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Shrinking Kinetics of Poly(*N*-isopropylacrylamide) Gels *T*-Jumped across Their Volume Phase Transition Temperatures

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ABSTRACT: The shrinking kinetics of poly(*N*-isopropylacrylamide) aqueous gels due to temperature jumps (*T*-jumps) across its volume phase transition temperature has been investigated as a function of the monomer concentration (C_{NIPA}), the destination temperature (T_{d}), and the cross-linker concentration (C_{BIS}). The following facts were disclosed. (1) The shrinking rate is T_{d} dependent and is slowest for $40 \leq T_{\mathrm{d}} \leq 45$ °C. (2) By reducing C_{NIPA} to the lowest concentration for gel formation (i.e., $C_{\mathrm{NIPA}} \approx 300$ mM), an anomalous rapid shrinking is observed. (3) The shrinking rate becomes smaller with increasing C_{BIS}. (4) Whenever a rapid shrinking takes place, characteristic changes in morphology, i.e., bubble formation, are observed on the surface of the gel. A mechanism of rapid shrinking of gels is proposed by taking account of bubble formation and phase separation.

1. Introduction

Responsive gels, such as temperature-sensitive and pH-sensitive polymer gels, have been developed for applications to drug delivery systems and actuators.[1] Poly(*N*-isopropylacrylamide) (NIPA) gels have been most extensively studied as a temperature-sensitive gel.[2,3] One of the drawbacks is that the rate of response is rather slow (a few hours for a millimeter-sized gel). This is, in principle, due to the fact that the kinetics of gel swelling and shrinking is governed by cooperative (collective) diffusion of the gel network.[3,4] Recent experimental studies, however, have shown that the rate of gel shrinking can be accelerated by designing special gels, such as (i) a gel which has a strong shrinking tendency introduced by dangling chains,[5−7] (ii) microporous gels prepared by γ-ray irradiation,[8] or (iii) a gel having a pathway for water molecules by incorporating hydrophilic chains or a high degree of porosity.[9] In the case of (i), a dangling chain in a gel can easily collapse by an external stimulus because one side of the dangling chain is free. With regard to (iii), Hirotsu developed a NIPA gel, for which the shrinking rate is 10^6 times faster than that for the conventional NIPA gels.[9] This gel was prepared from an NIPA monomer solution in the presence of poly(acrylamide) (PAAM). Although the hydrophilic PAAM chains are physically trapped in the NIPA network, the PAAM chains are thought to serve as a water reservoir as well as a pathway for rapid shrinking. However, the mechanism for rapid shrinking in the methods described above has not been fully elucidated. In addition, studies on the destination temperature, T_{d}, dependence of shrinking kinetics have seldom been reported in the literature although the shrinking rate is known to be affected by T_{d} of temperature jump (*T*-jump).

In our previous paper,[10] we discussed the shrinking/swelling behavior of cylindrical gels made of poly(*N*-isopropylacrylamide-*co*-acrylic acid) (NIPA/AAc) and poly(*N*-isopropylacrylamide) (NIPA) upon *T*-jump across the volume phase transition temperature, T_{c}. It was found that the shrinking process of NIPA homopolymer gels was strongly decelerated due to phase separation, while the swelling process was well reproduced by the Tanaka−Fillmore theory.[11] In this paper, we discuss the shrinking kinetics of NIPA gels as a function of the destination temperature (T_{d}), the cross-linker concentration (C_{BIS}), and the monomer concentration (C_{NIPA}). Then a possible mechanism for gel shrinking will be proposed. Furthermore, the cooperative diffusion coefficient on swelling is compared with that obtained by dynamic light scattering.

2. Experimental Section

2.1. Samples. Poly(*N*-isopropylacrylamide) (NIPA) homopolymer gels were prepared by redox polymerization. Aqueous solutions of NIPA monomers were polymerized in the presence of *N*,*N*′-methylenebisacrylamide (BIS; cross-linker). The monomer concentration was varied from $C_{\mathrm{NIPA}} = 300$ to 400, 690, and 1000 mM. The cross-linker concentration was also varied from $C_{\mathrm{BIS}} = 4.00$ to 8.62, 12.8, and 31.4 mM, to study effects of C_{BIS} on shrinking kinetics. The polymerization was carried out in a micropipet of 471 μm diameter for 20 h at 20 °C. The prepared gels were cut to 5 mm long cylindrical pieces and washed with an excess amount of distilled water for several days.

2.2. Swelling Degree Measurement. The sample was immersed in a thermostated chamber filled with distilled water. The *T*-jump experiments were carried out by exchanging the circulating water of which temperatures were set to two desired temperatures (i.e., the initial, T_{i}, and the destination temperature, T_{d}). The time required for *T*-jump was about 1 min. Images of gels during *T*-jumps were captured by an inverted microscope (TMD300, Nikon) coupled with an image processor (Algas 2000, Hamamatsu Photonics), and were recorded on videotapes. The degree of swelling, d/d_0, was obtained by measuring the diameter of the cylindrical gel, d, where d_0 is the gel diameter at preparation (i.e., the mold diameter) (=471 μm). When the shape of a gel became irregular on shrinking, the maximum width of the gel was measured. The measurement was repeated at least three times and its average was used as the value of d.

3. Results and Discussion

3.1. Shrinking Process. 3.1.1. Destination Temperature Dependence. Parts a−c of Figure 1 show

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series of micrographs of gels T-jumped from $T_i = 20$ °C to different destination temperatures T_d: (a) $T_d = 35$, (b) 45, and (c) 55 °C. The monomer and cross-linker concentrations of the sample were $C_{NIPA} = 690$ mM and $C_{BIS} = 8.62$ mM. These are typical concentrations for electrophoresis.[12] In the following discussion, we use this sample as a reference gel. In the case of $T_d = 35$ °C, the gel became like a knotty tree at $t = 4.5$ min. The knots grew with time up to $t = 10$ min, followed by their gradual disappearance as the gel entered a collapsed state ($t \geq 20$ min). Note that the gel became opaque for $t \geq 15$ min, indicating the presence of phase separation. On the other hand, a completely different shrinking behavior was observed when T_d was increased to 45 °C as shown in Figure 1b. Phase separation took place at $t = 55$ s. Instead of knot formation, small bubbles were formed on the surface of the gel (100 s $\leq t \leq$ 10 min). After disappearance of bubbles, the gel shrank quite slowly. It took more than 4000 min ($\approx$70 h) for this gel to reach a shrunken state (as is shown in Figure 2 below). By further increasing T_d to 55 °C, the bubble formation became dominant ($49 \leq t \leq 55$ s) as shown in Figure 1c, and the main part (seen as a black rod) of the gel shrank concurrently. Then, the bubbles disappeared ($t \geq 67$ s). These micrographs strongly suggest that both bubble formation and phase separation are highly correlated with the shrinking kinetics of gels.

The kinetics of swelling gel was treated by Tanaka and Fillmore.[11] The time variation of gel size, e.g., the gel diameter, can be described by a single-exponential function

$$\frac{|d(t) - d(\infty)|}{|d(0) - d(\infty)|} = \frac{|d(t)/d_0 - d(\infty)/d_0|}{|d(0)/d_0 - d(\infty)/d_0|} \approx \frac{6}{\pi^2}\exp(-t/\tau) \qquad (t \gg \tau) \quad (1)$$

where $d(t)$ is the gel diameter at time t and τ is the characteristic time for swelling. Note that $d(0)$ is not necessarily equal to d_0, the gel diameter at preparation, since a gel usually swells slightly when immersed in water at $T = T_i$. It was confirmed that eq 1 is also valid for the shrinking kinetics as far as the shrinking does not accompany phase separation.[13] However, the shrinking kinetics is completely different from that predicted by Tanaka and Fillmore when the size of gel changes drastically or a phase transition is accompanied.[14] This is ascribed to the fact that the theory is limited to the linear response regime and the cooperative diffusion coefficient is assumed to be invariant upon shrinking/swelling. Tomari and Doi[15] proposed a theory for the dynamics of volume transition of gels by incorporating a free energy change upon shrinking (or swelling). Their prediction was in accord with the experiment.[14] However, the theory did not take into account such interesting phenomena as bubble formation and wrinkling. Since these phenomena, as shown in Figure 1, seem to play a major role in the kinetics of shrinking, we reinvestigate the kinetics of gel shrinking by pursuing the condition for bubble formation.

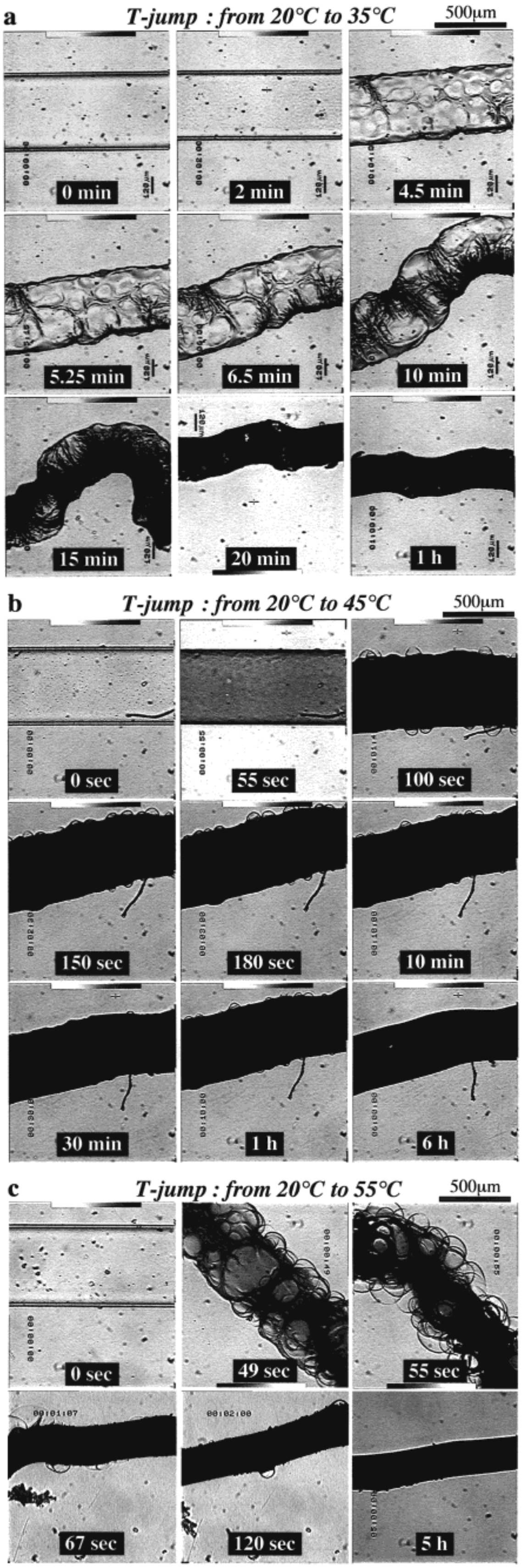

Figure 1. Series of micrographs showing the morphological changes of gels ($C_{NIPA} = 690$ mM; $C_{BIS} = 8.62$ mM) after T-jump from $T_i = 20$ °C to several destination temperatures: (a) $T_d = 35$ °C, (b) 45 °C, and (c) 55 °C.

Figure 2 shows the variation of the degree of swelling, d/d_0 ($\equiv d(t)/d_0$), of the gel ($C_{NIPA} = 690$ mM and $C_{BIS} = 8.62$ mM) after T-jump from 20 °C to several destination temperatures, T_d's. The solid lines are the fits with eq 1 for the case of $T_d = 30$ and 35 °C. The lines reproduce more or less satisfactorily the experimental results. This is the case of T_d (=30 °C) $\ll T_c$ or T_d (=35 °C) $\approx T_c$ ($\approx$34 °C).[2] In the case of T-jumps to 40, 43, and 45 °C; however, the shrinking process is decelerated by 2

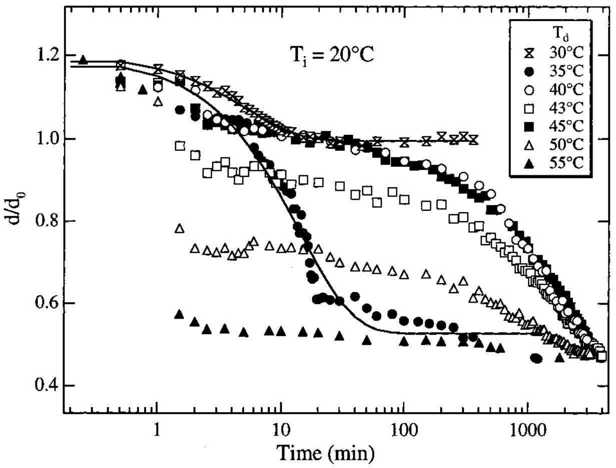

Figure 2. Variation of the degree of swelling, d/d_0, of the gel (C_{NIPA} = 690 mM and C_{BIS} = 8.62 mM) after T-jump from 20 °C to several destination temperatures, T_d's. The solid lines are the fit with eq 1.

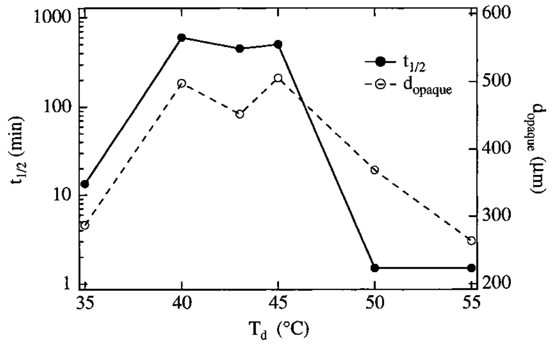

Figure 3. Destination temperature dependence of the time required for half-shrinking, $t_{1/2}$, and the gel size d_{opaque} at which the gel underwent phase separation.

orders of magnitude. Since analyses with a single-exponential function (eq 1) became no more applicable, we defined the time required for half-shrinking, i.e., $t_{1/2}$, by

$$\frac{d(t_{1/2}) - d(\infty)}{d(0) - d(\infty)} = \frac{d(t_{1/2})/d_0 - d(\infty)/d_0}{d(0)/d_0 - d(\infty)/d_0} = \frac{1}{2} \qquad (2)$$

The destination temperature dependence of $t_{1/2}$ is plotted in Figure 3. It is noteworthy that $t_{1/2}$ has a maximum in the region $40 \leq T_d \leq 45$ °C. This “slowing down” is not related to the critical slowing down discussed by Tanaka et al.[16] since our T_d is much higher than the temperatures (i.e., $T_c \approx 34$ °C) where the critical slowing down occurs. The slowing down of shrinking is due to the presence of phase separation (and/or absence of bubble formation), since it is observed when a phase separation takes place just after T-jump (See Figure 1). On the other hand, the rapid shrinking observed for T_d = 55 °C seems to be attained when a large number of bubbles are formed (Figure 1c). It is quite interesting that the “speeding-up” of shrinking took place at higher temperatures ($\gg$45 °C).

Also plotted in Figure 3 is the T_d dependence of the gel size d_{opaque} at which the gel underwent phase separation. As is shown here, the variation of d_{opaque} with T_d is similar to that of $t_{1/2}$. Hence, it is clear that the “slowing down” is due to occurrence of phase separation prior to gel shrinking. The phase separation leads to immobilization of network chains due to an increase in the mechanical modulus (i.e., the phase-separation-induced mechanical transition).[17] This results in suppression of the rate of solvent flow out of the gel. Hence, it is tempted to conclude that this immobilization is due to glass transition of poly-NIPA chains induced by an increased concentration upon phase separation. However, this speculation should be denied since the gel eventually shrinks and becomes transparent upon aging.

The “phase separation” discussed here is somewhat different from that observed in a polymer solution. Because of presence of cross-links, neither a macroscopic phase separation nor sedimentation is allowed, resulting in a localization of network chains on the order of the mesh size without a drastic change in the overall size of the gel. Ideally, the local concentration of the polymer-rich phase can reach that of the shrunken phase. The polymer fraction of the polymer-rich phase is then estimated to be 0.65−0.70, irrespective of the initial NIPA and BIS (cross-linker) concentrations. These values were obtained by volumetric measurement[18] and by differential scanning calorimetry.[19] After the phase separation, however, the gel eventually reaches the shrunken state by structural relaxation as shown in Figure 2.

3.1.2. Cross-Linker Concentration Dependence. Parts a and b of Figure 4 show series of micrographs of gels T-jumped from T_i = 20 °C to T_d = 45 °C, where (a) C_{BIS} = 4 mM and (b) C_{BIS} = 31.4 mM. The spherical object seen near the gel is a bubble, which was accidentally trapped in the sample chamber. The effect of C_{BIS} is clear from Figures 4a, 1b, and 4b. That is, in the case of low cross-linker concentrations (i.e., C_{BIS} = 4 mM), a bubble formation took place just after T-jump. This leads to a rapid shrinking. Contrary to this case, the gel with C_{BIS} = 8.62 mM (Figure 1b) and C_{BIS} = 31.4 mM (Figure 4b) showed a little (Figure 1b) or no bubble formation at all (Figure 4b). In addition, phase separation took place just after T-jump. As a result, the opaque gel kept its size for a long period of time (e.g., a few tens of hours) before reaching a uniform shrunken state.

Figure 5a shows the variation of d/d_0 with time after T-jump to 45 °C for gels prepared at different C_{BIS}'s. The behavior of the gel with C_{BIS} = 4 mM is rather exceptional. It shrinks quickly to a shrunken state, while the other gels shrank gradually with time. In Figure 5b is shown the $t_{1/2}$ vs C_{BIS} plot for gels T-jumped to several temperatures. For the case of T_d = 35 °C, the C_{BIS} dependence of $t_{1/2}$ seems to be small. However, for T_d = 45 and 55 °C, a clear C_{BIS} dependence was observed. That is, $t_{1/2}$ increased by a few hundred times when C_{BIS} was changed from 4 to 8.62 mM. This indicates that the shrinking rate is quite sensitive to C_{BIS} in this concentration range.

3.1.3. Monomer Concentration Dependence. Now, we discuss the monomer concentration dependence. Here, we varied C_{NIPA} by keeping the ratio of $C_{\mathrm{NIPA}}/C_{\mathrm{BIS}}$ fixed at 690/8.62. This means that the cross-link density is constant with respect to the network. Parts a and b of Figure 6 show a series of micrographs of gels T-jumped from T_i = 20 °C to T_d = 45 °C, where (a) C_{NIPA} = 300 mM and (b) C_{NIPA} = 1000 mM. Similar to the C_{BIS} dependence, the effect of C_{NIPA} is also clear (see Figures 6a, 1b, and 6b). In the case of (a) C_{NIPA} = 300 mM, the shrinking is governed by bubble formation (t

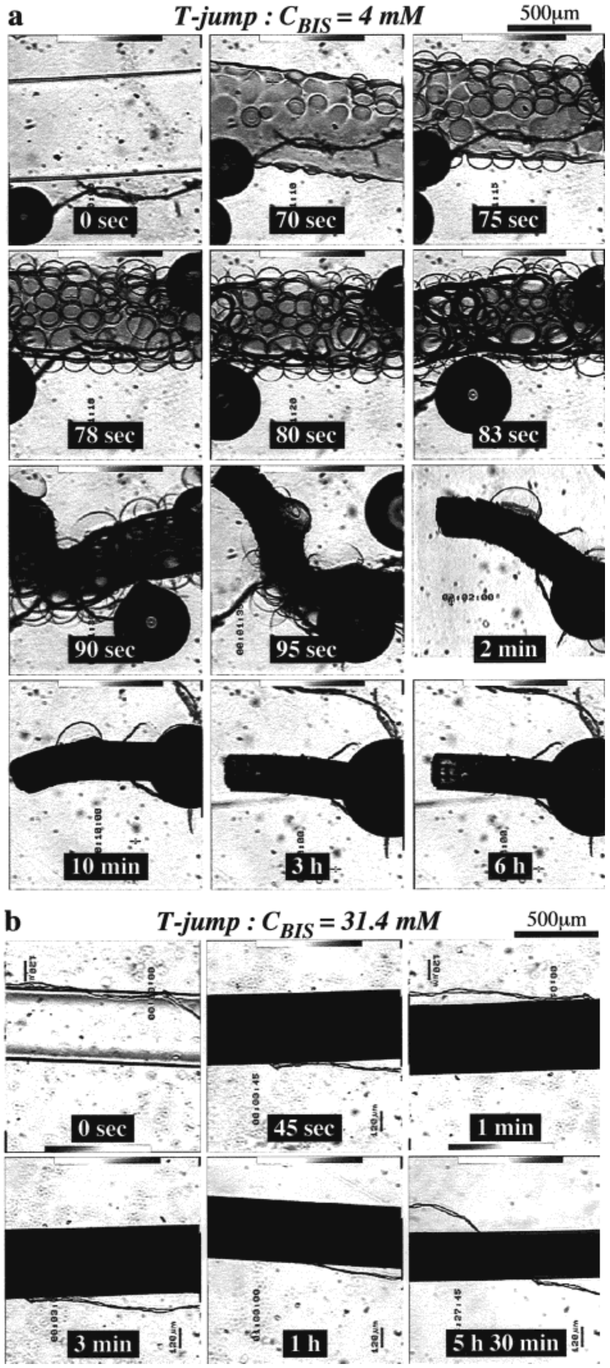

Figure 4. Series of micrographs showing the morphological changes of gels ($C_{NIPA} = 690$ mM) after *T*-jump from $T_i = 20$ °C to $T_d = 45$ °C with (a) $C_{BIS} = 8.62$ mM and (b) $C_{BIS} = 31.4$ mM. Comparison should be made with Figure 1b. Spherical objects in Figure 4a are bubbles accidentally trapped in the sample chamber.

< 85 s). When bubbles disappeared, the gel already reached a shrunken state. It should be noted that the gel became transparent after aging (≈6 h). This means that a gel eventually becomes homogeneous even in the shrunken state. This is a clear evidence that the gel at this temperature is not in a glassy state. On the other hand, no bubble formation took place at all for the gels with $C_{NIPA} = 1000$ mM (Figure 6b). The mobility of the gel network is strongly depressed just after *T*-jump ($t \geq 30$ s).

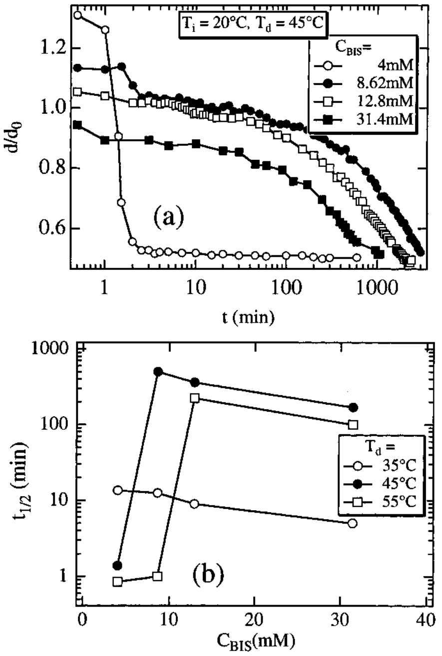

Figure 5. (a) Variation of d/d_0 with time after *T*-jump to 45 °C for gels prepared at different C_{BIS}. (b) C_{BIS} dependence of $t_{1/2}$ obtained for various T_d's.

Figure 7a shows the variation of d/d_0 with time after *T*-jump to $T_d = 45$ °C for gels prepared at different C_{NIPA}'s. As already discussed, the strong C_{NIPA} dependence is seen. That is, the NIPA gel prepared with $C_{NIPA} = 300$ and 400 mM shrank very rapidly when *T*-jumped to 45 °C. Figure 7b shows the variation of $t_{1/2}$ for *T*-jumps to $T_d = 35$, 45, and 55 °C. This implies that a rapid shrinking can be achieved for $C_{NIPA} \leq 400$ mM in the case of *T*-jump to $T_d \approx 45$ °C. Figure 7b also indicates that even for $C_{NIPA} = 690$ mM a rapid shrinking is attained by increasing T_d to 55 °C.

The findings discussed above clearly indicate that a rapid shrinking of gels can be achieved by simply reducing the monomer concentration and/or cross-linker concentration at gel preparation. Hence, it is not necessary to prepare a gel with a sophisticated chemistry[5] or to design complicated structures.[9,20] It is found that the shrinking kinetics is very sensitive to T_d, and a rapid shrinking is expected if T_d is high enough.

3.1.4. Shrinking Mechanism. Let us discuss the shrinking mechanism of NIPA gels on the basis of the experimental findings disclosed above. As shown in Figure 3, the shrinking rate was lowest for the case of $T_d = 45$ °C. It is obvious that the phase separation is strongly coupled with the shrinking kinetics. Therefore, we need to consider two types of driving forces, i.e., those for shrinking and for phase separation.

The thermodynamic driving force for shrinking is the change of osmotic pressure generated by *T*-jump. The osmotic pressure, Π ($\equiv -\partial F/V_s\partial f$), can be calculated on the basis of classical thermodynamics of swelling equilibrium for rubbers, Flory–Rehner (FR) theory, where F is the free energy of the gel and V_s is the solvent molar volume. We proposed a modified Flory–Rehner equation for gel swelling[18]

$$\frac{\Pi}{RT} = -\frac{1}{V_s}[\phi + \ln(1-\phi) + \chi\phi^2] + \nu\frac{C_0}{C_{ref}}\left[\frac{1}{2}\left(\frac{\phi}{\phi_0}\right) - \left(\frac{\phi}{\phi_0}\right)^{1/3}\right] \quad (3)$$

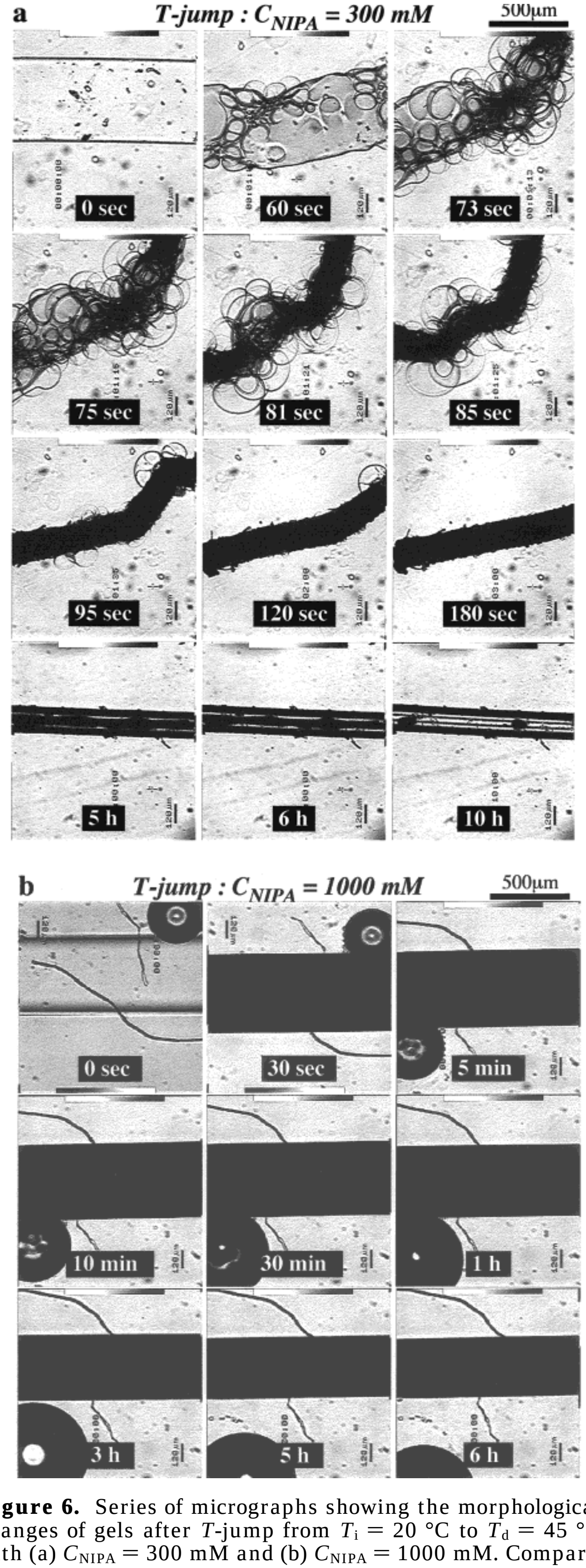

Figure 6. Series of micrographs showing the morphological changes of gels after *T*-jump from $T_i = 20$ °C to $T_d = 45$ °C with (a) $C_{NIPA} = 300$ mM and (b) $C_{NIPA} = 1000$ mM. Comparison should be made with Figure 1b. Note that C_{BIS} was also varied, keeping the ratio of C_{NIPA}/C_{BIS} fixed.

where *R* is the gas constant, χ is Flory's interaction parameter, and ν is the number of cross-links in the network at preparation, respectively. In eq 3, the factor, C_0/C_{ref}, takes account of topological constraints, where C_0 is the gel concentration at preparation and C_{ref} is the reference concentration. The details of the theory are given elsewhere.[18] By imposing a constraint $\Pi = 0$, one obtains the equilibrium swelling ratio, $\phi/\phi_0 \equiv (d/d_0)^3$ as a function of temperature. Figure 8 shows the result of experimental (open squares) and theoretical shrinking curves (dashed line) for NIPA gels with $C_{NIPA} = 690$ mM and $C_{BIS} = 8.62$ mM (open squares). As shown in the figure, the theoretical curve well reproduces the experimental shrinking curve. The left ordinate is the thermodynamic driving force for shrinking, i.e.

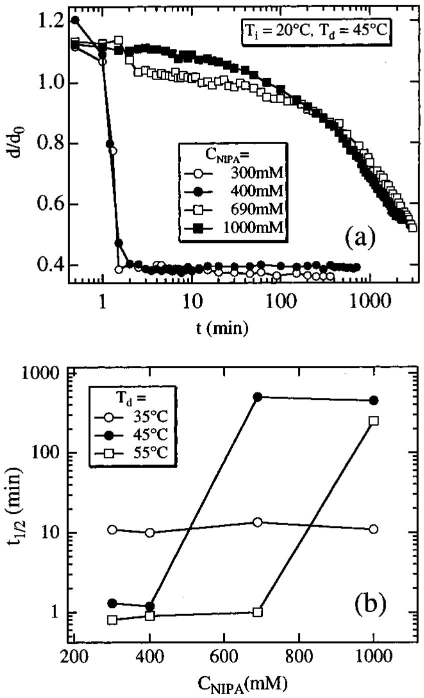

Figure 7. (a) Variation of d/d_0 with time for gels prepared at different C_{NIPA}'s. (b) C_{NIPA} dependence of $t_{1/2}$ obtained for various T_d's.

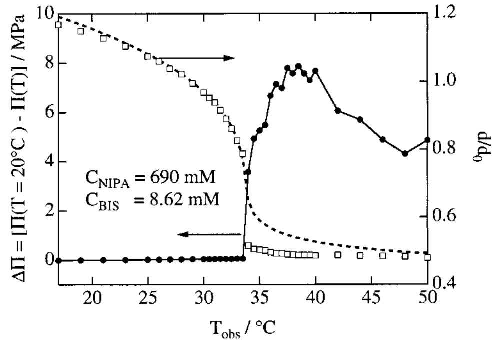

Figure 8. (Right axis) Temperature dependence of the equilibrium linear swelling ratios, experiment (open squares) and theory (dashed line). (Left axis) T_d dependence of the thermodynamic driving force, $\Delta\Pi(T_d)$, generated by *T*-jump from 20 °C. The parameters used for the theoretical calculation are given in ref 18.

$$\Delta\Pi(T) = \Pi(T) - \Pi_{noneq} \qquad (4)$$

where $\Pi(T)$ is the osmotic pressure at *T* and Π_{noneq} is the value with $\phi = \phi_{20°C}$. The variation of $\Delta\Pi$ indicates that a strong shrinking force ($\Delta\Pi > 0$) is generated by *T*-jump for $T > 34$ °C as far as the volume of the gel is the same as that at $T = 20$ °C. The value of Π evaluated from eq 3 is around 40 kPa for $T < T_c$, which reasonably agrees to the values reported by Geissler et al. for PAAM gels[21] On the other hand, $\Delta\Pi$ becomes an order of MPa by *T*-jump to $T_d > T_c$. However, phase separation takes place around T_c. This leads to the slowing down of shrinking kinetics by a factor of more than 100.

Kinetics of volume change can be described by

$$\frac{\partial f}{\partial t} = -\nabla \cdot D(\phi, T)\left(-\nabla \frac{\delta F}{\delta \phi}\right) \quad (5)$$

where D is the diffusion coefficient governing phase separation and $-\delta F/\delta\phi$ is the variation of the free energy of the system with respect to the local polymer concentration ϕ. The D is an increasing function of T since D is inversely proportional to the viscosity of the system. Note that T dependence of D also arises from the T dependence of ϕ. The nth mode characteristic time for shrinking, τ_n is given by[22]

$$\tau_n = d^2(\infty)/(4n^2\pi^2 D) \quad (6)$$

Therefore, its slowest relaxation time, τ_1 ($\approx t_{1/2}$) is an increasing function of T. This may be the reason a speeding-up effect becomes dominant for $T_d > 46$ °C. Therefore, it can be concluded that the slow shrinking (for $T_c < T_d < 46$ °C) is governed by phase separation and the subsequent speeding-up (for $T_d > 46$ °C) is a result of the temperature dependence of D. We had to give up a more quantitative discussion on the T dependence of $t_{1/2}$ since the functional form of $D\{\phi(T)\}$ is unknown.

In the case of gels with lower monomer concentrations, a phase separation leads to a rapid shrinking compared to gels with high C_{NIPA}. This is due to the presence of a large number of loops and dangling chains, which can respond to a drastic temperature change and shrink like a polymer chain with free ends. An increase in spatial inhomogeneities was observed by dynamic light scattering by Norisuye et al.[23] When C_{NIPA} was lowered to 100 mM while keeping $C_{BIS} = 8.62$ mM, a power law behavior was observed in the time−intensity correlation function. This indicates the presence of self-similar clusters with size distribution over 5 orders of magnitude. Though such a power law behavior disappears with increasing C_{NIPA}, it is easily expected that considerable amounts of defects (loops and dangling chains) are still present in the network at low C_{NIPA}'s. The rapid shrinking may accompany a characteristic change in morphology, such as bubble formation. Hence, we believe that the bubble formation is an evidence of inhomogeneous network structure characterized by a large population of loops and dangling chains. This allows the solvent to find many paths outgoing from the gel. Some of the fluxes may be captured by the outmost layer of the network, resulting in bubble formation. With increasing C_{BIS} and C_{NIPA}, the degree of completeness of a network structure becomes higher and the population of chains with free ends dwindles. Therefore, such bubble formation is not observed unless T_d is further enhanced to gain the mobility (i.e., a further increase in D). These are the reasons why $t_{1/2}$ has a unique T_d dependence.

3.2. Swelling Kinetics. We carried out a series of swelling experiments from various initial temperatures, T_i, to one destination temperature, $T_d = 20$ °C. Figure 9 shows a series of micrographs of a gel undergoing swelling after a T-jump with $T_i = 55$ °C. Although no bubbles are formed, a characteristic pattern appears on the surface. The characteristic size of the pattern grows with time at the beginning ($0 < t < 3$ min), followed by a uniform swelling ($t > 10$ min). Note that the swelling front is also seen at $t = 3$ min. Hence, it is clear that the swelling kinetics is quite different from the shrinking kinetics. A similar phenomenon was observed in spherical gels by Sato-Matsuo et al.[14] and was explained as buckling of the surface due to swelling at the surface with the inner part remaining in the shrunken state.[14,24] Hence, we will not discuss further the morphological change of gels upon swelling.

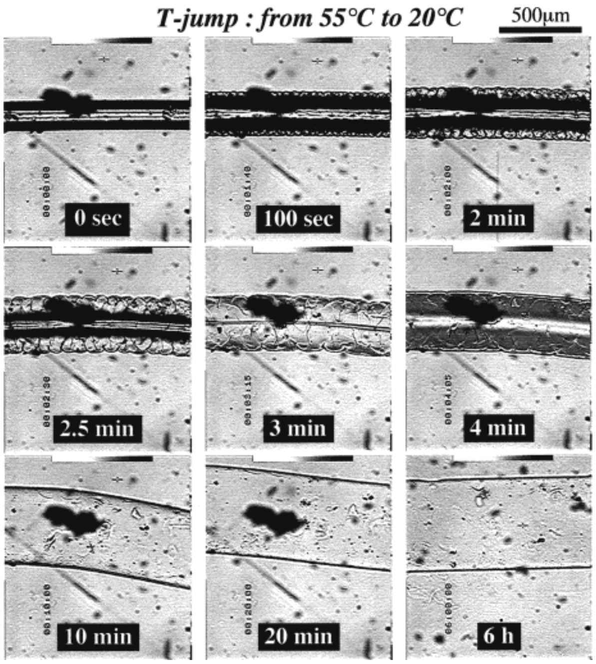

Figure 9. Series of micrographs showing the morphological changes of gels ($C_{NIPA} = 400$ mM and $C_{NIPA} = 5.00$ mM) during swelling after T-jump from $T_i = 55$ °C to $T_d = 20$ °C.

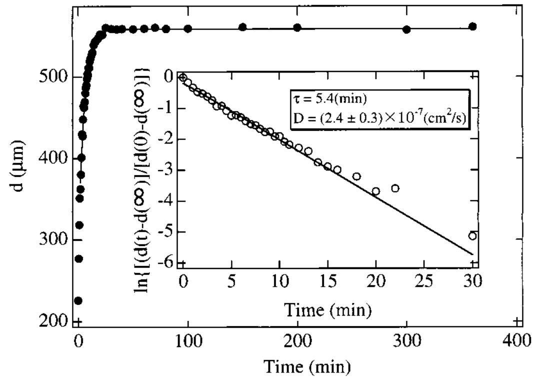

Figure 10. Variation of the gel diameter after T-jump from $T_i = 40$ to $T_d = 20$ °C for the gel with $C_{NIPA} = 690$ mM and $C_{NIPA} = 8.62$ mM. The inset is the semilogarithmic plot of the same data. The lines are the fit with eq 1.

Figure 10 shows a result of swelling kinetics, where a T-jump from 40 to 20 °C was carried out for a gel with $C_{NIPA} = 690$ mM and $C_{BIS} = 8.62$ mM. The data points nicely fell on the theoretical curve (eq 1), from which the cooperative diffusion coefficient was estimated to be $D = (2.4 \pm 0.3) \times 10^{-7}$ cm^2/s. This value is somewhat smaller than the cooperative diffusion coefficient obtained by dynamic light scattering (DLS) ($D = (4.38 \pm 0.02) \times 10^{-7}$ cm^2/s),[25] Variation of D with T_i for gels prepared with different monomer and cross-linker concentrations was also investigated. It was found that, unlike the shrinking process, the swelling kinetics was

Table 1. Comparison of the Diffusion Coefficients of the Gel with $C_{NIPA} = 690$ mM and $C_{BIS} = 8.62$ mM Obtained by Swelling/Shrinking Kinetics and by DLS

	from swelling/shrinking kinetics, D_{sw}(cm^2/s)	
T-jump	D_{sw} (10^7 cm^2/s)	$D_{sw}{}^0 \equiv 3D_{sw}/2$ (10^7 cm^2/s)
from 20 to 30 °C	1.7 ± 0.3	(2.50 ± 0.5)
from 30 to 20 °C	2.4 ± 0.3	(3.63 ± 0.5)

	from DLS, D_{DLS} (10^7 cm^2/s)	
T-jump	reactor-batch gel	swollen gel
30 °C	3.62 ± 0.02	
20 °C	4.48 ± 0.02	4.61 ± 0.02[a]

[a] Data taken from ref 34.

rather insensitive to the initial temperature T_i, in accord with Sato-Matuo and Tanaka.[14] The values of D were in the range of $(2-3) \times 10^{-7}$ cm^2/s.

3.3. Comparison of the Cooperative Diffusion Coefficients Obtained by Swelling Measurement and by Dynamic Light Scattering. Now let us compare the cooperative diffusion coefficients obtained by two methods, i.e., by dynamic light scattering (DLS) and by swelling experiment. Tanaka and Fillmore found a good agreement between the values of D obtained by the two methods ($D_{sw} = 3.2$ cm^2/s and $D_{DLS} = 3(\pm 0.5)$ cm^2/s) for PAAM gels with $C_{AAM} = 690$ mM and $C_{BIS} = 8.62$ mM.[11] Although their observation temperature was not given in the paper, it is expected to be around 25 °C (i.e., room temperature). This agreement, however, was obtained ignoring the nonergodic nature of gels. In other words, their DLS data were analyzed by assuming homodyne scattering, which leads to underestimation of D_{DLS} by a factor of up to 2. Geissler and co-workers pointed out this issue and proposed a heterodyne analysis.[26−28] As pointed out by Pusey and van Megen,[29] gels are nonergodic media. Hence, scattering intensity from a gel contains a large contribution of heterodyne scattering. Therefore, the contribution of heterodyne scattering has to be taken into account to evaluate D_{DLS}.[30,31]

Peters and Candau.[32] also reported a good agreement between D_{DLS} and D_{sw}. However, the important concept, i.e., the nonergodic nature of gels, was not introduced at the time of the works of refs 11 and 32. Hence, it is worth reconsidering this problem by taking account of the nonergodic nature of gels. We carried out two experiments on the gel ($C_{NIPA} = 690$ mM, $C_{BIS} = 8.62$ mM) in the opposite T-jump directions, i.e., from 20 to 30 °C and from 30 to 20 °C. The results are given in Table 1. The obtained values of D ($=D_{sw}$) were compared with those ($=D_{DLS}$) by DLS measurement at 20 and 30 °C. The values of D_{DLS} are about two times larger than those of D_{sw}. According to Li and Tanaka,[33] D_{sw} is dependent also on the shape of the gel, i.e., $D_{rod} = 2D/3$ (for a long narrow rod) and $D_{disk} = D/3$ (a thin disk). Since our gels were threadlike rod gels, the values of D_{sw} have to be corrected by multiplying by $^3/_2$, i.e., $D_{sw}{}^0 \equiv 3D_{sw}/2$ (shown in parentheses). Though the value of $D_{sw}{}^0$ becomes closer to D_{DLS} by this correction (25−45% smaller compared to D_{DLS}), there is still some discrepancy between $D_{sw}{}^0$ and D_{DLS}. Note that the value of $D_{sw}{}^0$ obtained for the T-jump from 20 to 30 °C (from 30 to 20 °C) has to be compared with D_{DLS} at 30 °C (at 20 °C).[34] Another fact, that the DLS measurement was conducted not for a swollen gel at equilibrium but for a reactor-batch gel, should be also considered. However, because the obtained value of D_{DLS} for a swollen gel, listed on the right column,[34] is very close to the one for a reactor-batch gel in this particular case (i.e., for the gel with $C_{NIPA} = 690$ mM, $C_{BIS} = 8.62$ mM), this cannot be the reason for the disagreement.

The theory of swelling kinetics[11] is constructed on the basis of several assumptions, such as (i) ignorance of the shear modulus, μ, and (ii) invariance of D with respect to temperature and/or the degree of swelling during swelling process, which certainly affect the evaluation of D_{sw}. With regard to (i), the diffusion coefficient is given by $D \equiv \{K + (^4/_3)\mu\}/f \equiv M_{os}/f$, where M_{os} and f are the osmotic modulus and the friction coefficient of the network, respectively. According to Peters and Candau,[32] the value of μ/M_{os} can be 0.3 or higher in many cases, so that the upward correction of D_{sw} by about 30% is reasonable. Though a direct evaluation of μ for the gels is necessary, the agreement of the diffusion coefficients obtained by the two methods seem to be reconfirmed at the same time.

4. Conclusion

Shrinking and swelling experiments were carried out on a series of NIPA gels prepared from several monomer (C_{NIPA}) and cross-linker (C_{BIS}) concentrations, where the initial (T_i) and destination temperatures (T_d) were chosen below and above the volume phase transition temperature. It was found that the shrinking rate was decelerated by more than 100 times due to phase separation. The shrinking rate was lowest for the case of $T_d \approx 45$ °C. For $T_d \gg 45$ °C, on the other hand, the shrinking became faster. This simply results in a high mobility of chains at elevated temperatures.

A gel with low monomer concentrations exhibited a faster shrinking compared to gels with high C_{NIPA}. This is due to presence of a large number of loops and dangling chains in the gel, which can shrink relatively freely without the constraint of cooperative motion of gels. It was also found that a rapid shrinking accompanies a morphological change, i.e., bubble formation.

In the swelling process, on the other hand, no significant T_i dependence was observed. This simply indicates that the gel swelling is mainly governed by the diffusion of incoming flux of the solvent and cooperative diffusion of the network chains at T_d. This means that the kinetics is solely dependent on T_d.

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