SHORT COMMUNICATIONS

Synthesis of Porous Poly(*N*-isopropylacrylamide) Gel Beads by Sedimentation Polymerization

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Poly(*N*-isopropylacrylamide) (PNIPA) gel has attracted much attention for a typical thermosensitive polymer gel, because it has lower critical solution temperature (LCST) at 32–4 °C[1–3] and relatively large volume change caused by a small temperature change around LCST. The volume change accompanies water absorption (swelling) or dewatering (deswelling) of PNIPA gel. Freitas *et al.*[4] investigated this application to concentration of an aqueous polymer solution, and proposed the industrial process. However, the process has not been practiced commercially because the volume change of millimeter-sized PNIPA gel is not satisfactorily fast, and it is very difficult to produce a large amount of millimeter-sized monodisperse PNIPA gels that is suitable for this process. One approach to improve swelling–deswelling rates was to synthesize porous PNIPA gels. Porous PNIPA gels have been prepared by several methods such as the incorporation of surfactants[5] or silica particles[6] during hydrogel preparation and their subsequent extraction, hydrogel preparation above its LCST,[7–10] and preparation using freezedrying.[11] Recently, Gotoh *et al.*[12] investigated preparation of a porous PNIPA gel plate reinforced with wire gauze by the phase separation polymerization of *N*-isopropylacrylamide (NIPA) above the LCST. It is found that the swelling-deswelling of the plate was so fast that it was suitable for dehydration of sludge such as rice-washed water.

On the other hand, Ruckenstein and coworkers[13,14] reported a preparation method of millimeter-sized monodisperse particles by sedimentation polymerization of droplets of aqueous monomer solution. Recently, Zhang and Cooper have investigated novel processes of sedimentation polymerizations such as oil-in-water-in-oil sedimentation polymerization[15] and compressed fluid sedimentation polymerization.[16] The common concept of sedimentation polymerization involves a formation of stable skin by the surface gelation of droplets descending a heat medium, since the sedimentation time is not enough to complete the polymerization of droplets. Porous PNIPA gel beads could be prepared by the sedimentation polymerization of aqueous NIPA droplets above the LCST if the polymerization gave a stable skin which prevented coalescence at the base of the reactor.

This communication reports the successful synthesis of the porous PNIPA gel beads which show high swelling rate by the polymerization of NIPA solution in aqueous DMF with a simple sedimentation polymerization apparatus (Scheme 1).

EXPERIMENTAL

A typical sedimentation polymerization of NIPA is as follows. NIPA (2.0 g, 18 mmol), *N,N'*-methylenebisacrylamide (MBAA) (27 mg, 0.18 mmol), and potas-
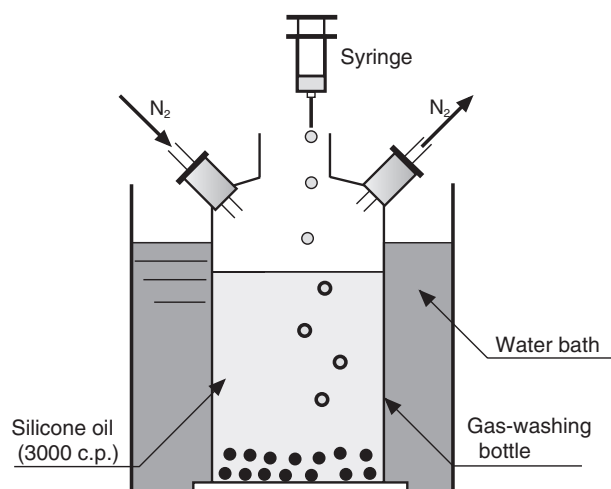
Scheme 1.

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sium persulfate (20 mg) was dissolved in 20 wt% aqueous DMF solution (8.0 g) at 20 °C under nitrogen atmosphere. Silicone oil (GE Toshiba Silicones Co., 3000 c.p.) was charged into a washing bottle in a water bath at 80 °C and nitrogen gas was bubbled into the silicone oil over 3 h. The monomer solution was injected dropwise into the silicone oil using a syringe with a needle (external diameter 1.5 mm). It was allowed to stand for 12 h at 80 °C under nitrogen stream. The resulting beads were washed from several times swelling–deswelling by temperature swing between 20 and 80 °C. The obtained beads were dipped in water and were stored in a refrigerator. The average diameter ($2R_0$) of a bead deswelled at 80 °C and the average weight of a dried bead are 2.49 mm and 2.63 mg. The average weight of a droplet of the monomer solution was calculated from that of ten droplets. SEM photographs were taken on a JEOL model JSM-5600.

Cylindrical porous PNIPA gel ($2R_D$: about 2.4 mm) was prepared from the copolymerization of a solution of NIPA (20 g), MBAA (270 mg), potassium persulfate (200 mg), and 20 wt% aqueous DMF (80 g) in Teflon tubes (internal diameter; 3.0 mm) according to the synthesis of poly(acrylic acid) gel.[17]

Swelling of the obtained gels was measured according to the method reported.[17] The swelling rate was evaluated by R_t/R_0, where R_0 and R_t are external radius of the gel deswollen in water at 80 °C and the gel swelled in water for t min, respectively. The equilibrium swelling ratio (R_∞/R_D) was measured, where R_D and R_∞ are external radius of the dried gel and the gel swelled in water for ∞ min, respectively.

RESULTS AND DISCUSSION

Sedimentation polymerization was carried out using a long cylindrical reactor containing a heat medium and surrounded with heating tapes[13] or a heating jacket.[16] The preparation of fine polymer beads by the polymerization needs enough time of sedimentation to form a stable skin on droplets of a monomer solution and fine temperature control of heat medium. A simple sedimentation polymerization apparatus (Scheme 1) consisting a 500 mL gas-washing bottle with 15 cm height of high viscous silicone oil (3000 c.p.) in a water bath was proposed. The sedimentation time of 3 mm diameter droplet of an aqueous monomer solution in this apparatus is about 14 min. The polymerization of NIPA solution containing 1 mol% MBAA and 2 wt% potassium persulfate was carried out using this apparatus at 80 °C. When the aqueous NIPA solution was used, a droplet of the monomer solution became clouded and the droplet coalescence did not occur during the sedimentation in the silicone oil.

However, the droplets on the bottom of the bottle were agglutinated gradually, and finally transformed into a polymer mass. A droplet isolated from the other droplets on the bottom produced a slightly distorted bead. In order to increase polymerization rate, the sedimentation polymerization was performed with small amounts of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) as a radical accelerator. However, fine beads (G-2) were not obtained from the polymerization of an aqueous NIPA solution. The sedimentation polymerization of an aqueous solution of monomers such as 2-hydroxylethyl acrylate and acrylamide solutions gave fine polymer beads under similar conditions. These results suggested that a large amount of the fine PNIPA gel beads were hardly prepared by the polymerization of an aqueous NIPA solution, although the polymerization of a separate droplet can produce a PNIPA gel bead. The observation of the polymerization by a video camera indicated that the skin layer resulting from the surface gelation of droplets shrank immediately and fresh monomer solution was soaked through the skin layer. The coalescence was attributed to the soaked solution. The temperature dependence on the equilibrium swelling ratio (R_∞/R_D) of cylindrical PNIPA gel was measured in various concentrations of aqueous DMF solution (Figure 1). The equilibrium swelling ratio increased above the LCST and decreased under the LCST with increasing the DMF concentration. Therefore, the thermosensitivity decreased in aqueous DMF solution. The addition of DMF to the polymerization solution could depress the shrinkage of the PINPA gel and generation of the pores resulting from phase separa-
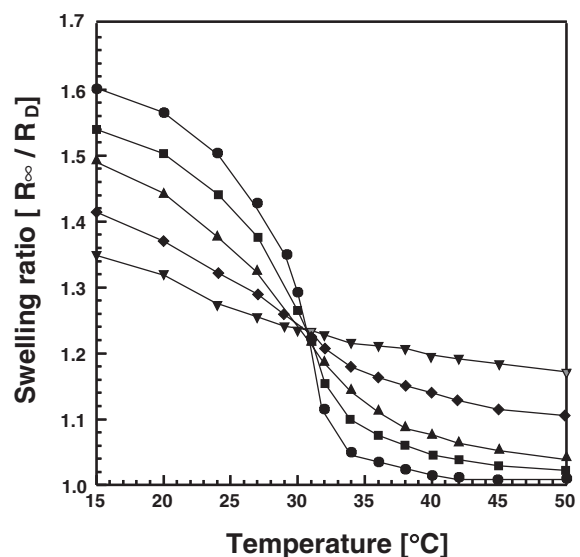

Figure 1. Equilibrium swelling ratio of cylindrical porous PNIPA gel in the various DMF concentrations in aqueous DMF solution as a function of temperature; (●) 0 wt%; (■) 10 wt%; (▲) 20 wt%; (◆) 30 wt%; (▼) 40 wt%.

tion polymerization above the LCST, and prevent a leak of monomer solution from the skin layer. When aqueous DMF (20 wt%) solution was used as a solvent, the leak was not observed, and the droplets on the bottom of the bottle were not agglutinated at all to produce fine beads (G-3). The rate of polymerization determined from average weights of a droplet of the monomer solution and a dried gel is 96–97%. Consequently, small amounts of DMF did not interfere with the polymerization, and the polymerization proceeded smoothly to give polymer beads. The addition of DMF also caused the solubility of NIPA to increase. The maximum solubility of NIPA is about 20 wt% in water, and 30 wt% in 20 wt% aqueous DMF solution at 20 °C. Since $2R_0$ of the beads was hardly dependent on the monomer concentration (20–30 wt%), the porosity of beads decreased with increasing the monomer concentration.

It is well-known that the shrinking rate of porous PNIPA is very fast.[18] Porous beads swollen in water shrank as soon as they were dipped in water at 80 °C. When the gels ($2R_0 = ca.$ 2.5–2.6 mm) shrunk at 80 °C was dipped in water at 20 °C, the swelling took place as shown in Figure 2. The swelling was evaluated by R_t/R_0, where $2R_t$ is external radius of the gel swelled in water for t min. The swelling of G-3 bead was very fast and was reached to the equilibrium swelling ratio after 5 min. However, two-step swelling was observed and the swelling was slower than that of G-1 bead obtained from the polymerization of aqueous NIPA solution. The swelling of obtained beads became slower and the two-step swelling became more distinguishing with increase of monomer concentration in the polymerization, because the
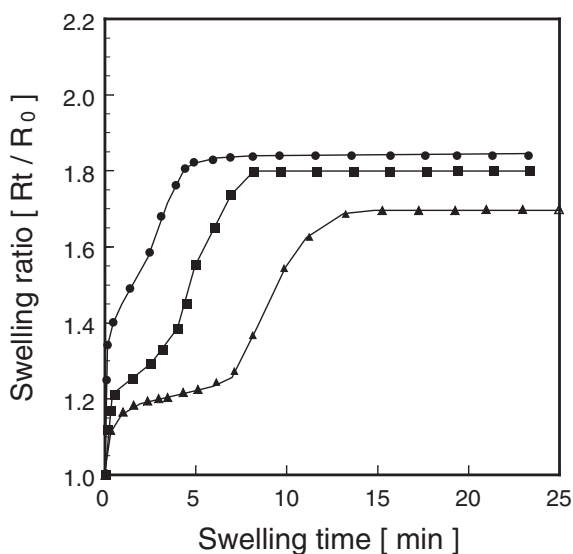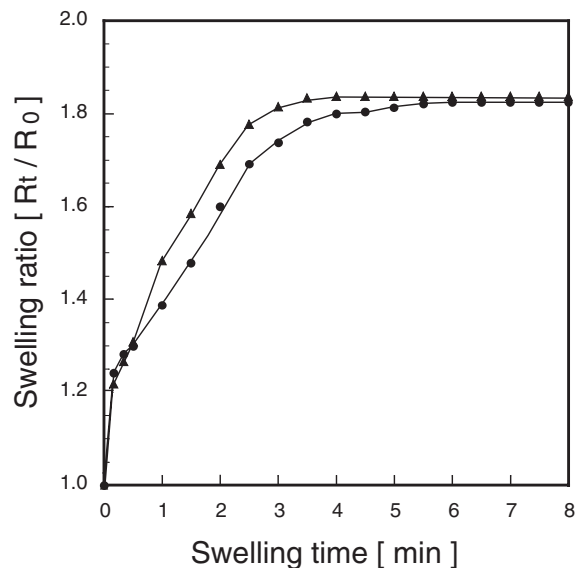

Figure 3. Swelling rate of beads in water at 20 °C; (●) G-3 ($2R_0 = 2.53$ mm); (▲) G-4 ($2R_0 = 2.54$ mm).

porosity of beads decreased with increasing the monomer concentration. G-4 prepared from the polymerization of NIPA solution in 20 wt% aqueous DMF solution containing TMEDA did not show two-step swelling and showed higher swelling than G-3 (Figure 3). Therefore, when TMEDA was used in the polymerization, the swelling behavior improved, and the porous PNIPA gel beads which show high swelling rate was obtained.

The gel beads swollen at 20 °C and shrunk at 80 °C in water had spherical shape and dense internal structure. When the gel beads were dried, the beads were distorted and the R_D can not be measured. Cross section photograph of the typical dried gel (G-3) are shown in Figure 4. The beads obtained from the sedimentation polymerization had complex morphology, while a cylindrical gel synthesized from the usual solution polymerization showed a simple porous morphology.[9] A big and irregular void appeared in the dried gel (Figure 4A). It seemed that the void came from the heterogeneous polymerization from the surface of the droplet. Since the swollen gel was preferentially filled in the void in water, the void could not be detected in the gel. G-3 had very complex structure consisting of high porous parts (Figure 4B) and dispersing nonporous strips into porous parts (Figure 4C). The strips were not detected in G-1 and G-4 beads prepared from the polymerization in water and in the aqueous DMF solution with TMEDA, respectively. The two-step swelling may be attributed to rapid swelling of the high porous part and relatively slow swelling of the strips.

From these results, it is concluded that the effective synthesis of porous PNIPA beads from the sedimentation polymerization require for the addition of DMF to
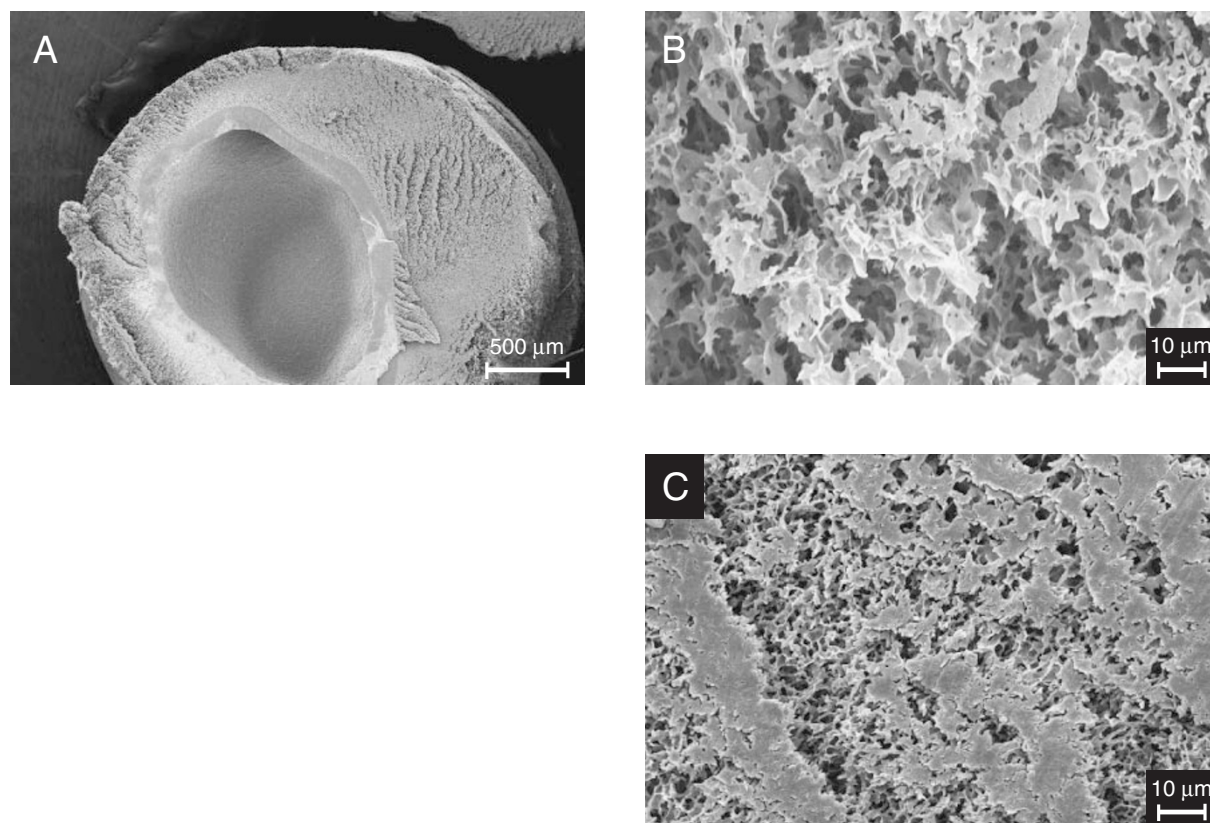

Figure 2. Swelling rate of beads in water at 20 °C; (●) G-3 ($2R_0 = 2.53$ mm); (■) G-5 ($2R_0 = 2.55$ mm); (▲) G-6 ($2R_0 = 2.58$ mm).

Figure 4. Cross sectional SEM Photographs; A) G-3 (×35), B) high porous part in G-3 (×1000), C) dispersing nonporous strips into porous parts in G-3 (×1000).

Table I. Synthesis of PNIPA gel beads by sedimentation polymerization[a]

Gel	Solvent[b] (wt%)	Conc. of NIPA (wt%)	TMEDA (mg)	$2R_0^c$ (mm)	Weight[d] (mg)
G-1	0	20	0	—[e]	—
G-2	0	20	40	—[e]	—
G-3	20	20	0	2.49	2.63[f]
G-4	20	20	40	2.50	2.61[g]
G-5	20	25	0	2.58	3.18
G-6	20	30	0	2.62	3.66[h]
G-7	20	30	60	2.61	3.66

[a]Sedimentation polymerization of the NIPA solution (10 g) was carried out with MBAA (1.0 mol%) and potassium persulfate (0.02 g) at 80 °C. [b]DMF content in the aqueous solvent. [c]Average diameter of a polymer bead deswollen in water at 80 °C. [d]Average weight of a dried gel. [e]Coalescence occur. [f]Conversion of NIPA: 96%, determined by average weight of a droplet (13.6 mg) [g]Conversion of NIPA: 97%, determined by average weight of a droplet (13.4 mg) [h]Conversion of NIPA: 97%, determined by average weight of a droplet (12.6 mg)

the aqueous NIPA solution. PNIPA beads which show high swelling rate are obtained in the further addition of TMEDA to counteract the decrease of porosity of the resulting beads.

Further studies on the sedimentation polymerization of NIPA under various conditions, and relationship between the swelling behavior and morphology are now in progress.

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