

## Kinetics and Phase Transition of Polymer Gels Under Mechanical Constraint

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We investigated the kinetics of volume change and the phase transition of thin-plate poly(*N*-isopropylacrylamide) gels under mechanical constraint along the surface (biaxial constraint). The bottom and/or top surfaces were chemically clamped on the glass slides, and the gel can swell and shrink only along the thickness direction in response to the temperature change. The swelling properties were discussed by comparing the data with the equation of states of gels on the basis of the Flory type free energy under the biaxial mechanical constraint. The characteristic time for the swelling process is compared with the prediction of the collective diffusion of the polymer network.

Key words: poly(*N*-isopropylacrylamide), biaxial mechanical constraint, kinetics, swelling ratio, volume phase transition, relaxation

### 1. INTRODUCTION

It has been well established that the kinetics of gel swelling and shrinking is governed by the collective diffusion of the polymer network relative to the solvent [1]. The kinetics is related to the elasticity (bulk modulus and shear modulus) as well as the friction between the polymer and the solvent [1-7]. The equation of motion of gel network was developed by Tanaka and Fillmore (TF) to describe the swelling kinetics of spherical gels for the case of zero shear modulus [1]. This TF model predicts that the relaxation time  $\tau$  of a spherical gel is proportional to the square of the diameter  $d$  and is inversely proportional to the collective diffusion constant,  $D$ :  $\tau \propto d^2/D$ . In accordance with this kinetic theory, a single exponential decay with time has been experimentally confirmed, which is valid for spherical, cylindrical, and disc gels [1-3]. The experimental results are qualitatively consistent with the theory, which is related to the fact that the swelling and shrinking of gels are isotropic and the gel can freely swell and shrink along the three-dimensional direction. On the other hand, the experimental observation has not been reported so far on the one-dimensional swelling and shrinking of gels under mechanical constraint.

In this paper, we report the swelling behavior and the kinetics of thin-plate poly(*N*-isopropylacrylamide) (NIPA) gels with rectangular surfaces under mechanical constraint. The swelling and shrinking were restricted along the two-dimensional direction in the surface; the gel could only swell and shrink along the one-dimensional thickness direction. The static swelling ratio was measured as a function of temperature including the transition temperature. The results were compared with the equation of state of gels under mechanical constraint. The time evolution of the thickness between two different swollen states was measured by abruptly changing the temperature. The effects of the gel sizes (surface lengths and thickness) on the kinetics were investigated on the swelling and shrinking processes. We discussed the phase transition of gels under the biaxial mechanical constraint in two different manners.

### 2. EXPERIMENTAL PROCEDURE

The thin-plate gels were prepared in water by a free radical polymerization reaction at the ice temperature [8] between two glass slides (for an optical microscope, 26.0 X 76.0 mm<sup>2</sup>) separated by thin spacers. The mixture of purified NIPA (main constituent, 7.8 g, Kohjin), *N,N'*-methylenebisacrylamide (cross-linker, 0.133 g, Wako), and *N,N,N',N'*-tetramethylethylenediamine (accelerator, 240  $\mu$ l, Wako) were dissolved in pure water (100 g, deionized and distilled water). After being fully saturated with nitrogen, the pregel solution was stored at the ice temperature, and the ammonium persulfate (0.04 g, Wako) was added to the solution to initiate the polymerization. The pair of two slides with spacers was immediately inserted into the solution. The pregel solution was brought into the thin space by capillary action. In order to chemically clamp the gel on the slides Bind Silane (Pharmacia) was used to rinse top and/or bottom slides before they were dipped into the pregel solution [8]. The gelling solution was stored at the ice temperature for at least 12 hours to allow the gelation process to be completed. We obtained two types of gels, designated here as "bottom-surface-clamped gel" and "both-surfaces-clamped gel". To obtain the dependence on the surface length, we changed one of the surface length  $a_0$ , while keeping the other length  $b_0$  at the width of the slide (26.0 mm). In this case, the thickness of the gel at gelation  $c_0$  was kept constant. To measure the dependence on  $c_0$ , on the other hand, several spacers with different thickness were used to obtain a different  $c_0$ . In this case,  $a_0$  was kept constant and  $b_0 = 26.0$  mm.

The sample was set in a small thermostat bath with water flow, and the water temperature was regulated to within  $\pm 0.05$  °C. A step-like temperature change in water flow was made from 30 (initial) to 11.5 °C (final) where the circulating initial water temperature was abruptly decreased to the final temperature by switching the water flow from one water-bath to another [9]. The thickness of the gel  $c$  was measured by an optical microscope apparatus equipped with a calibrated CCD (Charge Coupled Device) camera and a video processor.

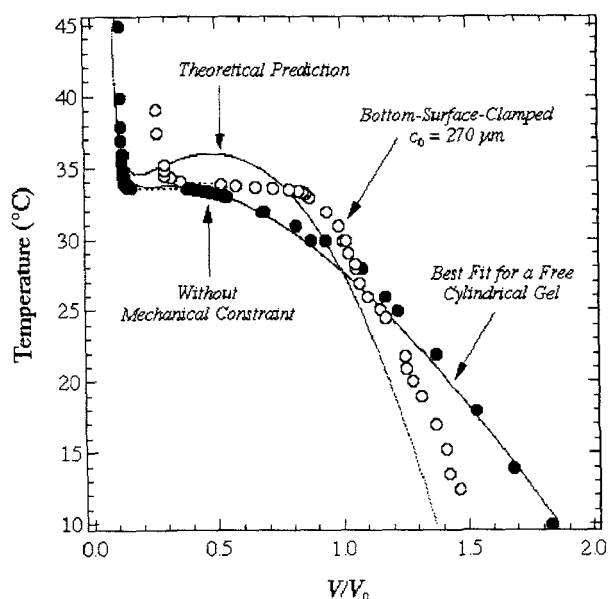


Fig. 1 Swelling curves of the gels with mechanical constraint (bottom-surface-clamped, open symbols) and without mechanical constraint (free, closed circles). Solid lines are the theoretical curves calculated on the basis of the mean field theory; first, the materials constants were determined by fitting the equation to the experimental data from the free gel, hereafter the theoretical prediction was obtained for the biaxial mechanical constraint using the same materials constants.

### 3. RESULTS AND DISCUSSION

#### 3.1 Swelling Curve

Figure 1 shows the swelling ratio  $V/V_0$  of the bottom-surface-clamped gel as a function of temperature on a heating process. In this figure,  $V_0$  is the volume at gelation and the swelling ratio is defined as  $V/V_0 = c/c_0$  under the biaxial mechanical constraint. Compared with the cylindrical gels without mechanical constraint (appended in Fig. 1, closed circles), we can see the following three properties; (1) the swelling ratio in the swollen state becomes smaller for  $V/V_0 > 1$  and larger for  $V/V_0 < 1$ , (2) the transition temperature slightly increased (about 0.2 °C), and (3) the transition width decreased (becomes almost continuous). The equation of state of the biaxially constrained gels on the basis of the Flory-type free energy [10], which is shown by the solid line in Fig. 1, can predict above (1) and (2), but not (3). And also the experimental swelling ratio in the collapsed state is evidently larger than the theoretical prediction. It is possible to explain these discrepancies between the experiments and the mean field theory in terms of the possible network imperfection [11] that might be introduced at gelation. The network structure of the present kind of polymer gels is not homogeneous by nature, but rather consists of microdomains, which should result in the inhomogeneous strain distribution under mechanical constraint. These frozen inhomogeneities should affect the swelling behavior. If the initial volume fraction of polymer and the effective number of polymer chains might be different from those of the cylindrical gels without mechanical constraint, the discontinuity of the phase transition and the swelling ratio at the collapsed state should be strongly modified.

In order to test these considerations, not only the macroscopic observations used in the present experiment but also the microscopic network structures in the same sample are desirable. This is an important subject for future investigations.

#### 3.2 Characteristic Times

By the kinetics experiments, we found that the time evolution of the thickness of each sample (bottom- or both-surfaces-clamped gels, and swelling or shrinking)

was well described by a single exponential;

$$c = c_1 + \Delta c (1 - \exp(-t/\tau)),$$

where  $c_1$  is the initial thickness,  $\Delta c$  is the total thickness change and  $\tau$  is the characteristic time. It should be noted that the slight deviation from the exponential immediately after the temperature change can be seen, which is similar to the results on the gels without mechanical constraint [1,2]. This could be due to extrinsic factors, such as the excess internal stress introduced by initial sample handling while the glass was being cut, or to intrinsic factors, such as an imperfection in the network structure [11]. The network structure at the mesoscopic level is constructed of highly cross-linked microgels connected by a loose network.<sup>11</sup> This unique structure can be introduced during the gelation process, which would affect deviation at the initial stage. We can calculate  $\tau$  as functions of  $a_0$ ,  $b_0$  and  $c_0$ , which is shown in Figs. 2 and 3. In the case of the bottom-surface-clamped gel (Fig. 2),  $\tau$  is scaled by  $c_0$  (the thickness at gelation) with the power of around 1.7, and not on  $a_0$  (the length of the constrained surface). On the other hand, in the case of the both-surfaces-clamped gel (Fig. 3),  $\tau$  is uniquely determined by  $a_0$ , and not by  $c_0$ . Note that  $\tau$  is scaled by neither  $a_0$  nor  $c_0$ , such as a simple square-power law. This observation implies that the relaxation along the thickness direction (within the present thickness range) is much faster than that perpendicular to the thickness direction. We found that  $\tau$  is well scaled by  $(a_0^2 + b_0^2)^{-1}$ , which indicates that the relaxation is essentially same as the two-dimensional diffusion with a square boundary condition, therefore the swelling and shrinking kinetics can be determined by the surface lengths  $a_0$  and  $b_0$ .

It is important, we believe, to take into consideration the possibility of the network orientation that might be introduced at gelation. During the polymerization the monomers in the pregel solution were first under the influence of thermal fluctuation, and after reaching the gel point the fluctuation was frozen into the gel network. Since the present polymerization is exothermic reaction, the thermal convection in a thin space between two slides should have an important role in determining the network structure. If the thin-plate gel might be oriented vertically, the kinetics should be strongly affected.

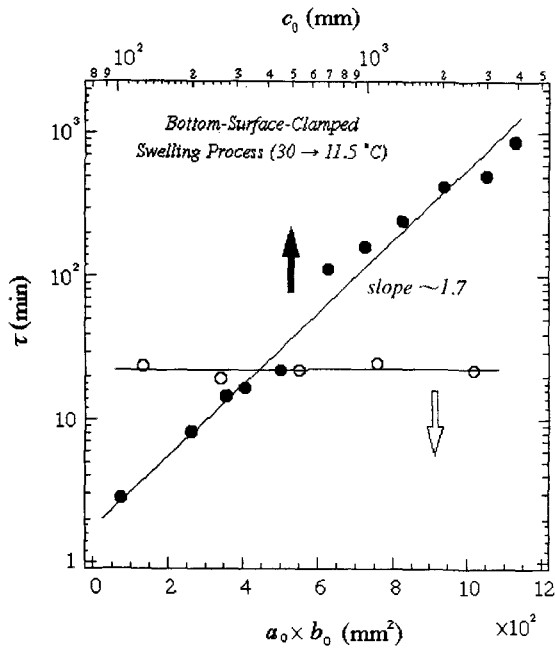


Fig. 2 Characteristic time of the bottom-surface-clamped gel with different  $a_0$  ( $b_0 = 26.0$  mm and  $c_0 = 0.44$  mm are constant, open circles) and with different  $c_0$  ( $a_0 = 33.0$  mm and  $b_0 = 26.0$  mm are constant, closed circles). The former is flat, while the latter is linear.

### 3.3 Effects of Mechanical Constraint on Kinetics

The present observation implies that the kinetics of the volume change for the bottom-surface-clamped gel can be well described by the collective diffusion of polymer networks along the thickness direction. In accordance with the kinetic theory, a single exponential decay was experimentally confirmed. Although the power is smaller than two,  $\tau$  of the bottom-surface-clamped gel is essentially governed by the relaxation of polymer network along the thickness direction.

In the case of the both-surfaces-clamped gel, on the other hand, the consistence of the results of  $\tau$  with the prediction of the two-dimensional diffusion equation implies that the relaxation along the surface directions is essentially important to determine the kinetics. It has been experimentally shown that the volume change of gels begins at the surfaces for spheres, cylinders, and plates [6,12,13], which indicates that the free surface has an important role in determining the kinetics. In the present case, the relaxation in response to a temperature jump is expected to begin at the unclamped side surfaces and can spread to the center portion with time. In a swelling process, the swelling develops from the outer (surface) to the inner (bulk) portions; the preceding (outer) swollen portion is compressed and the delayed (inner) portion is stretched along the one-dimensional thickness direction. Therefore, the observed thickness can be determined by the change in the free energy of the system  $\Delta G$  resulting from the average contributions of the outer and inner portions. According to the Flory-Huggins theory [10]  $\Delta G$  consists of two contributions of the osmotic term (mixing free energy)  $\Delta G_{\text{mix}}$  and the elastic term (elastic energy),  $\Delta G_{\text{el}}$ ;  $\Delta G = \Delta G_{\text{mix}} + \Delta G_{\text{el}}$ . We

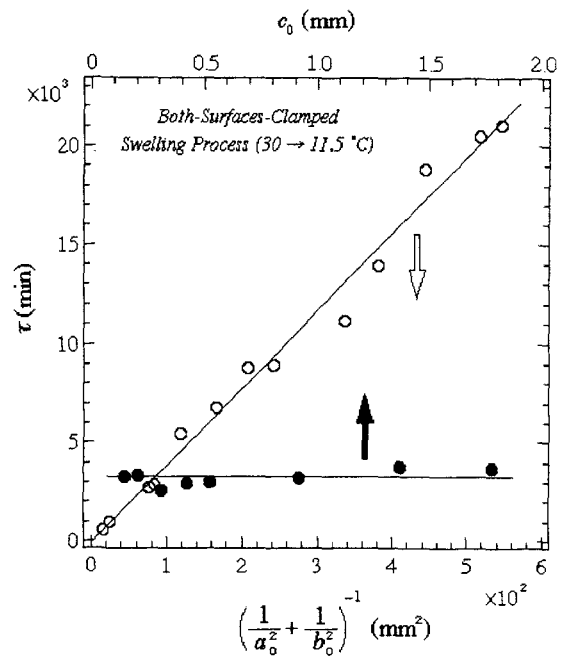


Fig. 3 Characteristic time of the both-surfaces-clamped gel with different  $a_0$  ( $b_0 = 26.0$  mm and  $c_0 = 0.90$  mm are constant, open circles) and with different  $c_0$  ( $a_0 = 9.5$  mm and  $b_0 = 26.0$  mm are constant, closed circles). The former is linear, while the latter is flat.

can estimate  $\Delta G$  in the present system by calculating the loss and the gain of  $\Delta G_{\text{el}}$  through the following first approximation. Suppose that there is a discrete boundary between the preceding and the delayed portions. If the sum of the changes in the elastic energies of the outer and of the inner portions is zero, one can assume,

$$S(c-c_f) + (a_0 b_0 - S)(c-c_i) = 0,$$

where  $S$  denotes the surface area of the preceded portion. This equation results in the thickness change,  $c - c_i = (\Delta c / a_0 b_0) S$ , which indicates that the time evolution of the thickness should be proportional to  $S$ . These primitive considerations suggest that the relaxation (single exponential decay) of the thickness is essentially equivalent to the two-dimensional diffusion, therefore the swelling and shrinking kinetics can be determined by the surface lengths  $a_0$  and  $b_0$  in the form of  $(a_0^2 + b_0^2)^{-1}$ . In order to confirm the above consideration, an additional experiment was conducted by changing  $b_0$ . As a result, the data traced on the straight line in Fig. 3, which successfully shows the validity of the model to the present system.

It is worth mentioning that the characteristic time  $\tau$  for the gels with a  $0.1 \times 0.1$  mm<sup>2</sup> surface (if the thickness is thin enough), estimated from Fig. 3, is roughly 1 min, which is on the same order as the absolute  $\tau$  for the cylindrical gels with 0.1 mm diameter.

The present fundamental findings, we believe, are of crucial importance not only for understanding the nature of the volume change of gels (the development of new science) but also in establishing the foundation for future practical applications of gels. This is because gels should be used practically under some mechanically restricted conditions.

#### 4. CONCLUSION

The swelling kinetics of two types of thin-plate NIPA gels under mechanical constraint (the top and/or bottom surfaces chemically clamped on the glass plates) were investigated by measuring the macroscopic thickness changes between two swollen states by the temperature jumps. The mean field theory on the basis of the Flory type free energy can predict the swelling ratio in the swollen state and the increment of the transition temperature for both gels. When the temperature is abruptly changed, the thickness of gels exponentially approached the equilibrium value except immediately after the temperature change. The size dependence for both gels were quite different each other. We found that the characteristic time of volume change is essentially governed by the relaxation of polymer network along the perpendicular to the free surface.

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