Kinetics of Volume Phase Transition in Poly(*N*-isopropylacrylamide-*co*-acrylic acid) Gels

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ABSTRACT: The shrinking/swelling behavior across the volume phase transition temperature, T_c, has been investigated for cylindrical gels made of poly(*N*-isopropylacrylamide-*co*-acrylic acid) (NIPA/AAc) and poly(*N*-isopropylacrylamide) (NIPA). NIPA/AAc gel shrank at $T_c = 43$ °C by quasistatic heating. On the other hand, the gel underwent a shrinking transition at a lower temperature, i.e., $T_c \approx 40$ °C, when a temperature jump was applied to the gel from 20 °C. More interestingly, the shrinking process consisted of three stages: (i) a uniform shrinking stage where the gel diameter decreases exponentially, (ii) a plateau stage where the gel shrinks further from both ends of the cylinder while the middle (swollen) part remains in the swollen state, and (iii) a collapsing stage where the middle part of the gel shrinks linearly with time. This sequential process was found to be characteristic of weakly charged gels with a large aspect ratio. To the contrary, the swelling process was fitted with a single exponential function given by the Tanaka−Fillmore theory on gel swelling. This interesting shrinking behavior was discussed by comparing the results of swelling kinetics. In the case of NIPA homopolymer gel, the shrinking process was strongly decelerated due to phase separation, while the swelling process was well reproduced by the Tanaka−Fillmore theory.

1. Introduction

Temperature-sensitive polymer gels have been investigated for applications in drug delivery systems,[1] actuators,[2] and so on, where quick responsive gels are desired.[3,4] However, since the process is diffusion controlled, the rate of gel swelling or shrinking is strongly dependent on the size of the gel. The smaller the gel, the quicker the gel swells or shrinks. A pioneering theory of gel swelling or shrinking was developed by Tanaka and Fillmore (TF).[5] The TF theory is based on the concept of cooperative diffusion of polymer network in a medium, where the gel is regarded as a continuum. According to the TF theory,

$$\tau \approx R^2/D \qquad (1)$$

where τ, R, and D are the characteristic time for gel swelling or shrinking, the size of the gel, and the cooperative diffusion coefficient, respectively. For typical polymer gels, D is on the order of $10^{-7}-10^{-6}$ cm^2/s, depending on the polymer concentration, cross-link density, etc. However, it is not easy to increase the value of D by a factor of 10^2 or more. Though several modified theories of gel swelling/shrinking have been proposed by Peter and Candau,[6] Li and Tanaka,[7] and Shibayama et al.,[8] the essential feature of eq 1 remains unchanged. Therefore, a reduction of gel size has been thought to be the only way to achieve quick response. In addition, the TF theory does not account for shrinking kinetics across the temperature of phase separation.

Recent experimental studies have shown that the rate of gel shrinking can be accelerated by designing special gels, such as (i) a gel having a pathway of water molecules through the gel incorporating hydrophilic chains or porosity, (ii) a gel which has a strong shrinking tendency due to the presence of dangling chains,[9−11] or (iii) microporous gels prepared by γ-ray irradiation.[12] In case ii, dangling chains in a gel can easily collapse upon an external stimulus because one side of the dangling chain is free. These modifications indicate the importance to bestow heterogeneous structure and/or architecture to gels in order to speed up the response rate. Recently, the understanding of gel inhomogeneities has been greatly advanced owing to extensive studies on gels by using light, X-ray, and neutron scattering.[13−17]

In the case of charged gels, the shrinking/swelling behavior becomes even more sophisticated. Due to the presence of charged groups, the solvent molecules are highly localized near the charged groups if the solvent becomes poor for the main constituent of the network. This leads to a discrete volume transition,[18] bubble formation,[19,20] and microphase separation.[21] Microphase separation in charged polymeric systems was first predicted by Borue and Erukhimovich[22] for weakly charged polyelectrolytes in a poor solvent. Shibayama et al.[21] reported the formation of microphase separated structure in temperature-sensitive weakly charged gels by small-angle neutron scattering.

Taking account of these unique features, we discuss the swelling/shrinking kinetics of weakly charged gels with an emphasis on microphase separation and spatial inhomogeneities and compare the kinetics with those of uncharged homopolymer gels.

2. Experimental Section

2.1. Samples. Poly(*N*-isopropylacrylamide) (NIPA) homopolymer gels and poly(*N*-isopropylacrylamide-*co*-acrylic acid) (NIPA/AAc) copolymer gels were prepared by redox polymerization. NIPA monomer, kindly supplied by Kohjin Chem. Co., Tokyo, Japan, was purified by recrystallization. An aqueous solution of a monomer mixture of NIPA (668 mM) and acrylic acid (AAc; 32 mM) was polymerized in the presence of *N*,*N*′-methylenebisacrylamide (BIS; cross-linker; 8.62 mM) in a micropipet of 471-μm diameter at 20 °C. Thus prepared gel

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was cut to a cylindrical piece 5 mm long and washed with an excess amount of distilled water.

2.2. Swelling Degree Measurement. The sample was immersed in a thermostated chamber filled with distilled water. The degree of swelling was measured by monitoring the diameter of the cylindrical gel, *d*, via an inverted microscope (TMD300, Nikon, Co., Ltd, Tokyo, Japan) coupled with an image processor (Algas 2000, Hamamatsu Photonics, Co., Ltd, Hamamatsu, Japan). The temperature of the chamber was increased either stepwise with $\Delta T \leq 3$ °C by ensuring thermal equilibrium (quasistatic heating) or by temperature jump (T-jump) with $\Delta T \geq 20$ °C. The temperature step is defined by $\Delta T = T_{n+1} - T_n$, where T_{n+1} and T_n are the temperatures of the gel at the $(n+1)$th and nth steps, respectively. In the case of the quasistatic heating, *d* was measured after an interval of 30 min whenever the temperature was increased. Then *d* was measured again after another interval of 30 min. If the difference in the values of *d* between two successive measurements was less than 5 μm, the temperature was increased again, and the same procedure was repeated. In this way, a quasistatic measurement of *d* was carried out. On the other hand, T-jump was carried out by switching the route of circulating water thermostated at two desired temperatures. The time required for a T-jump was about 1 min.

2.3. Small-Angle Neutron Scattering. Small-angle neutron scattering (SANS) experiments were carried out at the Research Reactor of the Institute of Solid State Physics, the University of Tokyo, located at the Japan Atomic Energy Laboratories, Tokai, Japan. Two types of NIPA/AAc gels having different sample dimensions were employed. One was a one-piece gel of disk shape, 4 mm thick and 25 mm in diameter, and the other was a smashed gel with a 500-μm sieve. In both cases, the gel samples were sealed in a quartz cell and thermostated at the desired temperature.

3. Results and Discussion

3.1. Quasistatic Heating of NIPA/AAc Weakly Charged Gels. Figure 1 shows (a) the variation of the linear swelling ratio, d/d_0, during a quasistatic heating process, where *d* and d_0 are the diameter of a cylindrical gel at observation and at preparation ($d_0 = 471$ μm), respectively, and (b) the time course of temperature variation during the cooling process. d/d_0 gradually decreased upon increasing the temperature up to 43 °C. In this process, the gel was kept at equilibrium swelling. The gel then underwent a discrete transition to a shrunken state at 43 °C. The shrinking process was monitored every 30 min. Some representative data points are shown with open circles. When the gel started to shrink at 43 °C, the time course of temperature variation as well as d/d_0 was plotted in Figure 1b. It took about 60 h for the gel to reach the shrunken state at 43 °C. Note that the volume transition temperature, T_c, of NIPA/AAc gels is dependent on the AAc concentration[23,24] as well as pH and salt concentration. After the gel reached the shrunken state, variation of *d* during a cooling process was studied. In this process, another interesting phenomenon was observed. When the temperature was lowered with a step $|\Delta T| \leq 0.5$ °C, no size change was observed on the gel. However, for $|\Delta T| \geq 0.7$ °C, a part of the gel started to swell like a bubble, followed by a gradual decrease to the shrunken state. A series of photographs in this process are shown in Figure 2. Note that the value of *d* here was taken as the diameter of the thickest part of the gel. This kind of strange behavior was observed in the cooling process in the temperature range of 37−43 °C. This indicates that the gel was in a highly frustrated state in this temperature range. Whenever a stimulus (e.g., $-\Delta T$, cooling) was applied to a gel, the gel feels a frustration whether to swell. In this particular case, for $|\Delta T| \geq 0.7$ °C, the gel swelled locally. On the other hand, for $|\Delta T| \leq 0.5$ °C, the gel remained in the shrunken state. However, even for the case of $|\Delta T| > 0.7$ °C, swelling could not go on, and the gel finally reached the shrunken state as long as the temperature was above 37 °C. This means that the shrunken state is more favorable thermodynamically for the gel in this temperature range ($37 \leq T \leq 43$ °C). A repetition of the d/d_0 vs temperature measurement using the same gel disclosed the following. In the second run, the equilibrium value of d/d_0 was about 1.6 (at $T = 37$ °C), which is significantly less than that in the first run, i.e., $d/d_0 \approx 2.0$ (at $T = 37$ °C). In addition, a discrete swelling took place around 38 °C (not at 37 °C). Therefore, it can be concluded that the presence of the gap in the temperatures for discrete shrinking/swelling was reproduced. However, a significant hysteresis in the loop of the temperature variation was also observed. Though the gel was washed with care before use, a small amount of residues, such as initiator and unreacted monomers, might be extracted during the shrinking/swelling processes. This is a possible reason such a significant hysteresis was observed during the successive loops. To understand this unique swelling/shrinking behavior, we carried out a temperature jump experiment.

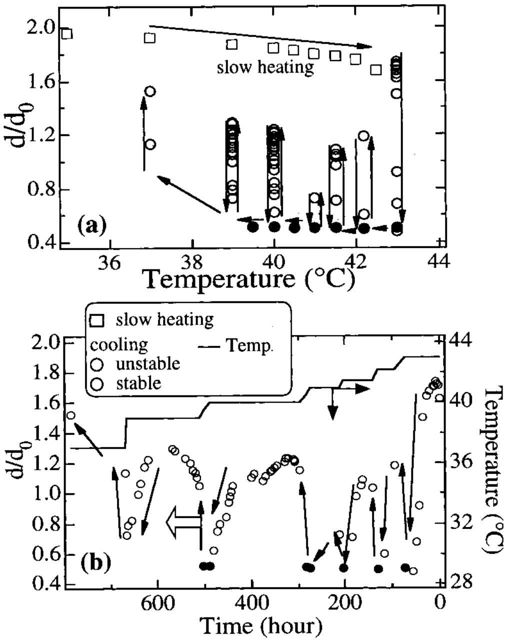

Figure 1. (a) Variation of the linear swelling ratio, d/d_0, during a quasistatic heating process (□), where *d* and d_0 are the diameters of a cylindrical gel at observation and at preparation, respectively. At $T = 43$ °C, the gel became unstable and underwent a shrinking transition (○). Subsequent cooling process was classified to unstable (○) and stable regions (●). For cooling with $|\Delta T| \leq 0.5$ °C, no changes occurred on the size of the gel, while a local swelling by bubble formation was observed for $|\Delta T| \geq 0.7$ °C. (b) Time course of temperature variation (solid line) as well as that of d/d_0 from the onset of shrinking transition at 43 °C.

3.2. Shrinking of NIPA/AAc Weakly Charged Gels by T-Jump. Figure 3 shows the variation of d/d_0 with time, *t*, after a temperature jump from 20 to 40 °C. Interestingly, the shrinking process can be characterized by three stages. In stage I, a rapid decrease in d/d_0 was observed, followed by a plateau region (stage II). Then, d/d_0 decreased again linearly with time (stage

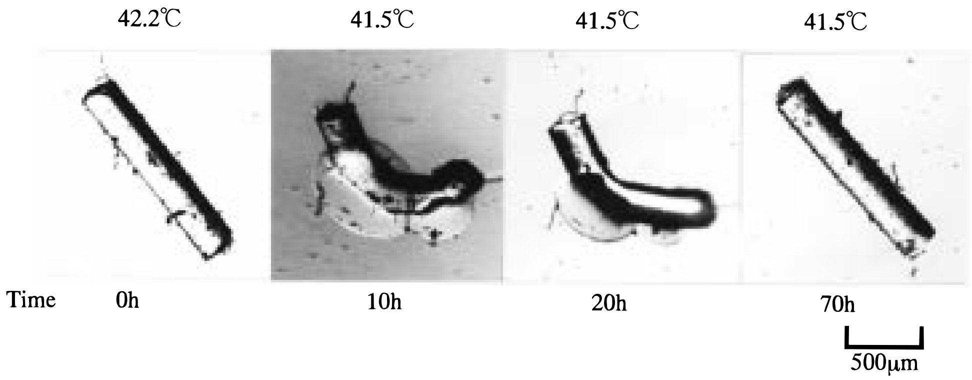

Figure 2. Series of photographs of NIPA/AAc gel during the cooling process.

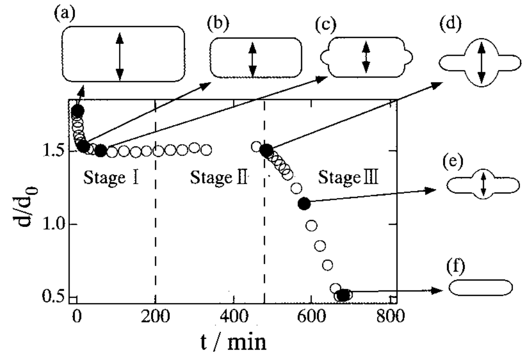

Figure 3. Variation of d/d_0 for NIPA/AAc gel after a T-jump from 20 to 40 °C. Shapes of the gel during the shrinking process were schematically shown with symbols (a) to (f). The arrow indicates where the d was measured.

III). In the plateau region, two coexistent phases were observed, as schematically depicted by (c) in the figure, and further collapsing to a fully shrunken phase took place from both sides of the gel. The value of d was again taken as the diameter of the thickest part of the gel. When the front of the shrunken phase reached the middle part (d), the swollen part started to shrink with time (e). Note that the shrinking transition occurred at 40 °C in the case of T-jump, while a higher temperature, i.e., 43 °C, was required for the gel to shrink in the case of the quasistatic heating.

Figure 4 shows the variation of $d(t)$ in stage I, where the experimental result was fitted more or less with the following equations,[5,7,8]

$$d(t) \approx d(\infty) + [d(0) - d(\infty)]\frac{6}{\pi^2}\exp(-t/\tau) \qquad (\text{for } t > \tau) \tag{2}$$

$$D = \left(\frac{d(\infty)}{2\pi}\right)^2 \frac{1}{\tau} \tag{3}$$

from which the cooperative diffusion coefficient D was estimated to be 2.6×10^{-7} cm^2/s. As shown in Figure 4, $d(t)$ in stage I is well fitted by the Tanaka–Fillmore theory for gel swelling/shrinking. On the other hand, $d(t)$ varies rather linearly in stage III, as shown in Figure 5, and the shrinking rate is estimated to be 2.9 μm/min in this particular case. The time required for stage II was roughly proportional to the length of the gel. This seems to be analogous to crystallization of chain molecules by folding.

T-jump experiments were carried out by changing destination temperature, T_d. Figure 6 shows the results of the variation of d/d_0 T-jumped to various T_d's from 40 to 60 °C. Each data set shows the presence of the plateau region, and an increase in d/d_0 is observed just before abrupt decrease. The increase in d/d_0 is due to the change of the shape from (c) to (d) in Figure 3, because the thickest part of the gel was measured. By careful observation, the case of T_d = 55 °C has another plateau region for 80 < t < 200 min. However, in general, the three-stage shrinking behavior was observed in all gels T-jumped to different temperatures.

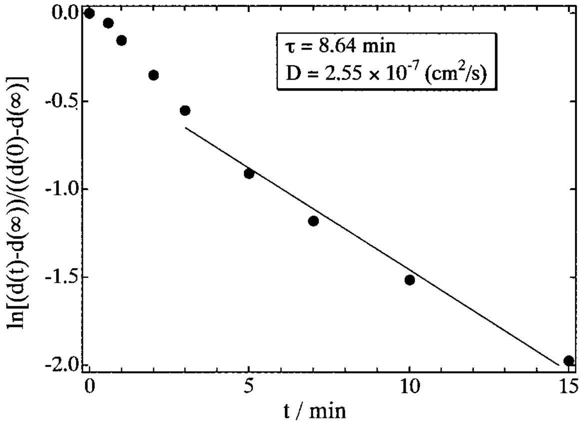

Figure 4. Time course of $d(t)$ for NIPA/AAc gel in stage I by T-jump from 20 to 40 °C. The solid line is obtained by fitting the data with the Tanaka–Fillmore theory for gel swelling/shrinking. The curve fit was conducted for $t > \tau$ (see eq 2).

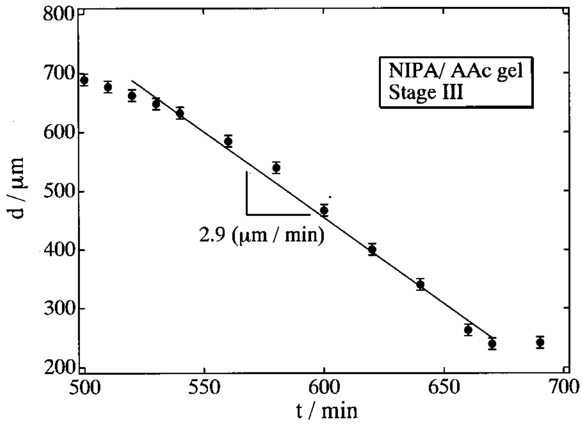

Figure 5. Time course of $d(t)$ for NIPA/AAc gel in stage III by T-jump from 20 to 40 °C. The variation of $d(t)$ was time linear, and the rate was evaluated to be 2.9 μm/min in this particular case.

Since the TF-type analysis was inappropriate for the gels having the three-stage shrinking, we estimated the

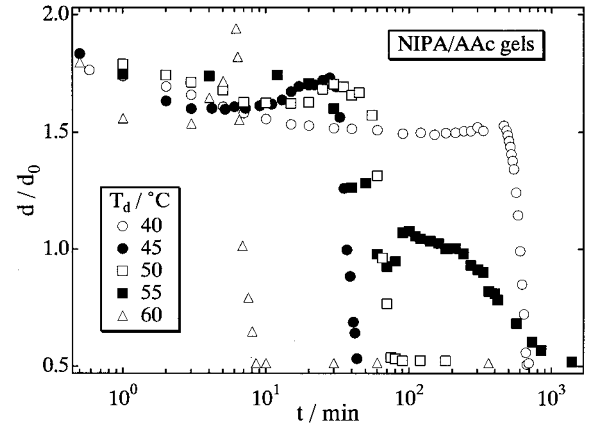

Figure 6. Time course of d/d_0 for NIPA/AAc gel T-jumped to various destination temperatures, T_d's.

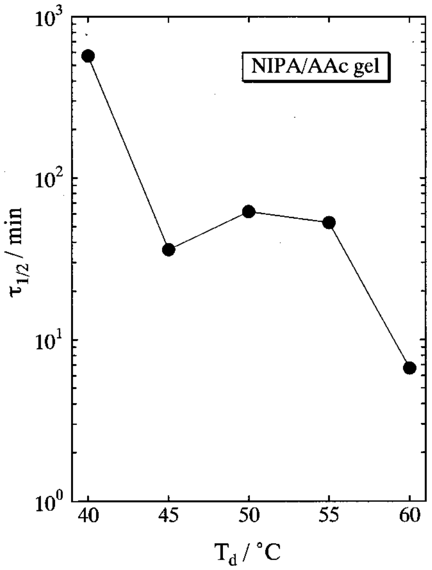

Figure 7. Variation of the half time, $\tau_{1/2}$, with destination temperature, T_d.

rate of the overall shrinking process by the half-time of shrinking, $\tau_{1/2}$, defined by

$$\frac{d(t=0) - d(\tau_{1/2})}{d(t=0) - d(\infty)} = \frac{1}{2} \tag{4}$$

Figure 7 shows the half-time,$\tau_{1/2}$, as a function of destination temperature. This shows that $\tau_{1/2}$ decreases with increasing T_d.

3.3. Swelling of NIPA/AAc Weakly Charged Gels by T-Jump. Figure 8 shows the change of d/d_0 during a swelling process by T-jump from several initial temperatures, T_i = 40, 50, and 60 °C, to one destination temperature, T_d = 20 °C. Contrary to the shrinking process, the swelling process is simply described with a single-exponential function and could be fitted with eq 1 (see the inset for the case of T_i = 50 °C). The evaluated values of D were in the range of (2.0−2.2) × 10^{-7} cm^2/s. Table 1 shows the values of cooperative diffusion coefficient during shrinking and swelling, D_{sh} and D_{sw}, for NIPA/AAc gels T-jumped to various temperatures (upward) and from various temperatures (downward), where D_{sh} was evaluated only in stage I. It is very interesting that D_{sh} is highest when the destination temperature was 45 °C, while D_{sw} is independent of the initial temperature. The independence of D_{sw} is in good agreement with that reported by Sato-Matsuo and Tanaka.[25] They observed that the characteristic time for swelling/shrinking of NIPA gels depends on the final state but is much less influenced by the initial state. However, the behavior of D_{sh} for NIPA/AAc is very different from that for NIPA gel. Sato-Matsuo and Tanaka observed a critical slowing down in D_{sh} at $T_d = T_c$ (≈34 °C), while D_{sh} of NIPA/AAc shows a speeding up around T_c (≈43 °C). In the next section, we discuss the mechanism of gel shrinking for weakly charged gels.

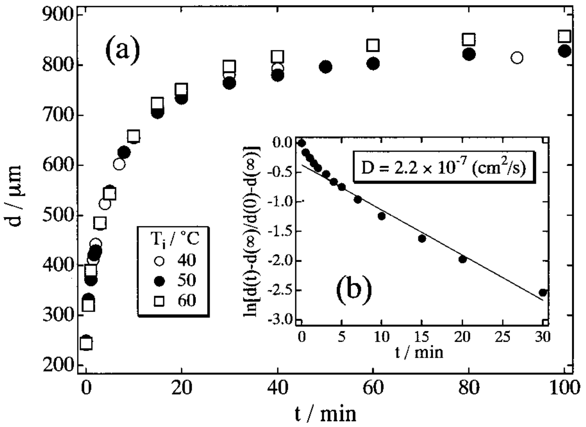

Figure 8. Variation of d for NIPA/AAc gel during a swelling process by T-jump to 20 °C in (a) linear plot and (b) semilogarithmic plot. The solid curve is the one fitted by Tanaka−Fillmore theory. Note that the fitting was conducted for t > 5 min according to the theory.

Table 1. Kinetics of Shrinking/Swelling Process for NIPA/AAc Gels

Shrinking (from 20 °C)					
T_d (°C)	40	45	50	55	60
$D_{sh(I)}$ (× 10^{-7} cm^2/s)	2.6	31	130	96	110
Swelling (from 20 °C)					
T_i (°C) 40 45 50 55 60					
D_{sw} (× 10^{-7} cm^2/s)	2.2	2.1	2.2	2.1	2.2

3.4. Shrinking Mechanism of NIPA/AAc Weakly Charged Gels. Figure 9 shows the comparison of the variations of d/d_0 for quasistatic heating (filled circles) and T-jump processes (open circles) for NIPA/AAc gels. In the case of quasistatic heating, the gel remains in a swollen state until 43 °C and then suddenly shrinks to the shrunken state as shown by filled circles. Note that it took 60 h to reach the shrunken state. On the other hand, a T-jump resulted in a steep decrease in d/d_0 in stage I, followed by a plateau region. It should be noted here that there is a significant difference in d/d_0 between the two processes, although both d/d_0's eventually reach the same value (i.e., $d/d_0 \approx 0.5$). This provides much insight into the shrinking mechanism of weakly charged gels. Now, we ask ourselves (i) why the charged gels have the intermediate size during the T-jump and (ii) why the value of d/d_0 is larger for the case of the quasistatic heating than that for the T-jump.

We propose the following mechanism for the shrinking process of NIPA/AAc gels. In quasistatic heating, a gel has enough time to adjust to a new equilibrium whenever the temperature is changed. Above the so-called Θ temperature of NIPA gels, i.e., ca. 34 °C, hydrophilic regions around the charged AAc segments are formed in the gel, as shown in the upper part of Figure 10. This is a kind of microphase separation, predicted by Borue and Erukhimovich,[22] in weakly

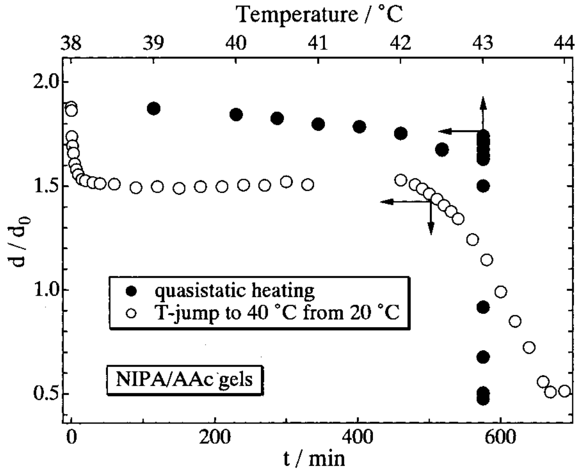

Figure 9. Comparison of the variations of d/d_0 of NIPA/AAc weakly charged gels for the quasistatic heating (●) and the T-jump processes (○).

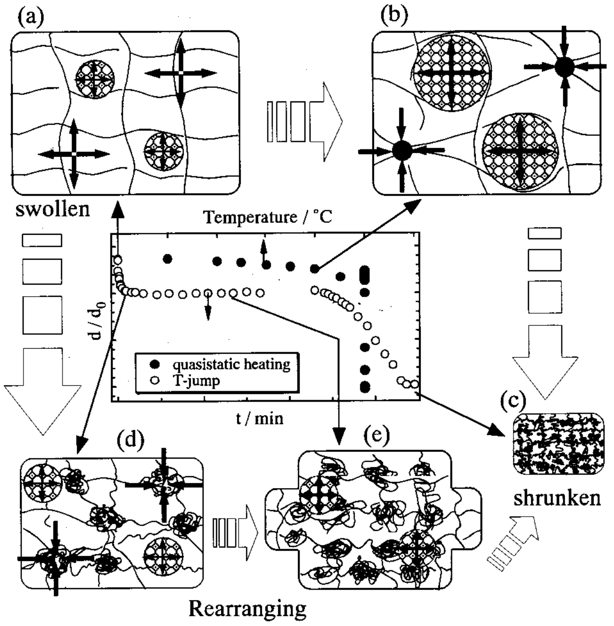

Figure 10. Proposed mechanism for the shrinking process of NIPA/AAc gels. In the case of quasistatic heating, microdomains are well developed, these domains maintain the swollen state as large as possible, as schematically shown in (b). For $T > T_c$, the gel undergoes a shrinking transition to the shrunken state (c). In the case of T-jump, it is not allowed to form well-developed microdomains (d), which leads to a squeezing process from (d) to (e) before reaching the shrunken state (c).

charged polyelectrolytes in a poor solvent. In a poor solvent, the polymer chains favor to collapse. However, the electrostatic interaction generated among charged groups prevents the polymer chains from collapsing because of the requirement for electroneutrality in the space. As a compromise, the system undergoes a microphase separation (b).[26] The formation of such hydrophilic regions has been already confirmed by small-angle neutron scattering.[21] The hydrophilic regions retain the swollen state until the attractive interaction (hydrophobic demixing) dominates the repulsive interaction (electrostatic interaction and/or Donnan potential). This is why the gel keeps a larger value of d/d_0 until 43 °C before shrinking to the shrunken state (c). Contrary to this, a T-jump does not allow the gel to form such a region, resulting in a less swollen state (at the plateau region) (d). This is why the gel treated by quasistatic heating has a larger swelling ratio than the T-jumped gel in the plateau region. Note that, in the plateau region, chain aggregation may occur in many places in the gel, as schematically shown in Figure 10e, and the aggregates evolve with time, Figure 10c. This type of chain aggregation and evolution has been predicted by Kuznetsov et al.[27] They studied the kinetics of the collapse transition of homopolymers and random copolymers by Monte Carlo simulations. The results show that the kinetic laws correspond to three stages, i.e., (1) the formation and growth of locally collapsed clusters, (2) a coarsening stage, and (3) a relaxation stage, where the overall size of the clusters decreases with time. A similar mechanism of chain collapsing is expected in the gel system studied here, although the cross-links decelerate the kinetics.

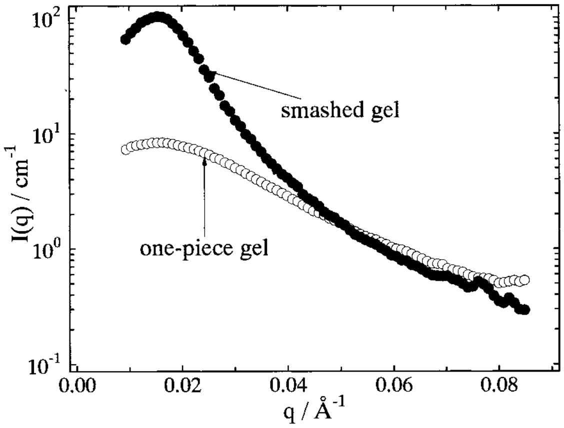

Figure 11. SANS intensity profiles of NIPA/AAc gels after T-jump: smashed gel (in equilibrium, ●) and one-piece gel (kinetically frozen, ○) observed at $t = 16$ min after T-jump.

Figure 11 shows a comparison of SANS intensity curves of smashed gels (in equilibrium) and of one-piece gels after T-jump to 40 °C. The smashed gels can easily attain thermodynamic equilibrium by temperature change compared with the one-piece gel because the size of individual gels is on the order of submilimeters. By T-jump, the scattered intensity, $I(q)$, increased with time, and a scattering peak appeared at $q = 0.014$ Å^{-1}. The intensity rise was confirmed to saturate at $t > 16$ min. On the other hand, it took several hours for the one-piece gel of this thickness (4 mm) to reach equilibrium because this is a diffusion-limited process. This figure indicates that the microdomain structure with characteristic spacing of $2\pi/q \approx 450$ Å is further developed in the smashed gels than in the one-piece gel. The significant difference in the SANS curves shown in the figure well supports the model of the shrinking process proposed above.

3.5. Shrinking Mechanism of NIPA Neutral Gels. The proposed mechanism of gel shrinking for weakly charged gels can be well contrasted by that for neutral gels, i.e., NIPA homopolymer gels. In the case of neutral NIPA gels, quasistatic heating results in a steep decrease in d/d_0 at the volume transition temperature T_c (≈34 °C), above which the gel size does not change with temperature.[28,29] Figure 12 shows the changes of d/d_0 of NIPA homopolymer gels for quasistatic heating (open squares) and T-jump processes from 20 °C (open and closed circles). In the case of T-jump, two destination temperatures were chosen, i.e., $T_d = 35$

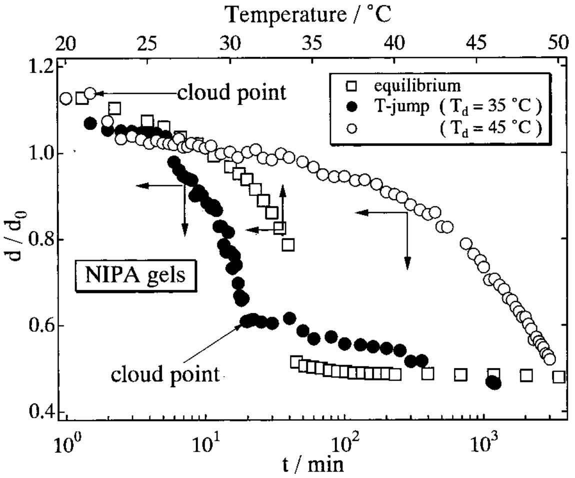

Figure 12. Changes in d/d_0 of NIPA neutral gels for quasi-static heating (□) and T-jump processes from 20 to 35 °C (●) and to 45 °C (○).

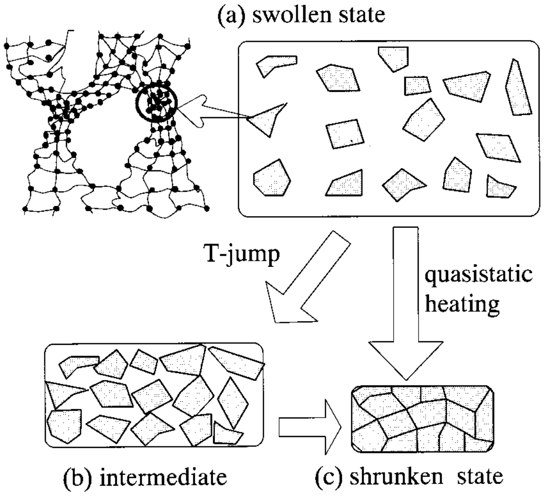

Figure 13. Shrinking mechanism of NIPA gels: (a) swollen state, (b) an intermediate state during shrinking after T-jump, and (c) shrunken state.

(solid circles) and 45 °C (open circles). Note that the former temperature is close to T_c ($\approx$34 °C), and the latter is much higher than T_c. In the case of the T-jump to 35 °C, the gel remained transparent even after the T-jump and then became cloudy after shrinking ($d/d_0 \approx 0.6$). At this point, a phase separation took place in the gel. On the other hand, in the case of a T-jump to 45 °C, the gel became cloudy just after the T-jump, indicating phase separation. The variations of d/d_0 were very different between the two T-jumps. In the case of a T-jump to 35 °C (solid circles), the final value of d/d_0 is close to that of the quasistatic heating (open squares). However, it took more than 2000 min for the gel T-jumped to 45 °C (open circles) to reach the same value of d/d_0 as shown in the figure. This means that the phase separation decelerates the rate of gel shrinking.

On the basis of the results of gel shrinking for NIPA gels, we propose a shrinking mechanism for NIPA gels as follows: NIPA neutral gels can be assumed to consist of lightly cross-linked and heavily cross-linked regions, as schematically illustrated in Figure 13a, where hatched parts indicate the heavily cross-linked regions. The presence of these kinds of regions is now well known as spatial inhomogeneities.[14,17,30,31] Now, if a gel is heated quite slowly, the cross-link-rich regions can adjust their position and/or orientation to fit a new equilibrium and finally reach an equilibrium shrunken state, as depicted in Figure 13c. However, in the case of a T-jump, the gel does not have enough time to reorganize. Therefore, the domains cannot move closer by heating, as shown in Figure 13b. Subsequent shrinking is attained by aging the gel at an elevated temperature, namely by taking a few tens of hours. This model is analogous to the mechanism proposed by Kuznetsov et al.[27] as discussed in Section 3.4. A skin formation by T-jump has been regarded as the most plausible reason for slow shrinking.[1,9,32] The skin referred to here is a thin layer of shrunken gel on the surface of a piece of gel, which prevents solvent from permeating across the boundary. However, at least in our case, we did not observe any evidence of skin formation. Such a skin may be formed at the onset of the T-jump. However, it would be due to an abrupt temperature jump. The estimated time for temperature equilibration in a gel is less than a few minutes. Thus, phase separation by a T-jump occurs not only at the skin but also at the inner part of the gel. Therefore, we believe that, even if a skin is formed by a T-jump, it cannot be a major reason for slow shrinking.

Table 2. Kinetics of Swelling Process for NIPA Gels

T_i (°C)	35	40	45	50	55
D_{sw} ($\times 10^{-7}$ cm^2/s)	2.2	2.1	2.2	2.1	2.2

The swelling process of NIPA gels was again very simple and was nicely reproduced by the TF theory. The results are listed in Table 2. As expected, D_{sw} did not depend on T_i, and the values of D_{sw} were very close to those of NIPA/AAc gels. These results agree well with those reported by Sato-Matsuo and Tanaka.[25]

4. Conclusion

The kinetics of swelling/shrinking for cylindrical gels made of weakly charged NIPA/AAc copolymer gels and of uncharged NIPA homopolymer gels was investigated as a function of time after a T-jump. In the case of NIPA/AAc gels, a three-stage shrinking process was observed. Stage I is a shrinking process from swollen to swollen phase, characterized by an exponential reduction in the gel diameter. In stage II, however, squeezing took place from both ends of the cylindrical gel, while the diameter of the gel in the swollen part remained constant. After the squeezing fronts from both sides met, the gel diameter decreased rather linearly with time. This unique behavior of gel shrinking was explained on the basis of the concept of microphase separation, characteristic of weakly charged gels in a poor solvent, and spatial inhomogeneities. In the case of NIPA neutral gels, the shrinking process was greatly decelerated by phase separation.

On the other hand, both types of gels showed the same swelling behavior, i.e., a single-exponential-type swelling behavior, which is in the context of the Tanaka–Fillmore theory of gel kinetics. The cooperative diffusion constant did not depend on the initial temperature as long as the destination temperature was fixed. This clearly indicates that the chain dynamics in a gel is simply governed by the destination temperature of the T-jump.

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