

Acceleration of Shrinking Rate Controlled by the Microstructure of Thermosensitive Gel

Norihiro Kato, Yasuzo Sakai, Yasue Hashimoto and Haruyoshi Suzuki

Department of Applied Chemistry, Faculty of Engineering, Utsunomiya University, 7-1-2 Yoto, Utsunomiya 321-8585, Japan
Fax: 81-28-689-6009, e-mail: katon@cc.utsunomiya-u.ac.jp

Shrinking kinetics of fast response gel is investigated. Microporous gel sheets (1.5 mm in thickness) prepared by a freeze-drying (FD) method and a modified method of temperature-induced phase separation (TIPS) respectively can reach to be equilibrium within 30-40 s and 10-20 s as temperature increase above lower critical solution temperatures of gels. The diffusional coefficients of the fast response gels are on the order of 10^{-4} cm²/s, where those of the non-porous conventional gels are on the order of 10^{-7} cm²/s. There are differences on microporous properties of these gels; interconnected pores generated by the TIPS method enable to drastically shorten the shrinking time due to the convection. In contrast, pores generated by freezing are disconnected, and not allowed to expel water with convection under the isothermal condition. However, this freeze-dry-treated gel can squeeze water out rapidly, causing the pores become interconnected to form channels which water can flow.

Key words: thermosensitive gel, microporous structure, freeze-drying, shrinking kinetics, fast response gel

1. INTRODUCTION

Keen interests are paid for thermosensitive polymers or gels, which alter their volume depending on temperature. Since control of the volume change rate is a significant technological problem for these gels, some methods have been reported to enhance the shrinking/swelling rates of thermosensitive gels. The volume change rate of gels is known to be relatively slow as compared with the rate of aggregation for linear polymers. It was reported that a porous structure of gels has an advantage to make the gel volume change fast. These methods include a gel preparation by γ -irradiation [1,2], the incorporation of surfactants during gelation [3], leaching of embedded soluble particles [4], the incorporation of other polymer during gelation [5], gel preparation on the hydrophobic mold [6], a modified temperature-induced phase separation (TIPS) method [7-9], and freeze-drying and subsequent hydration [10].

Construction of desired microstructure of polymer networks is indispensable technique for most applications of these gels. In our previous paper [10], a porous structure of thermosensitive poly(*N*-isopropylacrylamide), (PNIPA), gel was prepared by a treatment of the freeze-drying (FD) and re-swelling in water. PNIPA gel is a thermosensitive gel; a lower critical solution temperature (LCST) of PNIPA (31-35°C) depends on the polymer concentration and the volume phase transition occurred at around 34°C [11]. The FD-treated PNIPA gel can shrink approximately 10^3 times faster than the non-porous conventional gel. The FD-treatment is a simple and effective technique to improve the shrinking rate of thermosensitive gels, causing microporous structures. However, the properties of micropores formed by the FD-treatment are not studied well concerning the interconnectivity of micropores.

Gehrke and coworkers reported that the stimuli-response time of gels is drastically reduced by

decreasing thickness of pore walls or struts as the characteristic diffusional path length [8,9]. Also, microstructure of honeycombed pores can determine its volume change rate; the rate-limiting steps respectively may be the mutual diffusion process of water and polymer networks for closed cells, and a process of water convection for open cells [12]. Microporous structure of hydroxypropyl cellulose (HPC) gel can be also formed by the modified TIPS method [9,13]. Thermosensitive HPC gel has the LCST at around 43°C [13].

In this paper shrinking/swelling kinetics of microporous PNIPA gel prepared by the FD-treatment was compared with that of microporous HPC gel prepared by the TIPS method. The purpose of this research is to evaluate the shrinking/swelling properties of the FD-treated gel and to clear the role of micropores for fast shrinking.

2. EXPERIMENTAL

2.1 Materials

NIPA was purchased from Wako Pure Chemical. HPC (Mw 100,000) and Divinyl sulfone (DVS) were purchased from Aldrich and Kanto chemical, respectively. All other chemicals were of guaranteed grade or the best commercially available.

2.2 Polymerization of PNIPA gel

The cylindrical PNIPA gel crosslinked by 1 mol% of *N,N'*-methylenebisacrylamide (2 mm in diameter of the mold) was prepared in silicone tubes [10]. The swollen conventional gel rods (22°C) were frozen at -30°C after washing in water. The temperature inside gel was reached to -30°C within 3 min, of which the temperature was measured by a thermocouple embedded into the gel rod. Then the frozen gel was freeze-dried using FD-1 (Tokyo Rikakikai) and re-swollen in water at 22°C. The PNIPA gel sheet (1.5 mm in thickness) was also

prepared using the glass plates as the mold.

2.3 Synthesis of HPC gel

Synthesis of slab-shaped HPC gel was carried out according to the previous papers [12,13]. HPC was dissolved in NaOH solution (pH12) at room temperature. After 24 h, DVS was added to the solution at 22°C, and then the solution was thoroughly stirred for 20-30 s. The solution was poured between glass plates separated by a silicone rubber gasket (1.5 mm in thickness) and held together by clamps. The crosslinking reaction occurred over three different time/temperature intervals. After 2min from the addition of DVS, then the temperature was jumped to 49°C and the phase separation was allowed at the temperature above the LCST of the HPC solution for 5 min. After the phase separation period, the temperature was decreased below the LCST and the crosslinking reaction could occur before the reaction is quenched. Total reaction time was set to 24 h. After immersing the gel sheet in dilute HCl solution, the sol fraction was leached away in water.

2.4 SEM

The conventional PNIPA gel rod was equilibrated in water at 22°C. The gel rod was frozen at -30°C and then freeze-dried. The cross-section of the gel rod was observed by FE-SEM.

2.5 Measurement for shrinking and swelling

Gel rod The conventional PNIPA gel rod was equilibrated in water at 22°C, and then was cut into 60 mm. Also, the freeze-dried and re-hydrated PNIPA gel rod was cut into 60 mm after the equilibrium in water at 22°C. The PNIPA gel rods (the initial length: $L_0 = 60$ mm at 22°C) were transferred into water at 40°C. The gel length (L) was measured with time from pictures recorded by video-tape. $(L/L_0)^3$ was calculated as the shrinking ratio.

Gel sheet Weight change of the gel sheet was determined with time, when the temperature was jumped between 22 and 60°C. The dynamic gravimetric technique was used to determine the swelling kinetics of the FD-treated PNIPA gel sheet. The shrunken gel sheet at 60°C was immersed in water at 22°C for swelling. At desired intervals, the gel sheet was removed from the water, quickly blotted the surface with lint-free tissue papers, and weighed. Then the gel sheet was immersed in the water at 22°C again and allowed to swell. Weight increase of the gel sheet was measured until reaching equilibrium.

For the fast shrinking process of PNIPA gel and HPC gel, the equilibrium gravimetric technique was used to determine the shrinking kinetics. After weighing the gel sheet equilibrated at T_1 , the gel sheet was immersed in a water bath at temperature T_2 . After desired intervals (t), the gel sheet was removed from the water, blotted, and weighed. Then the gel sheet was placed in the original bath at T_1 and allowed to reach equilibrium. The gel sheet was immersed in the bath at T_2 again, and was removed from the water at $t + \Delta t$. The cycle was repeated until the weight of the gel sheet became independent of time.

2.6 Effective porosity

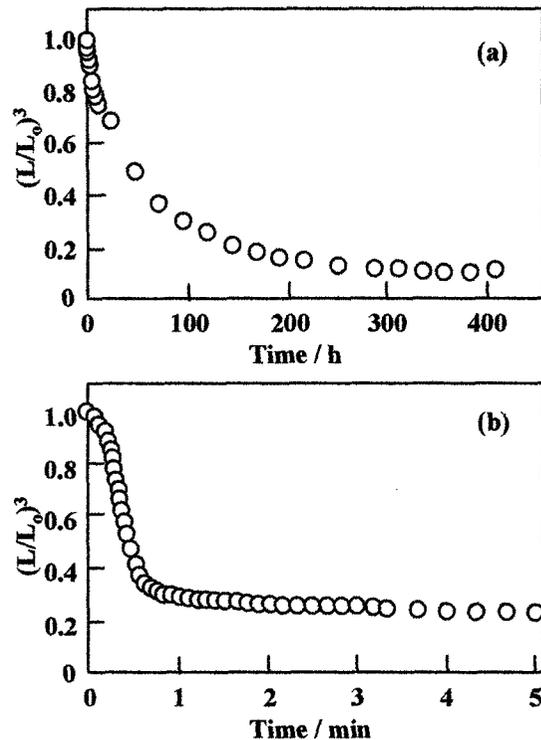


Fig. 1 Time evolution of the swelling ratio $(L/L_0)^3$ of PNIPA gels. (a) conventional gel, (b) freeze-dry treated gel. The temperature was jumped from 22 to 40°C. The rate of shrinking is accelerated drastically by freeze-drying.

Voids generated in thermosensitive gel sheets were measured as an effective porosity by the conventional methods [9,14]. The effective porosity was defined as the fraction of total gel volume occupied by interconnected pores through which water can flow. The gel sheet swollen at 22°C was weighed and placed between 10 layers of lint-free tissue paper. This assembly was placed between glass plates. When the mechanical pressure of approximately 10 kPa was applied to the gel sheet, expelled water was absorbed by the tissue paper. This procedure was repeated several times using fresh paper until the gel stopped expelling water under the pressure. From the mass lost, the effective porosity at 22°C was calculated.

3. RESULTS AND DISCUSSION

3.1 Fast shrinking of the FD-treated PNIPA gel

Effect of the microporous structure generated during the freezing process of PNIPA gel is studied in respect of the shrinking process. The PNIPA gel rods of 2 mm in diameter as the mold equilibrated at 22°C was heated to 40°C. Figure 1 shows the shrinking profiles of the conventional and the FD-treated gels. The empirical analysis of the time needed for half change of gel volume ($t_{1/2}$) was used for the results; $t_{1/2}$'s of the conventional and the FD-treated gels are 40 h and 30 s, respectively. This result clearly indicated that the microporous structure formed by the FD-treatment plays the important role to enhance water release. The conventional gel needed far longer time to equilibrate than it was expected from the diffusional coefficient of

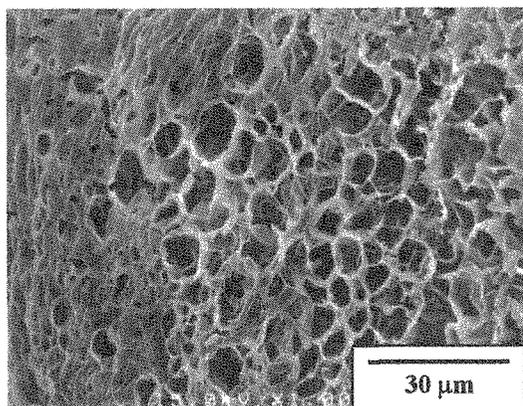


Fig. 2 Microporous structure of PNIPA gel. The surface of the gel was observed by field-emission electron microscopy (FE-SEM). Micropores are formed during the freezing process.

the homogeneous polymer network (10^{-7} cm²/s). This is because water located in the swollen gel is expelled through a hydrophobic skin layer formed around the surface of the gel [15].

The freeze-dried and re-hydrated gel can swell back to the nearly same size of the conventional gel. Therefore, the polymer contents for the conventional and the FD-treated gel rods are almost the same at 22°C. The phase transition observed by the FD-treated gel seemed to be a continuous process. When the gel became porous, some of the struts are considered to lock into position because of hydrophobic interaction or polymer entanglement, which results in a non-uniform polymer concentration. The struts comprise local regions with different transition temperatures from different polymer concentrations. A gradual change was observed for the degree of swelling because it includes all the struts.

Figure 1 shows that the volume change of the FD-treated gel became slightly smaller than that of the conventional gel. A possible explanation for the different volume change is as follows; For non-porous gel prepared at high initial polymer concentrations, equilibrium swelling degree and the change in volume becomes smaller. Since the struts of the microporous gels show similar behavior to homogeneous gels, it was not surprising to find a small change in volume for the microporous gels [16].

A SEM microphotograph for the morphology of the FD-treated gel shows the pores of 5-10 μm in diameter (Fig. 2). It was deduced that the polymer chains were gathered to form pores as the free water inside the gel froze. According to the pictures, the pores look like closed cells and most pores are disconnected. This result is also supported by an effective porosity of the gel. The effective porosity determined by the mass lost under the mechanical pressure is approximately below 0.1. Consequently, possible explanation for fast shrinking is that the pores alter to connect each other at the early period of shrinking and work as the connected channels through which water can flow.

3.2 Shrinking kinetics of microporous gels

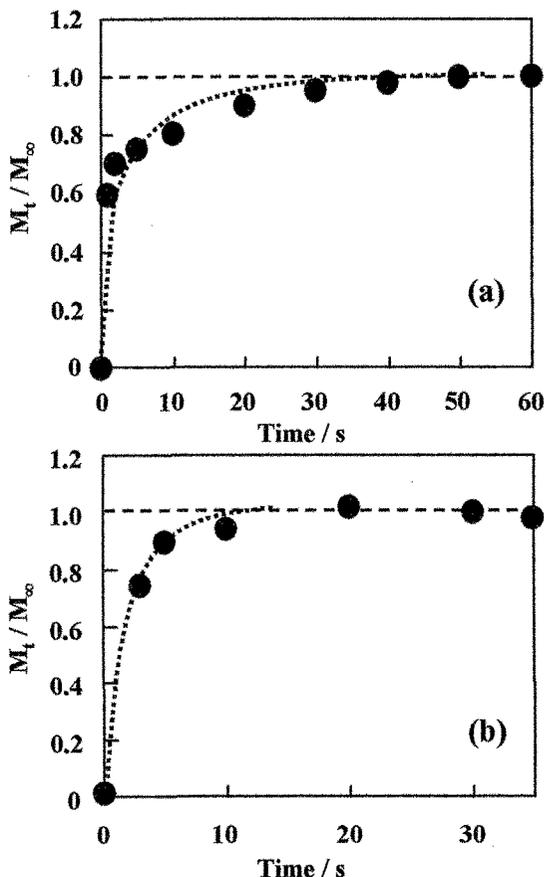


Fig. 3 Shrinking kinetics of microporous gel. (a) Microporous PNIPA gel (slab-shaped, 1.5 mm thick) prepared by freeze-drying was jumped from 22 to 50°C. (b) Microporous HPC gel (slab-shaped, 1.5 mm thick) was prepared by the TIPS method. Initial concentration of HPC and DVS are 7 wt% and 1.3 wt%, respectively.

Shrinking induced by temperature change for thermosensitive PNIPA gel and HPC gel were investigated using the slab-shaped gel. Sorption and desorption of rubbery polymer gels can be described by a single parameter, a diffusion coefficient (D) obtained from the solution of Fick's law of diffusion. For an expanding or contracting flat-sheet with an aspect ratio greater than 10, the mathematics of the swelling/shrinking problem are given as

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \left[\frac{8}{(2n+1)^2 \pi^2} \right] \exp \left[-(2n+1)^2 \pi^2 \frac{Dt}{L^2} \right]$$

where L is the half thickness of the gel sheet, M_t is the mass absorbed or desorbed at time t , M_∞ is the mass absorbed or desorbed at equilibrium [14].

Figure 3 shows the shrinking kinetics of microporous PNIPA gel prepared by the FD-treatment and that of microporous HPC gel prepared by the TIPS method. Rapid shrinking is observed for both gels; the gel weights of PNIPA and HPC gels can reach to be equilibrium at 30-40 s and 10-20 s, respectively. According to Gehrke, the TIPS method can generate the interconnected pores on the HPC gel; the effective

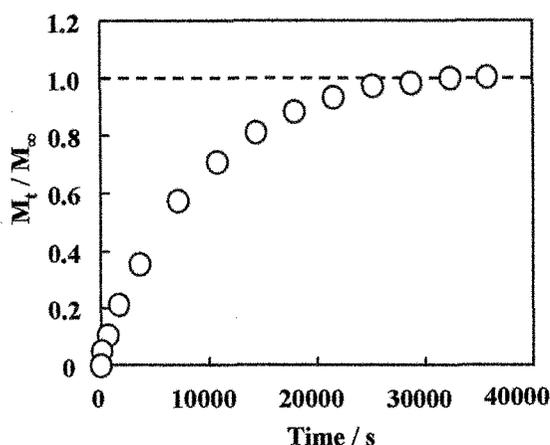


Fig. 4 Swelling kinetics of microporous PNIPA gel prepared by freeze-drying. The weight change of the gel was determined by the temperature-jump from 50 to 22°C.

porosity of the microporous HPC gel was determined as 0.80. Since water can flow through the interconnected pores, the microporous HPC gel can expel water rapidly.

We measured the temperature change inside gels using a thermocouple inserted in gels as the gel was immersed in the water at 50°C. It took approximately 10-15 s for the gel to reach the surrounding temperature. This result means that the process of heat transfer is supposed to be the rate-limiting step for shrinking of HPC gel, because the shrinking time is similar to the heat transfer time. On the contrary, the water desorption rate for the FD-treated PNIPA gel is a little slower than that for the microporous HPC gel with the interconnected pores. Therefore, the rate-limiting step for the FD-treated gel is considered to be the network motion or the convective flow through the partially connected pores.

As it is known the diffusion coefficient of the polymer chains is on the order of 10^{-7} cm²/s, the time required for network motion across the maximum strut thickness of 5 μ m is within a few seconds. In the case of the microporous gels, the time required for the network motion is determined by not gel thickness but strut thickness. This is because the pore shrinking is much faster than the actual volume change of the gel.

The diffusion coefficients of the PNIPA gel and the HPC gel are obtained to be on the order of 10^{-4} cm²/s. This result clearly indicated that the microporous structure is responsible for the drastic reduction of D.

3.3 Swelling kinetics of the FD-treated PNIPA gel

Swelling kinetics of the FD-treated PNIPA gel is determined as shown in Fig. 4. Compared with the shrinking process, water sorption rates were independent on the microporous structure of the gel. According to our previous studies, the micropores diminished and finally disappeared during the shrinking process. Consequently, the shrunken gel acts as the non-porous gel and the swelling kinetics are controlled by the gel thickness as the characteristic diffusional path length. Thus, the diffusional coefficient of the microporous PNIPA gel prepared by freeze-drying is obtained to be approximately 10^{-7} cm²/s, of which values for the

conventional PNIPA gel are caused by the mutual diffusion of the polymer network and water. Analyses of swelling kinetics for microporous HPC gels are now under consideration.

4. CONCLUSION

There are some differences of microstructure between the gel treated with freeze-drying and the gel prepared by the TIPS method; the values of effective porosity for these gels are 0.1 and 0.8, respectively. This result means that the micropores prepared by the phase separation (TIPS) are interconnected, through which water can flow. Thus, rapid shrinking was induced by the convective flow.

On the contrary, micropores prepared by freezing are disconnected each other. These pores formed by gathering and condensing the polymer chains physically, when the iceberg grows up inside the gel. However, these pores can easily alter to interconnect during the process of polymer aggregation (network motion) as temperature raise. Therefore, water can be expelled rapidly due to heating above the LCST of the gel.

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