Deswelling Kinetics of Poly(*N*-isopropylacrylamide) Gels at Volume–Phase Transition

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ABSTRACT: Shrinking kinetics after volume–phase transition was investigated for poly(*N*-isopropylacrylamide) (PNIPA) gels. Just after the temperature (T) jump beyond the transition temperature, the phase separation occurs in the gel specimen and simultaneously the gels shrink rapidly. PNIPA gels still continue to shrink with time, but the rate of shrinking is very small. In the course of the slow shrinking, homogenization also proceeds until equilibrium state is achieved. The relaxation time for the slow shrinking (τ_A) and the time required for the complete homogenization (t_a) are long, but the ratio of τ_A to t_a remains almost constant for the gels. The slow kinetics in shrinking reflects the deswelling properties of the gels in the collapsed state.

KEY WORDS Poly(*N*-isopropylacrylamide) Gel / Deswelling / Kinetics / Volume–Phase Transition / Phase Separation /

As well known, some kinds of polymer gels exhibit a volume–phase transition.¹ Extensive studies¹ have been made to clarify the physics of the phase transition of polymer gels, since Tanaka discovered that poly(acrylamide) gels in a mixture of water and acetone change the volume discontinuously around a certain solvent composition.² Theoretically, it is also shown³ that the transition can be described semi-quantitatively by the classical theory on the basis of the Flory-type free energy. The volume–phase transition for poly(*N*-isopropylacrylamide) (PNIPA) gels is realized by changing temperature, an easier variable to be controlled. The PNIPA gel is a better system for detailed studies on the volume–phase transition and actually has been used widely by many research groups.¹ The transition temperature for PNIPA gels is close to the room temperature, and the gels exist in the swollen state below the transition temperature, while above the transition temperature the gels are in the collapsed state.

Equilibrium properties of PNIPA gels both in swollen and collapsed states have become clearer at present,¹ and it is also well recognized that the swelling dynamics of the gels agrees well with the prediction from the linear theory^{4–6} as long as swelling (or deswelling) ratio is small enough. However, the dynamical properties in the volume–phase transition,⁷ which is accompanied by large volume change, remains unclear. In this study, kinetics in the course of shrinking after the volume–phase transition was investigated for PNIPA gels.

EXPERIMENTAL

PNIPA gels were prepared in water by radical polymerization of *N*-isopropylacrylamide (NIPA) using ammonium peroxodisulfate as an initiator and *N,N'*-methylene-bis(acrylamide) (BIS) as a crosslinker. The agent (*N,N,N',N'*-tetramethylethylenediamine) was used as an accelerator. Two types of PNIPA gels differing in NIPA concentration (c_0 ; $c_0=10$ and 15 wt% in this study) were prepared, but the molar ratio of BIS to NIPA

was fixed to be 1.66×10^{-2} for both types of gels. The gelation was performed in thin glass tube at 20°C for 24 h to obtain cylindrical gels. After gelation, the gels were washed and then kept in water at 25°C until equilibrium swelling was achieved. Gels at equilibrium were transparent, and the polymer concentration (c) at 25°C was 8.3 wt% for the gel prepared from the (pre-gel) solution with $c_0=10$ wt% and $c=11.0$ wt% for the gels with $c_0=15$ wt%. The specimens, with diameter (A) of *ca.* 500 μm and length of about 20 mm in the swollen state, were used for optical microscopy. For the microscopic observation, specially designed double-jacket water bath was used. The volume of water in the bath was *ca.* 3 cm^3 , and the temperature was controlled within $\pm 0.2^\circ\text{C}$. The temperature (T) jump was applied by transferring the gel specimen kept in water at T_i (initial T) into the water controlled at the temperature T_f (final T). Just after T jump, equilibration of the temperature within the gel specimens occurred very shortly compared with the time scale in this experiment. The water bath was equipped with an optical microscope (Nikon XTP-11) and A of the specimens after T jump was recorded using a video camera.

RESULTS AND DISCUSSION

Figure 1 shows the T dependence of the volume (V) for the cylindrical PNIPA gel prepared from the solution with $c_0=10$ wt%. Here, $V_\infty(T)/V_\infty(25)$ indicates the ratio of volume at T to that at 25°C, and was calculated from the values of equilibrium diameters at T and 25°C assuming that the change in size is isotropic. The volume ratio decreases gradually with increasing T in the region of T much lower than about 34°C, and shows a discontinuous change at about 34°C, indicating that the volume phase transition occurs around the temperature on heating. At T higher than the transition temperature (T_{tr}), the T dependence of the volume becomes very weak. The data points at high temperatures are a little scattered. This originates from the fact that the ratio

Figure 1. Plots of volume (V) against temperature (T) for PNIPA gel with $c_0 = 10$ wt%.

Figure 2. Optical micrographs for PNIPA gels with $c_0 = 10$ wt% before and after temperature jump from 24.5 to 51.0°C. Photograph (I) $A = 515 \mu\text{m}$ before temperature jump, (II) $A = 296 \mu\text{m}$ at 300 s after temperature jump, (III) $A = 245 \mu\text{m}$ at 36600 s, (IV) $A = 228 \mu\text{m}$ at 79800 s. A stands for the diameter of the gel specimen.

is plotted in the logarithmic scale. Actual deviation is not so large and the data upon cooling agree fairly well with those obtained on heating in the entire range of T examined. Usually, a hysteresis loop is observed on the V - T diagram of the gels showing a discontinuous volume-phase transition.¹ However, no hysteresis behavior was observed for the PNIPA gels examined in this study. This appears to be related to the stable range of temperature for the experimental apparatus. As stated in the experimental section, the water bath used in this study was stable to $\pm 0.2^\circ\text{C}$. The T window for the hysteresis may be too narrow, within $\pm 0.2^\circ\text{C}$, to be detected for the PNIPA gels. Similar curve was obtained for the PNIPA gel with $c_0 = 15$ wt%, but the curve did not show a discontinuity.

Figure 2 shows the transmission micrographs of the PNIPA gel with $c_0 = 10$ wt% before and after T jump. The gel at the initial temperature (T_i , in this case $T_i = 24.5^\circ\text{C}$) was transparent (photograph I). By the T jump to $T_f = 51.0^\circ\text{C}$, the specimen turn opaque and

Figure 3. Time dependence of the diameter of the cylindrical PNIPA gel (A) and the diameter of the black region in the gel shown in Figure 2 (a). Temperature jump applied is 24.5 to 51.0°C. Open symbols stand for A and filled symbols for a .

shrunk rapidly. In the course of shrinking, bubbles were observed on the surface of the gel. The bubbles, however, disappeared and the original (namely, cylindrical) shape recovered in a few minutes after T jump, although the color remained white (black in the figure, photograph II). The reduction in size was large in this process (in the time course from photograph I to II). As elapsed time increases further, the transparent domain emerges from the circumference and extends to the central region of the gel (photograph III). At this stage, A still continues to decrease. At about $t = 8 \times 10^4$ s, the whole gel recovers the transparency (photograph IV).

The T jump in this experiment is considered to occur almost under isochoric condition, and moves the system to the unstable region, causing the phase separation in the gel. Photograph II corresponds to the phase-separated state for the gel. Of course, the phase separation occurs not in global scale but in local scale, although the length of heterogeneity is larger than the wavelength of visible light. Two phases, polymer-rich and solvent-rich phases, coexist in the whole gel. Then, the system goes isothermally toward the isobar, which accompanies the reduction in dimension of the specimen. The decrease continues until equilibrium state corresponding to the isobar where osmotic pressure is vanished is achieved. At equilibrium, the whole gel recovers the homogeneous structure, namely, the homogenization is completed at the isobar (photograph IV). Since the homogenization requires draining of solvent, the homogeneous domain occurs from the circumference and extends in the inner direction with time. The transparent area (outer region of the gel) in photograph III corresponds to the homogeneous domain occurring in the course of shrinking. The homogeneous domain acts as a membrane through which water molecules are pumped out from the phase-separated domain in the course of shrinking, and c will be kept almost constant throughout the shrinking in the homogeneous domain.

In Figure 3 the time (t) dependence of A for the gel in Figure 2 is shown. The figure also contains the time dependence of the diameter (a) of the black region in Figure 2 (a). A large decrease of A occurs at $t = 0$, indicating the existence of the rapid shrinking process for the gel. The rapid shrinkage is observed as a vertical drop of A at $t = 0$, because the time scale in the figure is very large compared with that for the rapid shrinkage. After the large decrease at short times, the gel continues to shrink, although the rate of shrinking is very slow.

Figure 4. Semi-logarithmic plots of $\Delta A/\Delta A_0$ for PNIPA gel shown in Figure 3. Line is determined by the method of least squares.

Table I. Initial NIPA concentration (c_0), final temperature (T_f), equilibrium diameter (A_∞), relaxation time (τ_A), the time for complete homogenization (t_a), and the ratio $\Delta A_0^+/\Delta A_0$ for PNIPA gels

$c_0/\text{wt}\%$	$T_f/^\circ\text{C}$	$A_\infty/\mu\text{m}$	$\tau_A/10^4\text{ s}$	$t_a/10^4\text{ s}$	$\Delta A_0^+/\Delta A_0$
10	38.5	212	3.6	11	0.77
10	51.0	228	3.0	6.9	0.26
10	64.0	209	2.2	5.5	0.32
15	40.0	247	2.5	~7	0.91
15	50.1	236	2.5	6.5	0.84
15	57.8	242	2.1	5.0	0.63
15	64.8	240	1.5	3.5	0.62

This process corresponds to the change in photograph III to IV in Figure 2. At $t = 7 \times 10^4$ s, A becomes constant and approaches zero. The time at which $a=0$ is designated as t_a . As can be seen from the photograph III in Figure 2, a depends on the position measured, but large difference was not observed for the value of t_a measured at several points; the difference lay within $\pm 10\%$. This means that t_a gives the quantitative information on the rate of the homogenization of the gel. Similar behavior was observed for the other PNIPA gels examined in this study. Figure 4 represents a semi-logarithmic plot of $\Delta A/\Delta A_0$ against t for the PNIPA gel shown in Figure 3. Here, ΔA and ΔA_0 are defined using the initial and final values of A (A_0 and A_∞ , respectively) as

$$\Delta A = A - A_\infty \quad (1)$$

$$\Delta A_0 = A_0 - A_\infty \quad (2)$$

The data points at long times, which lie in the slow shrinking process, fall on a single line, and then we can estimate the longest relaxation time (τ_A) for the slow shrinking. The value of τ_A for the PNIPA gel is 3.0×10^4 s.

Table I summarizes τ_A and t_a together with the values of the other quantities (c_0 , T_f and A_∞) for the PNIPA gels. Both τ_A and t_a tend to decrease with increasing T_f for both types of gels, although τ_A at $T_f = 40.0$ and 50.1°C is identical to each other. However, the ratio t_a/τ_A for the gels remains almost constant lying in the range of 2–3. Assuming that the collective diffusion constant of the polymer network (D) is related to τ_A and A_∞ as

$$D \sim A_\infty^2/\tau_A \quad (3)$$

we can estimate the order of magnitude of D , although the validity of above relation is limited to the homogeneous system. It is shown by the simple calculation that, for the PNIPA gels, D is very small, in the order of $10^{-8}\text{ cm}^2\text{ s}^{-1}$. In some cases, slow dynamics can be observed as a result of the critical slowing-down,⁷ but clearly the slow dynamics observed in this study is not due to the critical slowing-down because the temperature range measured here is far from the transition temperature T_{tr} . We have shown⁸ that stress relaxation induced by re-swelling by the application of deformation^{9,10} occurs in the collapsed state of the PNIPA gels. The relaxation time for the stress relaxation cannot be compared directly with that obtained in this study, because the samples are different in size. Converting the relaxation time for the stress relaxation to D in terms of the relation (eq 3), comparison can be made for the dynamical properties of the gels in the collapsed state measured by the different experiments. The value of D estimated by the stress relaxation⁸ was also almost independent of temperature in the collapsed state and was in the order of $10^{-8}\text{ cm}^2\text{ s}^{-1}$, which agrees well with the order of the value obtained here. This suggests that the slow dynamics observed in this study is inherent in the swelling properties of the collapsed gels. We can also define the quantity $\Delta A_0^+/\Delta A_0$, which corresponds to the intercept of the line in the semi-logarithmic plots at $t=0$ (see, for example, Figure 4), and characterizes the degree of rapid shrinking. The values for the PNIPA gels are also tabulated in Table I. Although the order is inverted for the gels with $T_f = 51.0$ and 64.0°C , $\Delta A_0^+/\Delta A_0$ appears to decrease with increasing T_f for both types of gels. The value is rather low for the gels with $c_0 = 10\text{ wt}\%$ at high T_f .

CONCLUSIONS

The kinetics in shrinking after volume-phase transition was investigated for PNIPA gels in water. Just after T jump beyond the transition temperature, the gels underwent phase separation and also showed a rapid shrinkage. The gels continued to decrease as elapsed time increases further. Simultaneously, homogenization of the gels proceeded until equilibrium state was achieved. The values of τ_A and t_a were large, but the ratio was kept almost constant. The slow kinetics in the shrinking process is inherent in the deswelling properties of the gels in the collapsed state.

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