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

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ABSTRACT: Sedimentation polymerization of aqueous solutions of *N*-isopropylacrylamide (NIPA) was carried out to prepare porous poly(*N*-isopropylacrylamide) (PNIPA) beads. When small amounts of DMF and a radical accelerator were added to the monomer solution, the polymerization proceeded smoothly to give polymer beads with a very narrow size distribution. The rate of swelling of the resulting bead increased with increasing crosslinker content and was also affected by the type of crosslinker used. When amounts higher than 1 mol % *N,N'*-methylenebisacrylamide or 3 mol % diethylene glycol diacrylate (DEGDA) were used as a crosslinker, the resulting beads underwent rapid swelling in water at 20°C, reaching the equilibrium within 5 min. A cross-sectional photograph of a typical dried bead showed that it had a very complex morphology consisting of a large and irregular void, highly porous region, and nonporous region. The swelling rate was directly dependent on the morphology of the beads. PNIPA beads with well-developed porous areas show a high swelling rate. Although PNIPA beads produced from DEGDA had well-developed porous structures, they were able to effectively concentrate blue dextran from the dilute aqueous solution. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 842–850, 2007

Key words: stimuli-sensitive polymers; morphology; radical polymerization; separation of polymers; macroporous polymers

INTRODUCTION

The poly(*N*-isopropylacrylamide) (PNIPA) gel is thermally sensitive in its response to external temperature changes. It swells in water and absorbs large amounts of water at temperatures below the lower critical solution temperature (LCST) at 32–4°C,[1–3] but the swollen gel dewaters and releases the absorbed water at a temperature above the LCST. In addition, the swelling–deswelling change occurs rapidly by a small temperature change around the LCST. Their use has been investigated in many fields. One of the promising applications of PNIPA gels is a returnable water-absorbing polymer. Frettas and Cussler[4] investigated this application for concentrating aqueous polymer solutions and proposed an industrial process based on the application. The concentration or separation of an aqueous polymer solution and an aqueous dispersion of bacteria have been reported using thermosensitive gels such as PNIPA gels, poly(*N*-ethylacrylamide) gels, and their copolymer gels.[5–12] Champ

et al.[13] recently attempted to concentrate aqueous solutions of blue dextran with a thermosensitive gel using a practical semiautomated apparatus. Gotoh et al.[14] reported on a smart sludge dewatering system using a porous PNIPA gel plate reinforced with wire gauze. Millimeter-sized PNIPA gel beads have a suitable size and shape for this process because of their ease of handling in the separation and the negligible pressure drop in columns packed with these particles. However, there are two serious, practical limitations to their use. One is the slow swelling–deswelling of the gel, due to the fact that the process is diffusion-limited. To improve swelling–deswelling rates, porous PNIPA gels have been prepared by several methods such as the incorporation of surfactants[15] or silica particles[16] during hydrogel preparation and their subsequent extraction, heterogeneous polymerization at a temperature above the LCST,[17–20] and the use of freeze-drying.[21] Heterogeneous polymerization is a simpler and more economical method for the synthesis of porous PNIPA gels than the other methods.

The other difficulty involves the efficient production of a large amount of millimeter-size PNIPA beads with a very narrow size distribution. Although microgels of PNIPA have been investigated extensively,[22] few papers have been concerned with the synthesis of millimeter-size PNIPA beads. For example, Nayaman

et al.[6] examined the inverse suspension polymerization of aqueous NIPA solutions in paraffin oil, but produced PNIPA beads with a wide size distribution: 0.25–2.8 mm. Accordingly, pellet or desk type gels have been widely used instead of these size particles, but unfortunately, it may not always be practical to use pellet or desk type gels. Ruckenstein and Hong[23,24] proposed a new method for preparing millimeter-size monodisperse particles by the sedimentation polymerization of droplets of an aqueous monomer solution. Zheng and Cooper reported on some novel sedimentation polymerizations such as oil-in-water-in-oil sedimentation polymerization[25] and compressed fluid sedimentation polymerization.[26] Furthermore, sedimentation polymerization is useful for the synthesis of functional polymer beads such as complex polymers.[27] We recently investigated the chemical modification of beads prepared by sedimentation polymerization.[28]

In the previous study,[29] we reported the successful synthesis of porous PNIPA gel beads by the heterogeneous polymerization of an aqueous NIPA solution with a simple sedimentation polymerization apparatus (Fig. 1). The bead obtained by this procedure had a very complex structure consisting of a large and irregular void, highly porous region, and a non-
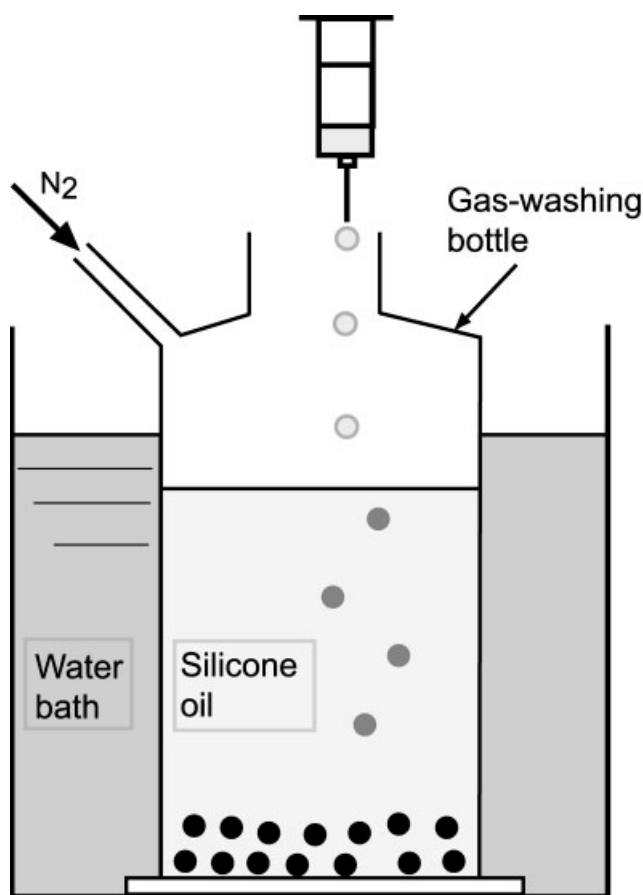
porous region. PNIPA beads with a more developed porosity would show more rapid swelling–deswelling. In this article, we report on the synthesis of porous PNIPA gel beads under various compositions. The internal morphology of the resulting beads was examined and relationships between morphology and swelling behavior are discussed.

MATERIALS

NIPA supplied by Kojin was recrystallized prior to use. Commercial silicone oil [poly(dimethylsiloxane), GE Toshiba Silicones, TSF451-3000, kinematic viscosity: 3000 mm^2/s at 25°C] was used as purchased. N,N'-methylenebisacrylamide (MBAA), diethylene glycol diacrylate (DEGDA), ethylene glycol dimethacrylate (EGDM), N,N,N'N'-tetramethylethylenediamine (TMEDA), blue dextran (Sigma, molecular weight, 2,000,000 g/mol), and potassium persulfate were used without further purification.

Apparatus

IR spectra were obtained on a Perkin–Elmer model IR-700 spectrophotometer. UV-spectra were obtained on a Shimadzu model UV mini 1240 spectrophotometer. Photomicrographs and SEM photographs were taken on a Keyence model digital microscope VH-6300 and a JEOL model JSM-5600, respectively.

Sedimentation polymerization of NIPA

A typical sedimentation polymerization of NIPA is as follows. NIPA (2.0 g, 18 mmol), MBAA (54 mg, 0.36 mmol), TMEDA (5.4 μL, 0.036 mmol), and potassium persulfate (20 mg) were dissolved in a 20 wt % aqueous DMF solution (8.0 g) at 20°C under a nitrogen atmosphere. Silicone oil (GE Toshiba Silicones, TSF451-3000) was charged in a washing bottle in a water bath at 80°C and nitrogen gas was bubbled through the silicone oil for over 3 h. The monomer solution was injected dropwise into the silicone oil via a syringe with a needle (external diameter 1.5 mm, 90° tip). It was allowed to stand for 12 h at 80°C under a stream of nitrogen. The resulting beads were washed several times by swelling–deswelling using temperature swing between 20 and 80°C. The resulting beads were placed in water and stored in a refrigerator. The average diameter $(\overline{2R_0})$ of a bead deswollen at 80°C and the average weight $(\overline{w})$ of a dried bead were 2.70 mm and 3.00 mg, respectively. Other preparations of PNIPA gel beads are summarized in Table I.

Measurement of swelling–deswelling rate

A sample was placed in water at 20°C. The change in external radius (R_t/R_0), where R_0 and R_t are the

Figure 1 Simple sedimentation polymerization apparatus.

TABLE I
Synthesis of PNIPA Gel Beads by Sedimentation Polymerization[a]

Gel	Conc. of NIPA (wt %)	Crosslinker (mol %)	$\overline{2R_0}^{\,b}$ (mm)	$\overline{w}^{\,c}$ (mg)	σ^{d} (%)
GM-1	15	MBAA (2.0)	2.60	1.85	4.23
GM-2	20	MBAA (0.6)	2.61		4.35
GM-3	20	MBAA (1.0)	2.50	2.66	3.26
GM-4	20	MBAA (2.0)	2.70	3.00	4.28
GM-5	20	MBAA (3.0)	2.78	3.28	3.04
GM-6	20	MBAA (5.0)	2.87	3.30	6.00
GM-7	25	MBAA (2.0)	2.83	3.84	3.21
GM-8	30	MBAA (2.0)	2.75	4.83	5.54
GD-1	15	DEGDA (2.0)	2.37	1.78	3.78
GD-2	20	DEGDA (1.0)	2.48		5.25
GD-3	20	DEGDA (2.0)	2.52	2.69	3.98
GD-4	20	DEGDA (3.0)	2.63		3.78
GD-5	20	DEGDA (5.0)	2.73		4.49
GD-6	25	DEGDA (2.0)	2.59	3.56	3.09
GD-7	30	DEGDA (2.0)	2.67	4.22	3.74
GE-1	20	EGDMA (2.0)	2.24	1.28	5.31

[a] Sedimentation polymerization of an NIPA solution (10 g) was carried out at 80°C.
[b] Average diameter of a polymer bead deswollen in water at 80°C.
[c] Average weight of a dried gel.
[d] The relative standard deviation.

external radius of the gel deswollen in water at 80°C and the gel swollen in water for t min, respectively, was periodically recorded by a digital video camera (Sony DCR-HC1000).

Measurement of equilibrium swelling ratio

Sample beads were immersed in water at the desired temperature T°C, and were allowed to stand for 1 day. The weights of the swollen beads W_T and W_{80} was measured at T°C and 80°C, respectively. The equilibrium swelling ratio was defined as W_T/W_{80}.

Concentrating of blue dextran

Dried PNIPA gel beads (w_0 g) were placed in 10 mL of an aqueous blue dextran solution (initial concentration of glucose unit c_0, 1.1 mM), and was allowed to stand for 1 day at 20°C. The swollen PNIPA gel beads (w_1 g) were separated from the mixture by filtration, and weighed. The concentration (c_1 mmol/L) of blue dextran in the filtrate was determined by measuring the absorbance of the sample at 630 nm on a UV-spectrophotometer. The separation efficiency η is defined as follows.[4]

$$\eta = \frac{\frac{c_1}{c_0} - 1}{\left(\frac{10}{10 - w_1 + w_0}\right) - 1} \times 100 \ (\%) \tag{1}$$

The conditions and results are listed in Table II.

RESULTS AND DISCUSSION

Synthesis of PNIPA gel beads

The sedimentation polymerization of water-soluble monomers using a long cylindrical reactor containing a heat medium such as paraffin oil[23] or supercritical carbon dioxide[26] which is immiscible with water has been reported previously. The preparation of well-formed polymer beads by polymerization requires a sufficient time of sedimentation to form a stable skin on the droplets of monomer solution and fine temperature control to prevent coalescence at the base of the reactor and convection due to temperature differences. We used a simple sedimentation polymerization apparatus (Fig. 1) consisting of a 500-mL gas-washing bottle with 15 cm height of highly viscous silicone oil (kinematic viscosity, 3000 mm^2/s at 25°C) in a water bath. The temperature and the control of the temperature distribution in the silicone oil could be easily adjusted. The sedimentation time for a 3-mm diameter droplet of aqueous monomer solution in this apparatus was about 14 min at 80°C. This is sufficient time to produce beads by the polymer-

TABLE II
Blue Dextran Separation Efficiency at 20°C Using PNIPA Gel Beads

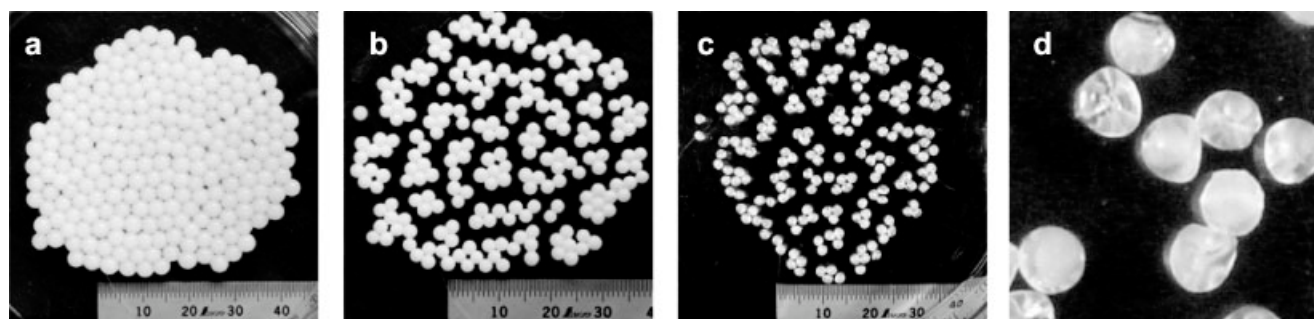| Gel	Crosslinker (mol %)	R_∞/R_0	η (%)
GM-3	MBAA (1.0)	1.86	6.0
GD-2	DEGDA (1.0)	1.56	42.3
GD-3	DEGDA (3.0)	1.30	93.7

Figure 2 Photomicrographs of PNIPA gel beads; (a) beads swollen in water at 20°C, (b) beads dewatered at 80°C, (c) dried beads, and (d) zoomed-in image of (c).

ization of an acrylate monomer such as 2-hydroxyethyl acrylate.[25] However, when the polymerization of an aqueous NIPA solution containing 1.0 mol % MBAA and 2 wt % potassium persulfate was carried out using this apparatus at 80°C, the droplets on the bottom of the bottle were agglutinated and the well-formed polymer beads were not produced. In a previous study,[29] we reported that the polymerization proceeded smoothly to give fine millimeter-sized beads when small amounts of DMF and TMEDA were added to the monomer solution. On the basis of this information, the polymerization of NIPA solutions with some crosslinkers in 20 wt % aqueous DMF containing 0.2 mol % TMEDA and 2.0 wt % potassium persulfate was carried out. The addition of DMF also caused the maximum solubility of NIPA to increase from about 20 wt % in water to 30 wt % in 20 wt % aqueous DMF solution at 20°C. Typical photographs of the resulting beads in water at 20 and 80°C, and the dried beads are shown in Figure 2. The

beads were cloudy. The beads swelled in water at 20°C, and the swollen beads were dewatered at 80°C. The swelling–deswelling was reversible. Both beads appeared to maintain a fine spherical shape and narrow particle size distribution in water. After drying, the beads were distorted, and the diameter could not be measured. Accordingly, the average diameter ($\overline{2R_0}$) and the particle size distribution of beads dewatered at 80°C were measured and these data are shown in Figure 3.

The polymerization was carried at various NIPA concentrations from 15 to 30 wt % with the content of crosslinker fixed at 2.0 mol % and at various crosslinker contents with the NIPA concentration fixed at 20 wt %. The copolymerization of NIPA with crosslinkers such as MBAA, DEGDA, and EGDM gave beads (GM-1-8, GD-1-7, and GE-1), respectively. The conditions for the reaction and results are listed in Table I. The relative standard deviation was about 3–6%, almost the same as that
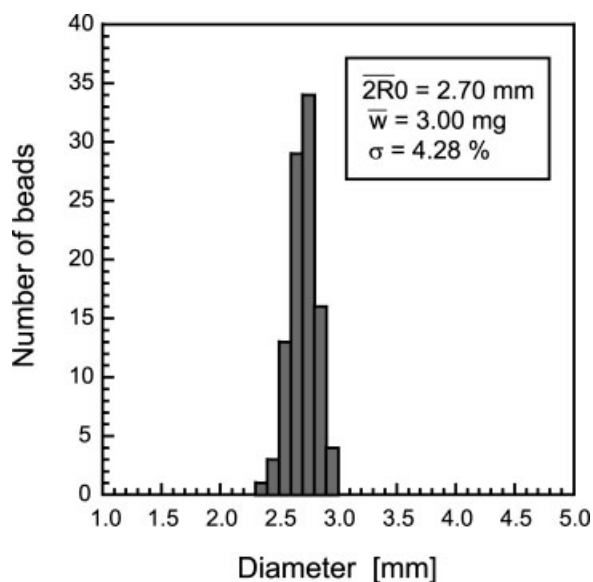

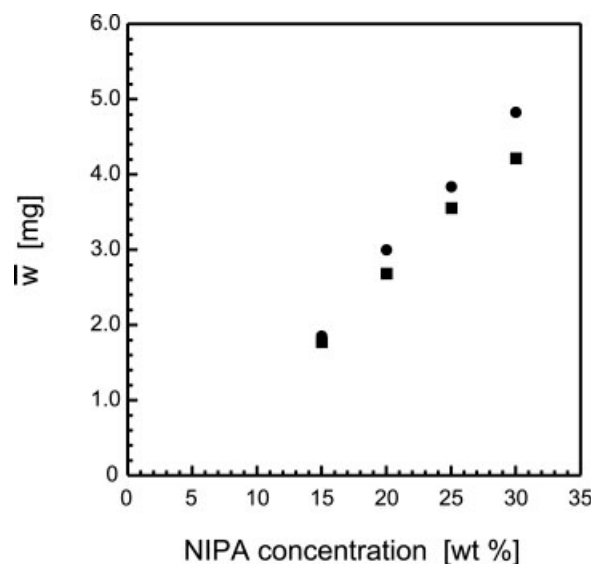**Figure 3** Typical particle size distribution of GM-3 beads dewatered at 80°C.

Figure 4 Relationship between NIPA concentration and the average weight of the PNIPA beads dewatered at 80°C.
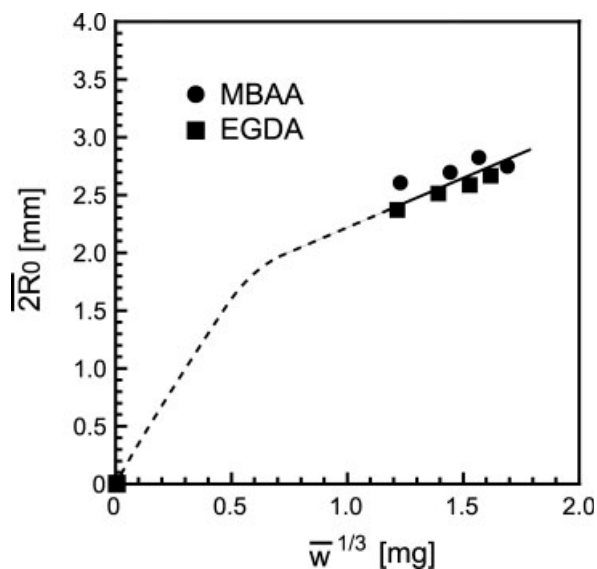
Figure 5 Relationship between the average diameter and the cube root of the average weight of the PNIPA beads dewatered at 80°C.

using a syringe reported previously[29] and by Ruckenstein and Hong.[23] These results suggest that a very narrow size distribution was achieved in all cases. Since the polymerization using MBAA proceeded almost quantitatively,[29] the average weight ($\overline{w}$) of the dried beads is proportional to the monomer concentration (Fig. 4). If the internal structure of the beads were homogeneous, $\overline{2R_0}$ beads should be directly proportional to the cube root of $\overline{w}$. However, Figure 5 did not show the direct proportionality between $\overline{2R_0}$ beads and the cube root of $\overline{w}$. This indicates that the internal structure of the beads is not uniform and the apparent porosity decreased with increasing monomer concentration.

Internal structure of beads

Typical cross-sectional photographs of dried GM-2 beads are shown in Figure 6. The beads obtained from the sedimentation polymerization had complex morphology, while a cylindrical gel synthesized using

the usual solution polymerization had a uniform porous morphology.[20] The gel obtained from the sedimentation polymerization roughly consisted of a large void encapsulated by two layers [Fig. 6(a)]. The inner layer was transparent and nonporous [Fig. 6(b)], while the outer layer was highly porous [Fig. 6(c)]. It seemed that the void was the result of heterogeneous polymerization from the surface of the droplet because the polymerization cannot produce enough polymers to fill the droplet. However, a void was not detected in the swollen bead since the void was preferentially filled with the swollen gel. The beads were greatly distorted after drying [Fig. 2(d)]. This can be attributed to the formation of voids.

Swelling–deswelling behavior of the PNIPA gel beads

The porous beads obtained were swollen and stored in water at 5°C. The swollen beads shrunk as soon as they were dipped in water at 80°C, and the shrinking is too fast to measure. Although nonporous PNIPA gels are known to form cracks during the deswelling, cracks were not detected during the swelling–deswelling cycles in the porous beads. The swelling of the various beads that were shrunk at 80°C was carried out in water at 20°C. The swelling was slower than the shrinking.

Effect of crosslinker on swelling behavior

The swelling of beads [GM-4, GD-2, and GE-1 ($2R_0 = \sim 2$–3 mm)] obtained by polymerization using 2.0 mol % MBAA, DEGDA, and EGDM as crosslinkers with the same NIPA concentration (20 wt %) was also measured (Fig. 7). It is known that a nonporous and uniform PNIPA gel swells slowly in water at a temperature below the LCST. For example, a nonporous cylindrical PNIPA gel ($2R_0 = \sim 4.8$ mm) prepared from amidation of poly(acrylic acid) gel required 40 h to reach equilibrium.[30] A GM-4 bead underwent rapid swelling reaching equilibrium within 3 min, where the GD-3 and GE-1 beads reached equilibrium after 50 and 280 min, respectively. The order of swelling rate was in
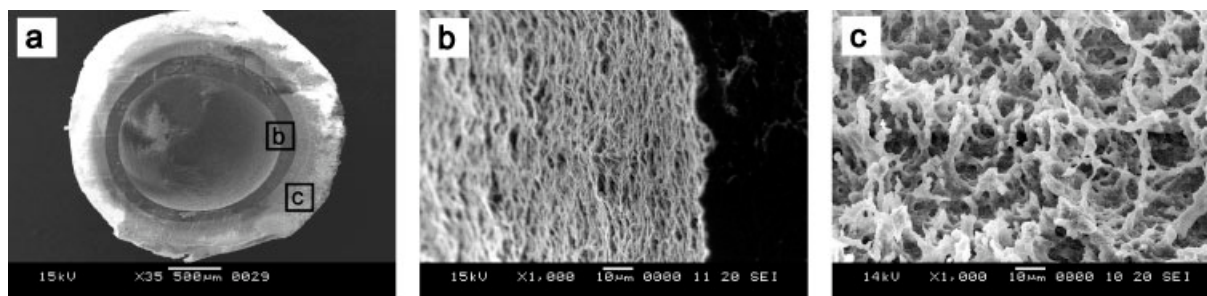

Figure 6 Cross-sectional SEM photographs of (a) GM-4, (b) nonporous region and interior surface in GM-4, (c) highly porous region in GM-4.
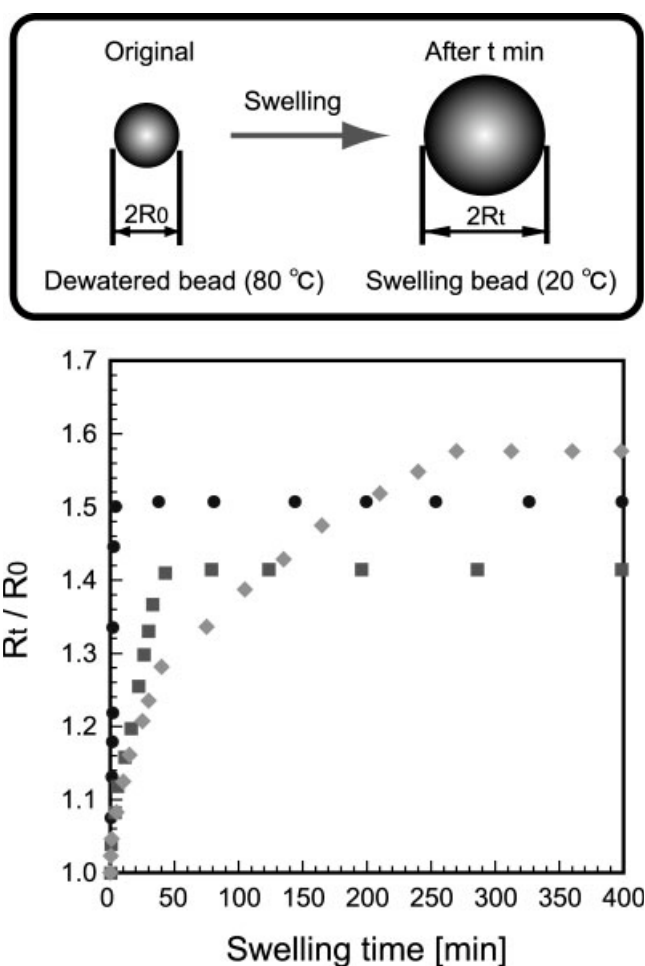
Figure 7 Swelling rate of beads in water at 20°C: ●, GM-4 ($2R_0$ = 2.51 mm), ▲, GD-3 ($2R_0$ = 2.78 mm), ◆, GE-1 ($2R_0$ = 2.17 mm).

general agreement with $\overline{w}$ and $\overline{2R_0}$. Therefore, when MBAA was used as a crosslinker, the polymerization proceeded smoothly, giving beads with well-developed porous structures. The equilibrium swelling ratio for these beads was measured in water over a wide temperature range (Fig. 8). The W_T/W_{80} values for these beads, where W_T and W_{80} are the weights of bead kept in water at T and 80°C, respectively, changed dramatically at a temperature around the LCST. The value for the GM-4 beads was smaller than that for GD-3 beads and larger than that for GE-1 beads at temperatures below the LCST. This indicates that the actual crosslink density of GM-4 beads was higher than GD-3 and lower than GE-1. These results can simply be attributed to the radical polymerizability of NIPA and crosslinkers as follows, which seems to decrease in the order: DEGDA > NIPA ≈ MBAA > EGDM. The polymerizability of EGDM was so low that the copolymerization of NIPA with EGDM did not proceed smoothly to give beads with a low crosslink density and low $\overline{w}$ When DEGDA, with a higher radical polymerizability than NIPA, was used as a crosslinker, the composition

ratio of DEGDA unit in the resulting gel was higher than the original composition ratio of DEGDA in the monomers at the beginning, but the DEGDA content decreased as the polymerization proceeded, and finally the homopolymerization of NIPA occurred because most of the DEGDA was consumed. The resulting polymer with a low crosslink density could be removed from the bead by washing. Therefore, copolymerization produced beads with a relatively high crosslink density and a slightly low $\overline{w}$. On the other hand, when MBAA with approximately the same polymerizability as NIPA was used as a crosslinker, the monomer composition ratio remained roughly constant during the polymerization. These results suggest that MBAA is the best crosslinker for the synthesis of porous PNIPA beads.

Effect of crosslinker content on swelling behavior

The crosslinker content is an important factor in the synthesis of porous PNIPA gels with rapid swelling–deswelling properties by the phase separation polymerization of NIPA. Figure 9 shows the swelling of the obtained gel beads for MBAA contents of 0.6, 1.0, 2.0, and 3.0 mol %, and DEGDA contents of 1.0, 2.0, 3.0, and 5.0 mol % with the concentration of an aqueous NIPA solution fixed at 20 wt %. Although the equilibrium swelling ratio of the resulting bead decreased with increasing crosslinker content, the swelling rate became higher with increasing crosslinker content up to a certain value, and the swelling ratio was then saturated within 3–5 min when the content exceeds this value. The values of the MBAA and DEGDA contents are 1.0 and 3.0 mol %, respectively. The glaring difference between the values
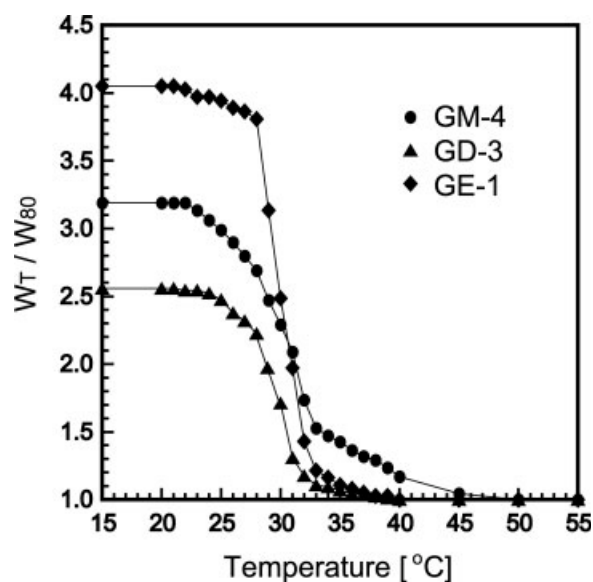

Figure 8 Equilibrium swelling ratio of PNIPA gel beads in water as a function of temperature.
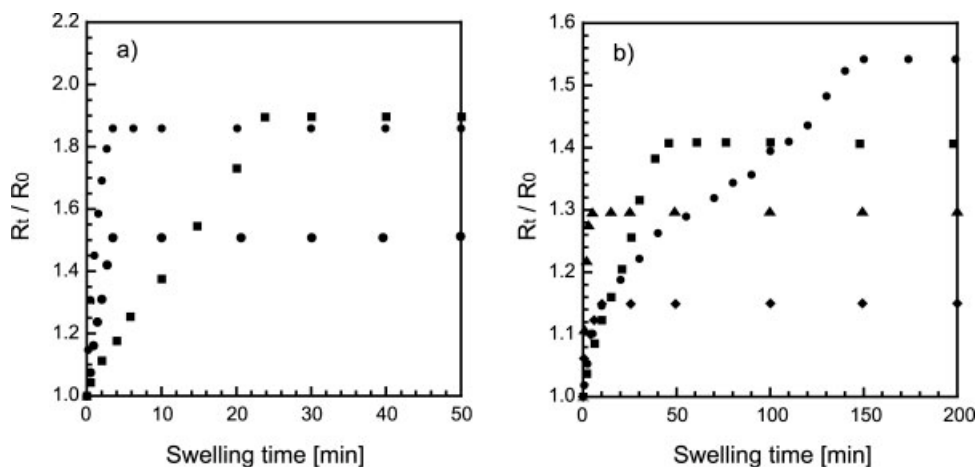
Figure 9 Swelling rate of beads prepared by the polymerization of NIPA containing various crosslinker contents in water at 20°C; (a) using MDAA as a crosslinker: ■, 0.6 mol % ($2R_0$ = 2.72 mm); ●, 1.0 mol % ($2R_0$ = 2.56 mm); ○, 2.0 mol % ($2R_0$ = 2.51 mm); (b) using DEGDA as a crosslinker: ●, 1.0 mol % ($2R_0$ = 2.66 mm); ■, 2.0 mol % ($2R_0$ = 2.78 mm); ▲, 3.0 mol % ($2R_0$ = 2.97 mm); ◆, 5.0 mol % ($2R_0$ = 2.60 mm).

may be explained by the difference between their copolymerizability with NIPA. Cross-sectional photographs of the dried beads are shown in Figure 10. The porous layer increased, and nonporous layer and the void decreased with increasing crosslinker content. The developed porous structure leads to an increased swelling rate. However, the effect of the type of crosslinker on the morphology could not be observed.

Effect of concentration of aqueous NIPA solution on swelling behaviors of the obtained beads

The swelling of beads resulting from polymerization at concentrations of an aqueous NIPA solution (15, 20, 25, and 30 wt %) with the content of crosslinker fixed at 2.0 wt % were carried out in water at 20°C. The swelling behavior is shown in Figure 11. The swelling rate would be expected to decrease with increasing monomer concentration because the appa-
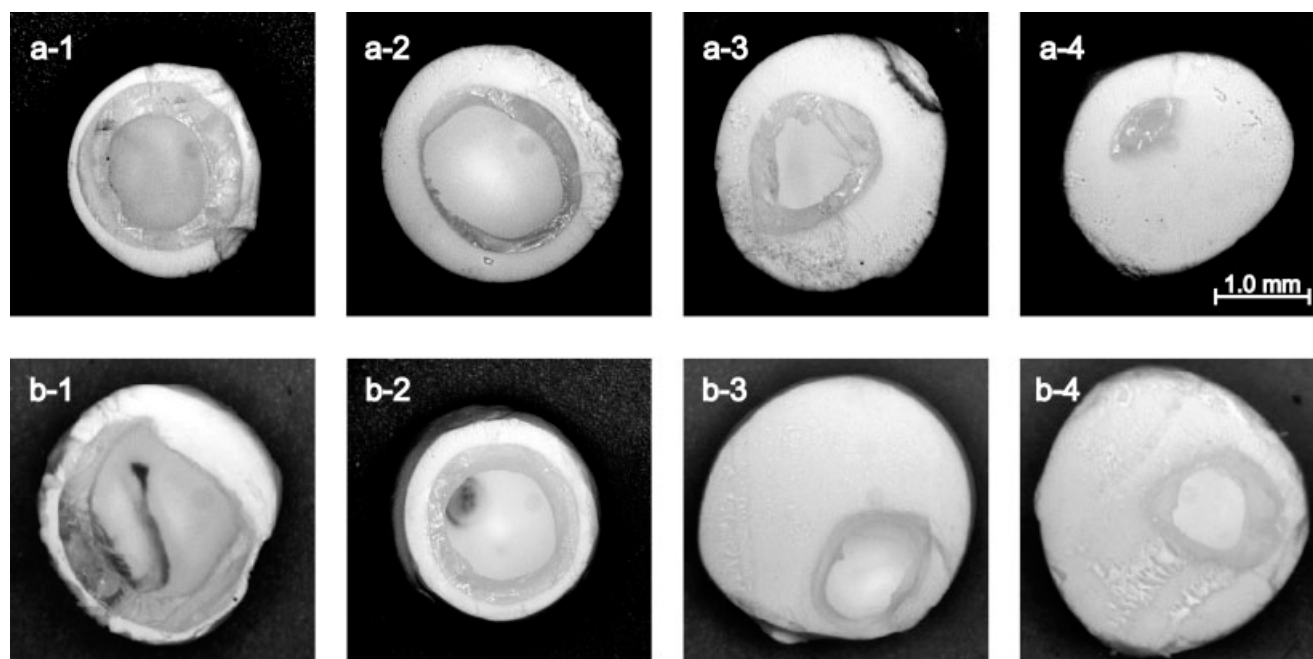

Figure 10 Cross-sectional photographs of beads prepared by the polymerization of NIPA containing various crosslinker contents; (a-1) MBAA 1.0 mol %, (a-2) MBAA 2.0 mol %; (a-3) MBAA 3.0 mol %, (a-4) MBAA 5.0 mol %, (b-1) DEGDA 1.0 mol %, (b-2) DEGDA 2.0 mol %, (b-3) DEGDA 3.0 mol %, (b-4) DEGDA 5.0 mol %.
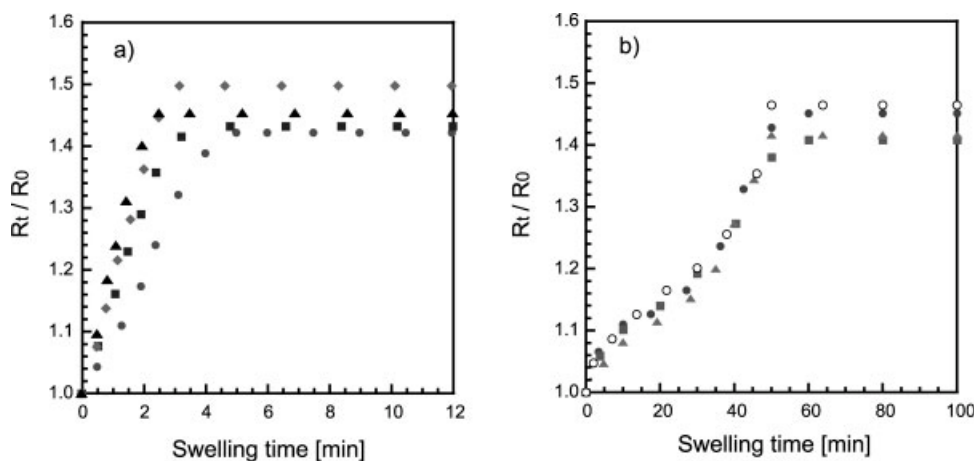
Figure 11 Swelling rate of beads prepared by the polymerization of various NIPA concentrations in water at 20°C; (a) using MDAA as a crosslinker: ▲, 15 wt % ($2R_0 = 2.53$ mm); ◆, 20 wt % ($2R_0 = 2.51$ mm); ■, 25 wt % ($2R_0 = 2.78$ mm); ●, 30 wt % ($2R_0 = 2.85$ mm); (b) using DEGDA as a crosslinker: ○, 15 wt % ($2R_0 = 2.61$ mm); ▲, 20 wt % ($2R_0 = 2.71$ mm); ■, 25 wt % ($2R_0 = 2.85$ mm); ●, 30 wt % ($2R_0 = 2.73$ mm).

rent porosity decreased, as described above. In addition, the porous layer showed a tendency to become thinner and the void became bigger with increasing NIPA concentration, as evidenced by microscopic observations (Fig. 12). However, the beads showed almost the same swelling rate, and the swelling behavior was not significantly affected by the concentration of NIPA.

Concentrating blue dextran

Nonporous hydrophilic polymer gels such as PNIPA can absorb large quantities of water and low molecu-

lar weight solutes, while excluding larger molecules. The swelling of gels in an aqueous solution of larger molecules causes the latter molecules to be concentrated. Blue dextran can be effectively concentrated from the aqueous dilute solution using PNIPA gels[4,10,13] since the molecules are too large to penetrate into the polymer network. The concentration of blue dextran from the aqueous dilute solution using the resulting porous PNIPA beads was tested (Table II). When GM-3 with 1.0 mol % MBAA units was used, the separation efficiency is 6.0%. Such PNIPA beads with well-developed microporous structures would not be expected to concentrate the blue dex-
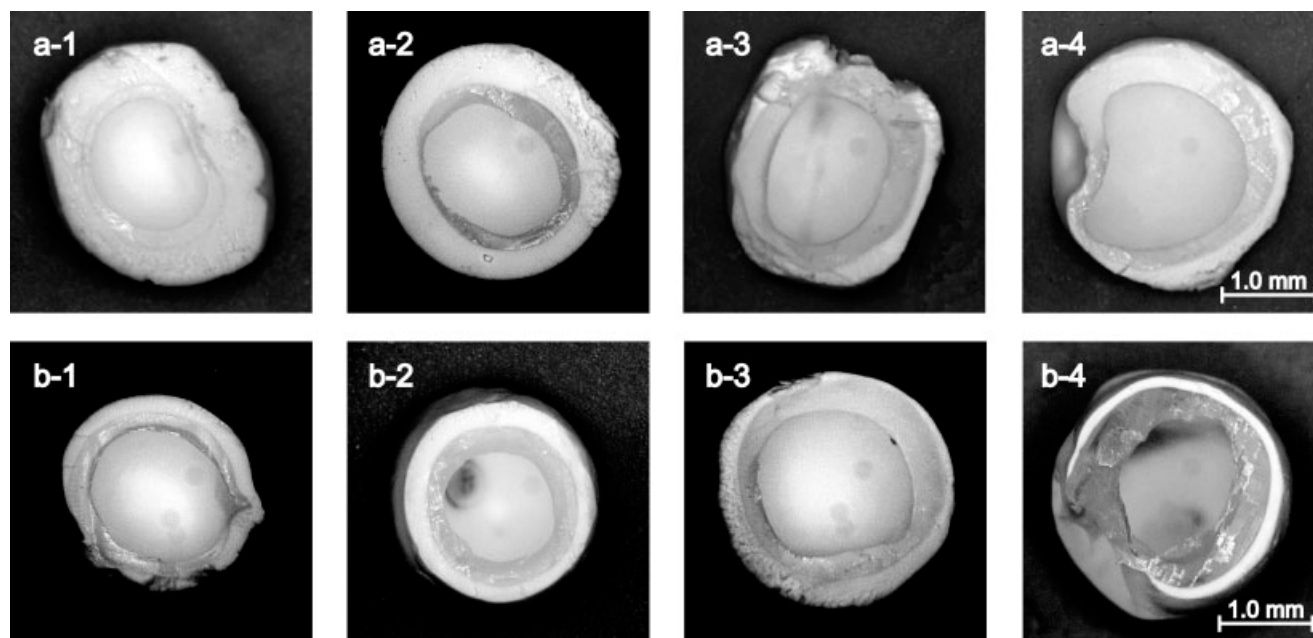

Figure 12 Cross-sectional photographs of beads prepared by the polymerization of various NIPA concentrations: (a-1) 15 wt % MBAA, (a-2) 20 wt % MBAA, (a-3) 25 wt % MBAA, (a-4) 30 wt % MBAA, (b-1) 15 wt % DEGDA, (b-2) 20 wt % DEGDA, (b-3) 25 wt % DEGDA, and (b-4) 30 wt % DEGDA.

tran solution very effectively. However, the separation efficiency of GD-2 and GD-3 with 1 and 3 mol % units of DEGDA were 42.3% and 93.7%, respectively. The efficiency and swelling rate increased with increasing DEGDA content of the beads, and GD-3 showed a nearly quantitative separation efficiency and high-speed swelling-deswelling behavior. This suggests that dry GD-3 is porous, but swollen GD-3 has a few pores that are larger than a blue dextran molecule. As DEGDA showed a higher polymerizability than NIPA, a distribution of crosslink density occurred in GD-3 beads. Kayaman et al.[6] reported that the separation efficiency of a low molecular weight compound increased when PNIPA beads coated with protein molecules were used. We estimated the microstructure and swelling mechanism of GD-3 as follows. The heterogeneous polymerization of NIPA with DEGDA gives well-developed porous beads with a relatively high density of crosslinking. However, the final stage of the polymerization produces a nonporous thin PNIPA film with a low crosslink density since the concentration of monomers is so low that porous polymers cannot be produced in the polymerization. Accordingly, the polymerization leads to the surface of the porous beads being coated with a nonporous thin film. When GD-3 beads were dipped in water, the thin film swelled rapidly, and, consequently, the swollen film plugged the pores.

CONCLUSIONS

Porous PNIPA beads were prepared by the sedimentation polymerization of a solution of NIPA in aqueous DMF. The resulting beads have a balloon-like morphology consisting of a large void encapsulated by two layers. The inner layer was transparent and nonporous, while the outer layer was highly porous. The morphology and swelling–deswelling behavior of the beads were markedly dependent on the crosslinker used and the content of crosslinker. Dried beads prepared by the polymerization of NIPA using 3 mol % DEGDA as a crosslinker have a well-developed porous structure, but few pores are available after swelling in water. These results indicate that GD-3 beads are suitable water-absorbing polymers for the concentration of aqueous polymer solutions, although the equilibrium swelling ratio is not sufficiently high.

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