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Microporous, Thermosensitive Organic-Inorganic Hybrid Hydrogel Prepared by Freezing

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Summary: Thermally triggered shrinking rates of poly(*N*-isopropyl-acrylamide) (PNIPA) -based organic-inorganic hydrogel could be accelerated by applying the ice templating method. Freezing and subsequent rehydration of gels is an effective way to prepare the porous polymer network that leads to rapid expelling of pore water. The shrinking coefficients obtained by fitting Fick's law to the data increased two orders of magnitude as compared with the conventional gel before freezing. The microstructure of gels generated during freezing gels had advantage to expel the pore water rapidly probably due to the PNIPA aggregation through the hydrophobic interaction.

Keywords: hydrogel; microporous polymers; *N*-isopropylacrylamide; organic-inorganic composite; stimuli-sensitive polymers

Introduction

Micropore formation is an effective way to enhance rates of shrinking as well as solute release from responsive gels.[1] In our previous papers, a simple way to prepare the microporous, fast-response gels was reported; the freezing and subsequent rehydaration of gels easily alters the microstructural properties.[2–4] When the solvent sorption by gels can be described as a simple diffusion-controlled process, response time of gels to the environmental change can be drastically reduced by decreasing the characteristic diffusion path length. Hence fast-responsive gels can be created by reducing the strut thickness of pores instead of reducing the gel sample size. The hydrogel became porous by ice templating and its microporous structure could be basically controlled by nucleation of ice crystals and their growth rates. As the useful way to control the macropore size and stimuli-responsive rates of gels, honeycomb-like structure could be controlled by adjusting the water content of gels prior to freezing. This method has already applied to crosslinked vinyl polymers including poly(*N*-isopropylacrylamide) (PNIPA) gel, cellulose ether gels containing hydroxypropyl cellulose (HPC) gel, and crosslinked DNA gels. Thus this research could extend the method on the organic-inorganic (O-I) hybrid gel to control its microstructure and shrinking rates. Matějka and coworkers reported the thermosensitive PNIPA gels crosslinked by the silsesquioxane (SSQO) like multifunctional polysiloxane network.[5] The objective of this research is to investigate the microporous properties and the weight change kinetics of such crosslinked PNIPA based O-I gel after applying the ice templating method.

Materials and Methods

NIPA and [3-(methacryloyloxy)propyl]trimethoxysilane (MPTMOS) were respectively purchased from Wako Pure Chemical and Aldrich. The PNIPA-based O-I gels were synthesized by copolymerization of NIPA and MPTMOS. The sol-gel process for the MPTMOS sidechains could be

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initiated by adding *N,N,N′,N′*-tetramethylethylenediamine (TEMED) as the hydrolytic condensation of trimethoxysilanes.[5] After adding the initiator TEMED, ammonium peroxodisulfate solution was mixed to the aqueous solution of NIPA and MPTMOS [NIPA/MPTMOS = 95/5, 90/10, 80/20, 70/30 (mol/mol)] at 10 °C. The pregel solution was poured into the mold (20 × 20 × 1.5 mm) and then the reaction was allowed to proceed for 24 h at 22 °C. Temperature dependence of the equilibrium swelling degree Q ($Q = M_s/M_d$) was determined with increasing the temperature, where M_s and M_d respectively are the weights of the swollen and dried gel samples. To make the gels porous, swollen gels at 22 °C were put into a glass flask and then frozen by immersing the flask in the cooling bath at −20 °C. After freeze-drying (FD) the gels, the gel surfaces were observed by SEM.

The shrinking profiles of the conventional and the FD-treated gels were determined after reswelling at 22 °C. The initial mass of the gel was determined after blotting it with a lint-free tissue paper. Then the gel was immersed in water at 60 °C. At the desired intervals, the gel was separated from water and blotted before weighing. Then the gel was returned to the original bath at 22 °C until the gel reached equilibrium again. This process was repeated with a small increase of time for heating until the gel weight became independent of time. Fick's law of diffusion can be applied to the desorption process of gel sheets,

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

where D and L repectively are an effective diffusion coefficient in a polymer-fixed frame of reference and the initial thicknee of the gel sheet.[6] The fractional mass change (M_t/M_∞) could be calculated as the mass of water desorbed at time t (M_t) divided by the mass of the water desorbed at equilibrium (M_∞).

The squeezable fractions of pore water was determined as follows.[7] It was measured by applying a mechanical pressure of 10 kPa for 1 min and determined the gel weight before and after. The mass of the expelled water (M_{sq}) was divided by the dry mass (M_d) of the gel.

Moreover, a homologous set of polyethylene glycol (PEG) with a wide range of molecular weights (200–4,000,000) was used to probe accessibility of the pore water. The solute hydrodynamic radius (r) was calculated by the Mark-Houwink-Sakurada equation as the function of the molecular weights of PEGs.[8] The PEG accessible water fraction was noramlized by the total mass of water in gels to determine its cumulative distribution.

Results and Discussion

As the PNIPA based O-I networks with polysiloxane structures covalently attached to the PNIPA, gels could be formed by crosslinking with inorganic SSQO-domains. Any gel sheets possessed lower critical solution temperatures (LCSTs) at around 31–32 °C. The equilibrium swelling degree ($Q = M_s/M_d$) at 22 °C, squeezable fraction of gels (M_{sq}/M_d) at 22 °C, and the ratio of the equilibrated weights between 22 and 60 °C as shrinking ratios were summarized in Table 1.

Water mass in the gels decreased with increasing the alkoxysilane moieties of MPTMOS. After the freeze-drying and subsequent rehydration, the Q and the shrinking ratio of the FD-treated gels had a tendency to decrease irrespective of the MPTMOS contents. The interconnectivity of macropores could be generally evaluated by squeezable fractons (M_{sq}/M_d). The M_{sq}/M_d remained low even after the FD treatments.

A SEM image of FD-treated gel surface was shown in Figure 1a. Macroporous, heterogeneous structure could be observed on the FD-treated gel surface as well as the PNIPA gels crosslinked with *N, N′*-methylenebisacrylamide.[2] By ice templating

Table 1.
Swelling properties of poly(NIPA/MPTMOS) gels.

MPTMOS	Conventional gel			FD gel		
mol%	Q	M_{sq}/M_d	Shrinking Ratio	Q	M_{sq}/M_d	Shrinking Ratio
5	29.9	3.3	18.8	15.7	2.0	8.6
10	26.1	2.6	16.3	11.2	0.7	6.0
20	22.1	1.3	14.0	10.3	0.7	5.0
30	19.9	2.0	12.7	8.8	1.0	4.0

method, the free water froze in the gel, causing the polymer chains gather and then condense. The generated structure is stable in aqueous solution probably due to the hydrophobic interaction and the polymer entanglements. The result of the squeezable fractions and the SEM image indicated that the most of the generated macropores were the closed cells of which interconnectivity was low. Figure 1b shows the cumulative distribution of PEG accessible water fractions determined from the batch size-exclusion experiments of poly(NIPA/MPTMOS) gels with or without the FD-treatment. After applying the ice templating method, the mean size of micropores was considered to meaningfully decreased. The PEG 4,000,000 (r = 38 nm) was size-excluded from the conventional gel without freezing, while the PEG 20,000 (r = 4.6 nm) became to size-exclude from the FD-treated gel. It was plausible that the macropore occupied the large space in the gel and then the polymer concentration inceased at the macropore strut. Accordingly, the shrinking kinetics of the O-I gel was investigated in respect of effects of such morphologic change.

The representative shrinking profiles of the conventional and FD-treated poly (NIPA/MPTMOS) gel [NIPA/MPTMOS = 95/5] were shown in Figure 2. The swollen gel sheet at Q = 29.9 was frozen at –20 °C

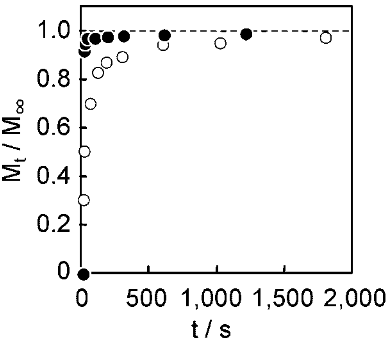

Figure 2.
Weight change kinetics of poly(NIPA/MPTMOS) [NIPA/MPTMOS = 95/5] gels with or without the freezing treatment. Temperature of gels with (●) or without the freezing treatment (○) altered from 22 to 60 °C.

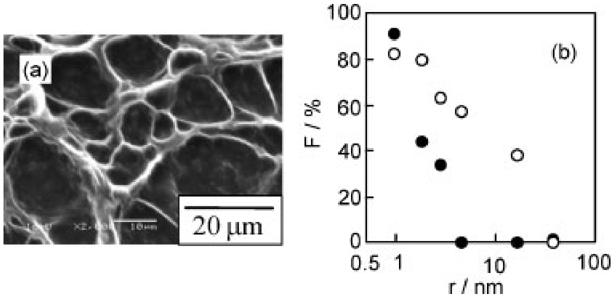

Figure 1.
a. A SEM microphotograph of the freeze-dried poly(NIPA/MPTMOS) gel [NIPA/MPTMOS = 95/5]. The swollen gel at 22 °C was frozen and then freeze-dried. Figure 1b. Cumulative distribution of PEG accessible water fractions in the poly(NIPA/MPTMOS) gel before (○) and after (●) the FD-treatment.

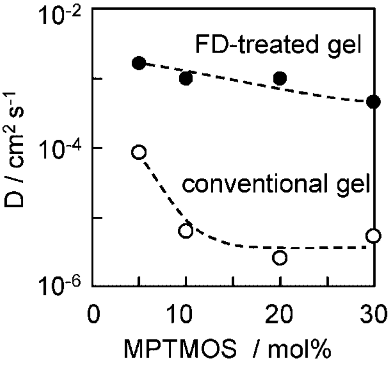

Figure 3.
Relationship between the effective diffusion coefficients and the MPTMOS contents of gels.

and then rehydrated at 22 °C. The shrinking profiles were determined by weighing the gel sample through the abrupt temperature change to 60 °C. The FD-treated gel could shrink faster than the conventional gel; it took about 2–3 min to reach equilibrium while the conventional gel took over 2–3 h. Effective diffusion coefficients (Ds) could be obtained by fitting the Fick's law to the data (Figure 3).

Shrinking of any gels could be accelerated after the ice-templating method was applied. For the 30 mol% MPTMOS gel, the D (4.3×10^{-4} cm^{2}s^{-1}) was two orders of magnitude larger than that of the conventional gel (5.0×10^{-6} cm^{2}s^{-1}). The magnitude of Ds indicated that the shrinking of the FD-treated gel was probably limited by the convection of pore water. It was reported that the convective flow through the porous materials could be described by the same differential equation of the Fick's law with greater transport coefficients.

The possible explanation for the fast shrinking of the FD-treated O-I gel was that the pores easily connect each other in the beginning of the shrinking process due to the polymer aggregation. The pore water could be squeezed out through the temporarily generated interconnected channels. During freezing the O-I gels, the macroscopic and microscopic change of the polymer networks appeared; generated macropores were closed cells which were partitioned by heterogeneous, thin pore walls. The ice templating method could expand to the PNIPA based O-I gel, of which crosslinking points were the SSQO domains, for the simple and effective way of fast response gel preparation.

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