }^\circ\text{C}$ .

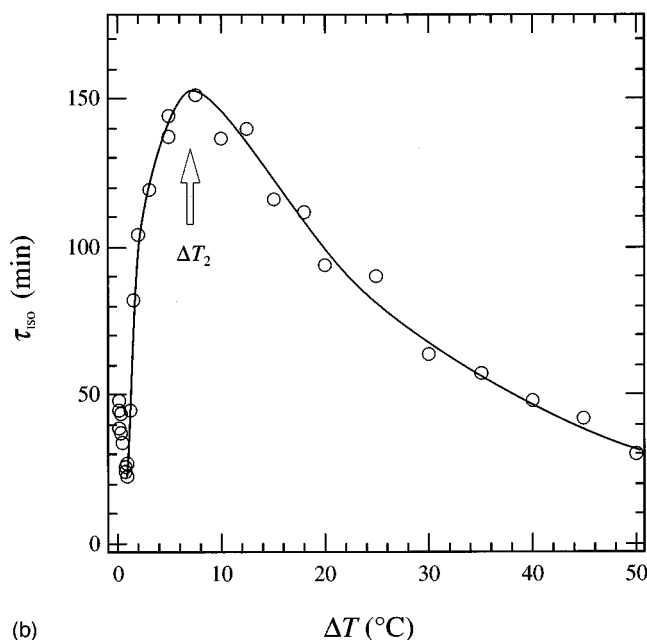
Figure 4 shows the time,  $\tau_{\text{CON}}$ , to complete the swollen to collapsed phase transition in the continuous heating process;  $\tau_{\text{CON}}=(T_{\text{END}}-T_{\text{ONSET}})/v_T$ . One can see that  $\tau_{\text{CON}}$  decreases with increasing  $v_T$  and increases after reaching its minimum at around  $0.03 \text{ }^\circ\text{C min}^{-1}$ . One can expect that a crossover phenomenon of two competing shrinking mechanisms starts at around this characteristic  $v_T$ .

### D. Phase transition velocity on steplike temperature change

Figure 5 shows the time,  $\tau_{\text{ISO}}$ , to finish the swollen to collapsed phase transition in the isothermal process after a steplike temperature increase,  $\Delta T$ . To take this measurement, the solvent temperature was quickly increased beyond the transition point from  $33.6 \text{ }^\circ\text{C}$  (just below the transition



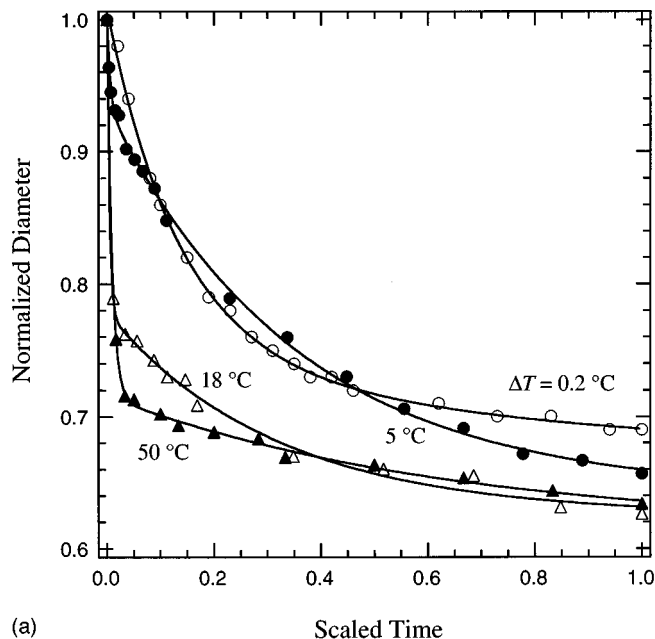
(a)



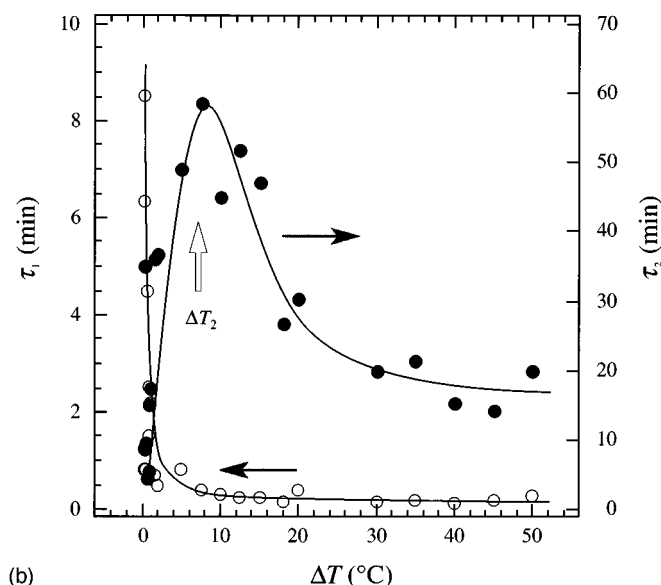
(b)

FIG. 5. Times,  $\tau_{\text{ISO}}$ , from onset to end of the swollen to collapsed phase transition as a function of the degree of "super-heating,"  $\Delta T$ , on isothermal process after several steplike temperature increases beyond the transition point. The initial temperature was  $33.6 \text{ }^\circ\text{C}$  (just below the transition point).  $\tau_{\text{ISO}}$  exhibits a minimum at  $\Delta T=0.9$  (final temperature= $34.5 \text{ }^\circ\text{C}$ ) (a), and a maximum at  $\Delta T=7.5$  (final temperature= $41.1 \text{ }^\circ\text{C}$ ) (b). Lines added are to guide the eye.

point). One can see that  $\tau_{\text{ISO}}$  decreased with increasing  $\Delta T$ , reaching a minimum at  $\Delta T=0.9 \text{ }^\circ\text{C}$  (final temperature= $34.5 \text{ }^\circ\text{C}$ ) [Fig. 5(a)]. Then it steeply increased, reaching a maximum at  $\Delta T=7.5 \text{ }^\circ\text{C}$ , and rapidly decreased in the larger  $\Delta T$  [Fig. 5(b)]. When  $\Delta T$  approached zero,  $\tau_{\text{ISO}}$  rapidly increases. This can be attributed to a critical slowing-down of the gels, which has been reported in bulk gels in the vicinity of the discontinuous volume phase transition.<sup>25</sup> We have two characteristic super-heating degrees,  $\Delta T_1$  ( $0.9$ ) and  $\Delta T_2$  ( $7.5 \text{ }^\circ\text{C}$ ) (see Fig. 5). It should be noted that this characteristic  $\Delta T_1$  should correspond to the minimum  $v_T$ , above



(a)



(b)

FIG. 6. (a) Time course of the diameter change on the steplike temperature increases for  $\Delta T=0.2$  ( $<\Delta T_1$ ), 5 ( $>\Delta T_1$ ,  $<\Delta T_2$ ), and 18, 50 °C ( $>\Delta T_2$ ). Solid lines added are the best fits by double exponential functions. (b) Characteristic times for the diameter changes on the isothermal processes obtained by the best fits. Lines added are to guide the eye.

which the coarse pattern could appear (see Sec. III C and Fig. 4). The transformation from the minimum at  $\Delta T_1$  to the maximum at  $\Delta T_2$  suggests a crossover of two competing mechanisms characterized by the appearance of the coarse pattern. The absolute value of  $\tau_{\text{ISO}}$  in the smaller range of  $\Delta T < \Delta T_1$  is much smaller than that in the larger range of  $\Delta T_2 < \Delta T$ . One can see that the dominant phase transition mechanism would transfer one to the other through the crossover range of  $\Delta T_1 < \Delta T < \Delta T_2$ .

#### E. Characteristic times of isothermal process on steplike temperature change

The diameter was measured as a function of time on the isothermal process after steplike super-heating from the ini-

tial temperature of 33.6 °C. Typical examples of diameter change vs time are shown in Fig. 6(a). In this figure, time in the horizontal axis is scaled by respective  $\tau_{\text{ISO}}$ , while diameter in the vertical axis is normalized by the respective diameter at 33.6 °C. One can see that the scaled time course depends on the final temperature (the degree of superheating,  $\Delta T$ ) and that it can be well described by double exponential functions (solid lines), indicating two relaxation processes with two time constants,  $\tau_1$  and  $\tau_2$ . Figure 6(b) shows  $\tau_1$  and  $\tau_2$  against  $\Delta T$ . With increasing  $\Delta T$ ,  $\tau_1$  decreases rapidly and takes a very small value when  $\Delta T$  exceeds  $\Delta T_2$ . On the other hand,  $\tau_2$  exhibits a behavior similar to that of  $\tau_{\text{ISO}}$  and shows a maximum at  $\Delta T_2$ . It was difficult to identify a minimum at  $\Delta T_1$  because of the scattering of the data points. The absolute value of  $\tau_2$  is much larger than  $\tau_1$ . As will be discussed later,  $\tau_1$  is related to the formation of the collapsed surface skin layer, while  $\tau_2$  is related to the relaxation of the phase-separated bulk networks through the collapsed skin layer growth.

## IV. DISCUSSION

### A. Conformation change

In the present study, several interesting features appeared in the swollen to collapsed phase transition of neutral NIPA gels. The results indicate that the macroscopic conformation change (the surface pattern and the growth of collapsed skin layer) is related to the characteristic times,  $\tau_{\text{CON}}$ ,  $\tau_{\text{ISO}}$ , and  $\tau_2$  against  $v_T$  or  $\Delta T$ . First, the fine pattern was observed on both processes under all conditions of  $v_T$  or  $\Delta T$  at the first stage of phase transition. This was due to the formation of the collapsed surface skin layer, indicating that the phase transition started at the surface. In the second stage, the time course of the macroscopic behavior depended completely on the absolute value (smaller and larger) of  $v_T$  or  $\Delta T$ . In the case of the isothermal process, it is interesting to observe that  $\tau_{\text{ISO}}$  reached its minimum at  $\Delta T_1$  and its maximum at  $\Delta T_2$ ;  $\tau_{\text{ISO}}$  decreased with increasing  $\Delta T$  in the ranges of  $\Delta T < \Delta T_1$  as well as of  $\Delta T_2 < \Delta T$ . Evidence of the existence of the crossover behavior in the range of  $\Delta T_1 < \Delta T < \Delta T_2$  suggests the existence of two different shrinking mechanisms. The former decrement corresponds to the initial decrement of  $\tau_{\text{CON}}$  with increasing  $v_T$  on the continuous heating process (see Secs. III C and D). The most possible explanation lies with the traditional phase separation phenomena. The macroscopic conformation change during the phase transition in some binary systems can be interpreted in terms of the phase separation of two mechanisms of nucleation growth (coarsening) and spinodal decomposition.<sup>26-28</sup> In the present system, the phase transition can be controlled by the nucleation mechanism in the metastable region ( $\Delta T < \Delta T_1$ ). On the other hand, the phase transition is dominated by the spinodal decomposition in the unstable region ( $\Delta T_2 < \Delta T$ ). In the intermediate range ( $\Delta T_1 < \Delta T < \Delta T_2$ ), the transition comes into the crossover region.

## B. Thermally activated nucleation and phase transition velocity

The critical difference between the traditional nucleation phenomena and the phase separation in the present study is that the gel is a network of cross-linked polymers swollen in liquid. The network in a polymer gel system is continuously connected to form a dilute three-dimensional solid with a complicated structure. The phase separations occur not only between the swollen and the collapsed networks but also between the respective network and the solvent.<sup>18</sup> Even if the embryos (or clusters) of the collapsed phase emerged in the swollen network, they could not remain in the local potential minimum, which is too small to fall into the swollen nuclei because of the surrounding networks. This is because the energy gain from the network volume change will not exceed the loss of the elastic energy from the boundary strain. Therefore, thermally activated nucleation could be strongly suppressed in bulk gels by the distortion of the elastic field in three-dimensional gels.<sup>29,30</sup> In spite of these considerations, however, the present study suggests that thermally activated nucleation is expected on the surface at the first stage of the transition. Of the various possibilities being considered, the imperfection of the surface structure is essential; the nucleation can experimentally occur on the gel surface, leading to the formation of a stable surface layer of the new phase. This is because the network surface structure is far from the perfect lattice; it has many defects. Nucleation could start with such portions. Therefore, the volume phase transition takes place by means of the nucleation mechanism, when the gel stays between the binodal and the stability limit (spinodal) of the swollen state of the gel.

When the phase transition starts, the initial collapsed portion can emerge on the surface through the nucleation mechanism, which corresponds to the macroscopic fine pattern. The characteristic time,  $\tau_1$ , may be related to the network relaxation during the formation of the initial collapsed skin layer. This can be attributed to the fact that, in the present study, the temperature was continuously increased in all experiments; even on the isothermal processes the temperature jump to the unstable region was conducted with finite velocities. Therefore, just after the temperature exceeds 33.6 °C, the embryos were able to become nuclei of the new collapsed phase at the interface between the collapsed skin layer and the unchanged swollen core, and the coarsening of nuclei increased the collapsed volume from the outside. This phase separation by the nucleation mechanism could continue until the temperature was forced into the unstable region. If the phase transition ended in the metastable region, the formation and coarsening of nuclei would continue until the gel reached a completely collapsed state. This nucleation mechanism is characterized by two factors of the formation rate as well as the coarsening velocity of the nuclei. According to the classical nucleation model,<sup>28,31</sup> the formation and the coarsening rates of nuclei depend on the degree of ‘‘super-cooling’’ (how deeply the gel state can be brought into the metastable region; in the present case,  $\Delta T$ ). The formation rate (probability) of nuclei is assumed to be proportional to  $\exp(-G_V/k_B T)$ , where  $G_V$  is the minimum formation energy of the nuclei and  $k_B$  is the Boltzmann con-

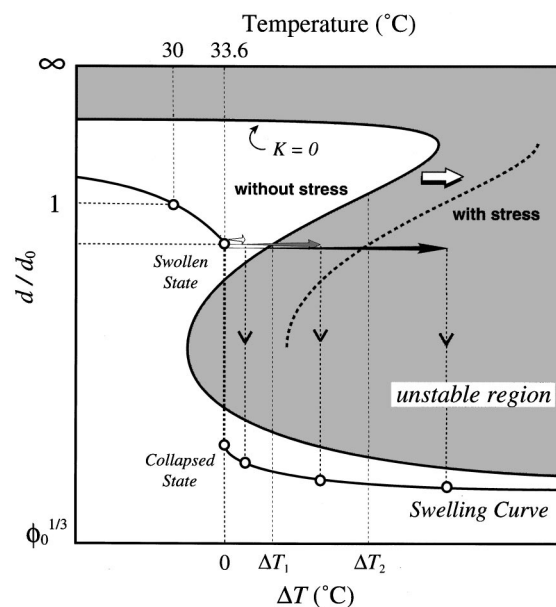


FIG. 7. Schematic phase diagram of the linear swelling ratio,  $d/d_0$  vs temperature (or temperature jump,  $\Delta T$ ), where the shaded area represents the unstable region. The equilibrium diameter change from the swollen to collapsed state is also schematically plotted. Phase separation on the isothermal processes are shown in three different  $\Delta T$ 's in the smaller (nucleation), intermediate (crossover), and larger (spinodal decomposition) ranges. The effects of stress by the phase coexistence at the interface on the  $K=0$  curve are expressed by the broken curve.

stant. This formula is proportional to  $\exp(-C/\Delta T^2)$ , where the positive coefficient  $C$  has a negative correlation with temperature,  $T$  [roughly,  $\propto (k_B T)^{-3}$ ]. On the other hand, the coarsening of nuclei is expected to be a thermal activation process; therefore, it could be in the form of  $\exp(-G_C/k_B T)$ , where  $G_C$  is the activation energy. This formula also decreases with increasing  $T$  ( $\Delta T$ ) since  $G_C$  does not depend on  $T$ . From these expressions, one can expect that the number of nuclei and the coarsening velocity will both increase with increasing  $\Delta T$ , which can accelerate the phase transition, resulting in the initial decrement of  $\tau_{ISO}$  in the range of  $0 < \Delta T < \Delta T_1$ . As for the second decrement of  $\tau_{ISO}$ , the relaxation velocity increases with  $\Delta T$  in the range of  $\Delta T_2 < \Delta T$ ; the larger the  $\Delta T$ , the faster the phase-separated state by spinodal decomposition turns into the collapsed state. We believe that this behavior could be attributed to the increment of the diffusion constant of polymer networks with  $\Delta T$ .<sup>25</sup> It should be noted that the reason for the extremely large time constant is that the relaxation during the coarsening process of nuclei requires cooperative motions of the phase boundary at the interface between the collapsed skin layer and the swollen core portion. This is because neighboring domains in the interface are under mechanical constraint.<sup>8–10,32</sup>

## C. Phase diagram and crossover of two mechanisms

The above considerations can be clearly expressed by the phase diagram of the present system. In the literature, the phase diagram of polymer gels has been experimentally determined,<sup>1,33</sup> and it has been reported that the unstable region, defined by the bulk modulus  $K < 0$ , was theoretically

calculated by the mean field theory.<sup>18</sup> In Fig. 7, the unstable region is schematically drawn in the diameter vs temperature plane of the present system. The swelling curve is also schematically plotted in this figure. Three passes from the swollen to collapsed phase transition on the isothermal processes can be considered in this plane; typical examples are drawn in the cases of smaller, intermediate, and larger  $\Delta T$ . According to the classical model,<sup>26–28</sup> one might expect that the transformation from the nucleation to spinodal decomposition mechanism would take place at  $\Delta T_1$ . However, the present experimental observations are not consistent with this estimation; as mentioned in Sec. III D, a crossover phenomenon of two competing shrinking mechanisms can be observed in the characteristic time,  $\tau_{\text{ISO}}$  or  $\tau_2$ , against  $\Delta T$  in a large range of  $\Delta T_1 < \Delta T < \Delta T_2$ . Evidence of the existence of crossover cannot be explained by the simple phase diagram. Of the various possibilities to explain the discrepancy, two important facts should be taken into account for the existence of  $\Delta T_2$ . One is the rapid formation and growth of nuclei to form the collapsed surface skin layer. This is because the temperature of gel does not instantly change even after switching the water flow. Therefore, even if the temperature exceeds  $\Delta T_1$ , the surface nucleation cannot be ignored since the relaxation time of temperature control is much larger than that of the collective diffusion of a polymer network relative to water (less than 1 min for the gel with 100  $\mu\text{m}$  size, therefore, approximately 1 msec for the gel with 1  $\mu\text{m}$  size<sup>5,6</sup>). The other is the stress-induced modification of the phase diagram of the swollen state in the vicinity of the interface. Just above  $\Delta T_1$ , the coexistence of the stable and metastable states plays an important role, realized by the temperature gradient in the polymer networks at the initial stage of temperature jump. It is, therefore, necessary to take into account that the locally collapsed skin layer is subject to stress by proximity to the swollen portion, which is at a maximum at the boundary between the two phases. According to the phase transition in mechanically constrained NIPA gels, it has been established that the mechanical stretching induces the increment of the transition temperature;<sup>9,10,32</sup> the collapsed state just above the transition point can return to the swollen state upon application of a small tensile stress. Such an effect may be understood in terms of the mean field theory; the stress in the transitional boundary region between two phases can affect the free energy of the system. Hence, the diameter vs temperature curve should be modified as schematically shown by the broken curves in Fig. 7. When  $\Delta T$  exceeds  $\Delta T_2$ , these effects can be ignored since the collapsed skin layer will become too thin to affect the relaxation process of the phase-separated network by the spinodal decomposition.

It should be noted that the network structure of the present kind of polymer gels is not homogeneous by nature, but rather consists of microdomains,<sup>24</sup> resulting in inhomogeneous strain distribution at the microscopic level. These frozen inhomogeneities affect the phase transition velocity. In order to verify these considerations, not only macroscopic observations but also kinetic experiments at the microscopic

level in the same sample are desirable. This is a subject for future investigations.

## V. CONCLUSION

We have observed the conformation changes during the shrinking phase transition of neutral poly(*N*-isopropylacrylamide) gel. The results can be summarized as follows. All gels start to shrink from the surface, showing a fine pattern. The collapsed portion develops from the collapsed surface layer to the core portion in different manners depending on the temperature drift rate,  $v_T$  or the degree of “superheating,”  $\Delta T$ . If  $v_T$  or  $\Delta T$  is small enough, the phase transition is governed by the nucleation mechanism. When it exceeds the threshold, the spinodal decomposition has an important role. The phase transition velocity has a strong correlation to the surface patterns, which can be determined by the phase diagram of the polymer gels. The results have been discussed qualitatively in terms of nucleation, spinodal decomposition, and inhomogeneous stress distribution during phase separation.

The results of the present study show identical properties for the polymer gels of submillimeter diameter; if the diameter is comparable to the skin layer, we cannot observe the second stage; if the gel is ionized, the phase coexistence can be observed. Further experiments, including those for different shapes of gels and for ionized gels, are desirable.

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