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ORIGINAL CONTRIBUTION

Fast responsive poly(*N, N*-diethylacrylamide) hydrogels with interconnected microspheres and bi-continuous structures

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Abstract We prepared thermo-responsive polymer hydrogels by γ-ray irradiation of aqueous solutions of *N, N*-diethylacrylamide at different temperatures below and above its lower critical solution temperature (LCST). Poly (*N, N*-diethylacrylamide) gel had a transparent and homogeneous structure when the radiation-induced polymerization and crosslinking were carried out below the LCST (25 °C) of the polymer. On the other hand, cloudy and heterogeneous gels were formed at temperatures above the LCST of the polymer (>35 °C). From environmental scanning electron microscopy observations, the gels prepared at 35 and 40 °C were seen to show sponge-like bi-continuous porous structures, while those prepared at 50 °C showed a porous structure consisting of interconnected microspheres. For temperature changes between 10 and 40 °C, gels with porous structures showed rapid volume transitions on a time scale of about a minute, not only for shrinking but also for swelling processes, which is in remarkable contrast to the porous poly(*N*-isopropylacrylamide) hydrogels.

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Introduction

Polymer hydrogels consist of a three-dimensional network of crosslinked polymers swollen in an aqueous medium. Some kinds of hydrogels can change their shape and volume reversibly following changes in external physical and chemical conditions such as temperature, solvent composition, ionic strength, pH, electric field, and light [1–3]. Recently, stimuli-responsive polymer hydrogels have been attracting the attention of many researchers and are playing a part in a variety of fields, such as chemical engineering, medicine and pharmacy, life sciences, biotechnology, agriculture, etc. To perform well in these systems, the polymer hydrogels need their volume transitions to respond rapidly. Since the swelling rate of a hydrogel is proportional to the square of its linear size [4], small gels, such as microspheres, fine fibers, and thin films, show a fast responsiveness. However, these small or fine gels are not always suitable for application as devices.

In order to improve the response time without simultaneously decreasing the gel size, the synthesis of macro-porous hydrogels by a phase separation of thermo-responsive polymers is very effective. Poly(*N*-isopropylacrylamide) (PNIPAM) is a well-known example of a typical thermo-sensitive polymer; its aqueous solution exhibits a phase separation at a lower critical solution temperature (LCST) [5]. Several researchers have prepared porous and heterogeneous PNIPAM gels by a radical copolymerization of *N*-isopropylacrylamide (NIPAM) with a crosslinking monomer above the LCST [6–8]. Compared with homogeneous PNIPAM hydrogels synthesized below the LCST, these hydrogels have both a larger pore volume and an increased surface area; in addition, they show a rapid volume transition upon temperature alteration.

For the crosslinking methods, the γ-ray irradiation appears to be an effective and reproducible method to prepare fast response porous and heterogeneous hydrogels [9, 10]. These porous PNIPAM gels can be synthesized by radiation polymerization using an aqueous solution of NIPAM without a crosslinking monomer [11–13]. Just after the irradiation begins, the radiation-induced polymerization produces an exothermic reaction, and during the course of the irradiation, radioactive heating takes place. These two factors keep the temperature of the monomer solution close to the radiation source (^{60}Co) above the LCST. The following phenomena occurred simultaneously under these irradiation conditions: a radiation-induced polymerization of the monomers, an irradiation-produced phase separation of the polymers, and a crosslinking reaction of the phase-separated polymers. Thus, a heterogeneous and opaque gel with a phase separated, porous structure was formed. The advantages of this method are its easy reproducibility and adaptability to copolymerization with other water-soluble, functional monomers such as acrylic acid [12, 13].

Recently, using Fourier transform infrared spectroscopy and differential scanning calorimetry (DSC) measurements, Maeda et al. investigated the temperature dependences of hydrogen bonds and hydration states of thermo-responsive poly(*N*-monoalkylacrylamide)s [14, 15] and poly(*N, N*-dialkylacrylamide)s [16, 17] on the phase separation. They revealed that the presence of the amide proton of poly(*N*-monoalkylacrylamide) such as PNIPAM, as a hydrogen bond donor is important to its phase transition behavior [14, 17]. In the case of poly(*N*-monoalkylacrylamide), the hydrogen bonding between C=O and water below the LCST is partially broken and that intra- and inter-molecular hydrogen bonds between the amide groups (C=O ··· H–N) form during the coil-to-globule transition. From the resulting DSC curves, the transition temperature region of PNIPAM is very narrow (ca. 1 °C). This narrow phase transition appears to result from the cooperative formation of C=O ··· H–N hydrogen bonds.

On the other hand, a poly(*N, N*-dialkylacrylamide) such as poly(*N, N*-diethylacrylamide) (PDEAM) does not contain amide protons, since only dehydration between C=O and water takes place during the coil-to-globule transition [17]. In this case, the transition temperature region of PDEAM obtained from the DCS measurement is over 15 °C and much wider than that of PNIPAM.

The phase transition behavior of PDEAM hydrogel is also different from that of PNIPAM gel. In the case of homogenous structures, the PDEAM gel exhibits a thermo-responsive volume transition, which gradually decreases on increasing the temperature [18, 19], whereas the PNIPAM hydrogel shows discontinuous volume transition at around the LCST (33 °C) [20].

Although the porous PDEAM gels have been reported [8], the preparation method was the radical copolymerization with crosslinking monomer and their porous structure was observed at the freeze-drying states. While the crosslinking by radical copolymerization completed in a considerably short period which corresponds to the initial phase separation stage, the γ-ray crosslinking requires far longer time. This slow crosslinking process makes possible to obtain various phase separated gel structures compared with the conventional method. In addition, we can observe gel structures in the wet states directly by an environmental scanning electron microscope (ESEM). ESEM is considered to be a suitable method for structural observation of the highly hydrated porous gels to avoid drastic structural changes of specimens during freezing and drying [13].

In the present work, we prepared macro-porous PDEAM gels by γ-ray polymerization and crosslinking under different temperatures and investigated the relationship between the phase-separated porous structures and the responsive properties of the PDEAM hydrogels.

Experimental

Materials

N, N-diethylacrylamide (DEAM) (Kohjin, Tokyo, Japan) was purified by distillation under reduced pressure before use. Tert-butyl alcohol (Wako Pure Chemical Industries, Osaka, Japan) was distilled before use. All other materials were used as received.

Synthesis and characteristics of linear PDEAM

The LCST of the polymer is a decisive factor in the phase separation process; it plays an important role in forming the porous structures of gels. Therefore, we examined the LCST of the linear polymer in aqueous solution. Dissolved in tert-butyl alcohol (100 mL) were 12.72 g of DEAM (0.1 mol) and 164 mg of α, α′-azobisisobutyronitrile (1 mmol). After purging with nitrogen gas at room temperature for 30 min, the polymerization was carried out at 60 °C for 6 h. After completion of the polymerization, the solvent was evaporated and the remaining solid was dissolved in deionized water. PDEAM was purified by dialysis using a Spectra/Por Membrane (Spectrum Laboratories, MWCO 1,000) in deionized water at 10 °C for 20 days and then freeze-dried. The number-average molecular weight (Mn) was determined to be 8,200 (Mw/Mn 1.6) by gel permeation chromatography (column: Shodex K-805L & KF802, eluent: chloroform) calibrated with standard polystyrene. The cloud point of PDEAM aqueous solutions (0.5 wt.%) was 29.8 °C determined from the 50% transparency at 500 nm while raising the temperature continuously (heating rate 1 °C/min).

Preparation of the PDEAM gels at different temperatures

Five grams (39.3 mmol) of DEAM was dissolved in 20 mL of deionized water and purged with nitrogen gas. The solution was then transferred into several sealed glass test tubes (inner diameter 10 mm). We irradiated the DEAM solution with a ^{60}Co γ-ray source under temperature control using the equipment previously reported [10]. Circulating water from a thermostatic water bath (Lauda, RM6) enabled us to regulate the equipment's temperature. The temperature of the equipment during the irradiation was kept constant at 25, 30, 35, 40, and 50 °C. The dose rate and time of radiation were 7.19 kGy h^{-1} and 11 h 40 m, respectively; we monitored the equipment's temperature during irradiation by thermocouple. The respective products prepared at 25, 30, 35, 40, and 50 °C were labeled as PDEAMG-25, PDEAMG-30, PDEAMG-35, PDEAMG-40, and PDEAMG-50. After irradiation, the gels prepared in glass tubes were washed several times with a large amount of water at 5 °C.

Measurements

For the swelling measurement, we used cylinder shape gels that were cut into 7.5 mm long at 50 °C and observed changes in their size and shape with a video system. A Hi-8 videocassette recorder (SONY; EVO-9650) equipped with a CCD camera system (Olympus; CS230 CCD camera, Kenko; Macro lens ×10) recorded the images of the volume transition; to measure the size of the gel under various conditions, we used an image analysis system (Kenko, Measure unit MC-50). We calculated the degree of swelling in diameter, $d/d_{50\,^\circ\mathrm{C}}$ from the diameter of the gel under various conditions (d) and the diameter at 50 °C $(d_{50\,^\circ\mathrm{C}})$.

ESEM observation

The ESEM images were obtained by the method reported previously [13]. The swelling of gels in deionized water at 3 °C was examined with the ESEM (Philips, XL30 ESEM-FEG) operated at 15 kV. The gels, which were prepared in the glass test tubes described above, were cut into small pieces using a razor blade. We observed the sliced surface of these pieces. The pieces were placed on the cooling stage of the ESEM adjusted to 3–5 °C and maintained above a saturated water pressure of 0.76–0.87 kPa (5.7–6.5 Torr). Under these conditions, the ESEM showed a water layer covering the sample surface. To prevent inordinate dehydration of the samples, the vapor pressure in the chamber was lowered gradually until the sample surface appeared. The ESEM images were usually observed at a vapor pressure of 0.33–0.56 kPa (2.5–4.2 Torr). Since exposure to an electron beam over 5–7 min causes damage to the samples or local evaporation, we observed samples for only 2–3 min, during which no destruction of the structure was observed in our samples.

Results and discussion

Formation of the PDEAM gels under various temperatures

PDEAM gels were formed by γ-ray-induced polymerization and crosslinking. Below the LCST of the polymer (25 °C), we obtained a transparent and homogeneous PDEAM gel (PDEAMG-25). On the other hand, cloudy and heterogeneous PDEAM gels (PDEAMG-30, PDEAMG-35, PDEAMG-40, and PDEAMG-50) were formed at temperatures near and above the LCST of the polymer (30, 35, 40, and 50 °C). We studied the thermal volume changes of the PDEAM hydrogels in water at various temperatures. Figure 1 shows a plot of the degree of swelling in length $(d/d_{50\,^\circ\mathrm{C}})$ of the gels against the temperature. At first, we set the temperature of the water at 10 °C, and then raised it stepwise to 50 °C. The system was thermally equilibrated at each temperature over 3 days. All the gels showed a continuous thermal volume transition, and they swelled at a lower temperature region and shrank gradually on increasing the temperature. The swelling curves of the all the gels were almost the same and not dependent on differences in their synthesis temperatures.

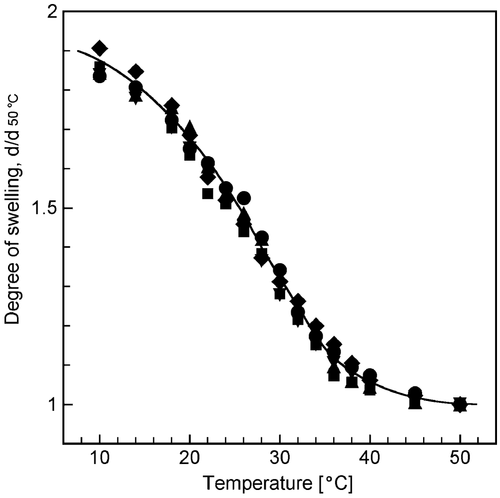

Fig. 1 Degree of swelling in length $(d/d_{50\,^\circ\mathrm{C}})$ of the gels plotted against the temperature. PDEAMG-25 (*filled square*), PDEAMG-30 (*filled triangle*), PDEAMG-35 (*filled circle*), PDEAMG-40 (*inverted filled triangle*), PDEAMG-50 (*filled diamond*)

ESEM images of the PDEAM gels prepared at different temperatures

To avoid drastic structural changes of specimens during freezing and drying, ESEM is considered to be a suitable method for structural observation of the highly hydrated samples, such as porous hydrogels prepared by γ-ray irradiation with phase separation [13]. The structures of the PDEAM gels prepared by the irradiation at the different temperatures were observed directly by ESEM (Fig. 2). The ESEM image of the PDEAMG-25 prepared below the LCST can be seen in Fig. 2a. The structure of this gel is homogeneous, and the fractured part is flat and smooth. A porous structure is not produced by the irradiation, since the temperature during radiation is lower than the LCST of PDEAM.

Figure 2b shows the ESEM image of the PDEAMG-30 prepared at 30 °C, around the LCST of the polymer. The sliced surface of the gel was irregular and rough and many discontinuous depressions were observed on the surface. These depressions, which might have been caused by slicing the gels, have many independent and unconnected small pores. It seems that these pores were formed by the small water droplets that slightly phase separated around the LCST.

On the other hand, the precise porous structures were observed in the gels prepared at 35, 40, and 50 °C, since the temperatures during radiation were higher than the LCST of

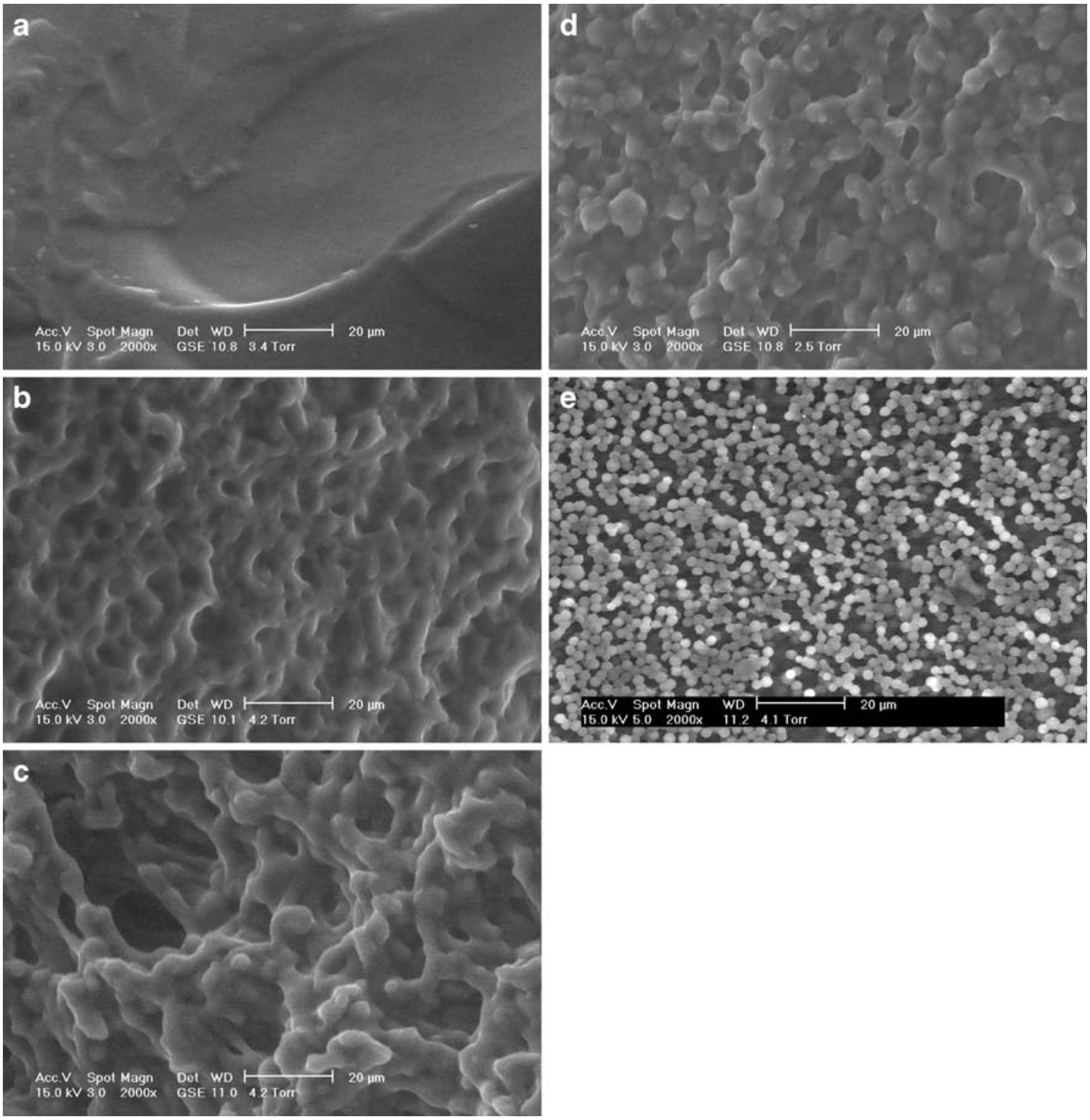

Fig. 2 ESEM micrographs of the gels. **a** PDEAMG-25, **b** PDEAMG-30, **c** PDEAMG-35, **d** PDEAMG-40, **e** PDEAMG-50. All at same magnification

the polymer. The shape and size of the gel pores varied depending on the irradiation temperature. In Fig. 2e, a porous structure consisting of interconnected microspheres approximately 1.8–3.5 μm in diameter was observed for PDEAMG-50. This structure, which consists of interconnected microspheres, was also previously observed in the γ-ray-prepared macro-porous PNIPAM hydrogel [13].

Kawaguchi et al. synthesized independent and monodisperse microspheres using a dilute monomer solution [21]. In this case, inhibition due to low monomer concentration (2.6%) resulted in the formation of dispersed small gel droplets. However, the monomer concentration in this study was very high (DEAM concentration 20%), and the gel clusters were close to each other during the polymerization. In our opinion, the phase separation is an important factor for the formation of micro-droplet structures at high polymer concentrations. The crosslinking reaction of the gel preserved the micro-droplet structure formed at the intermediate phase separation stage, which also obstructed the further coarse-graining processes of the droplets.

In PDEAMG samples prepared at 35 and 40 °C, the ordinary bi-continuous porous structures were observed, as shown in Fig. 2c and d. In these conditions, the initial bi-continuous porous structures may be preserved during the irradiation, since the phase separation speed was slower than that of the PDEAMG-50.

Thermal volume changes of the PDEAM gels

The thermal shrinking and swelling behaviors of the PDEAMGs were studied in deionized water. Figures 3 and 4 show the time profiles of the volume change of these gels. They underwent a thermal contraction when, after swelling to equilibrium at 10 °C, they were immersed in water at 40 °C. The porous gels prepared above the LCST, such as PDEAMG-35, PDEAMG-40, and PDEAMG-50, showed a rapid contraction; the time required for them to shrink to their equilibrium state was approximately 2 min.

It is remarkable that these gels also swelled rapidly when the shrunken gels were immersed again in water at 10 °C (Fig. 4); they completely recovered their original size and shape within 2 min. In the case of PNIPAM porous gels, they show a fast volume transition at shrinkage process, but the response time of the swelling was 15 times longer than that of the shrinkage [11]. The slow swelling of PNIPAM can be explained as follows. The amide proton of PNIPAM plays an important role as a hydrogen bond donor for its phase transition [14, 17]. The hydrogen bonding between the C=O of PNIPAM and water below the LCST is partially broken and that the intra- and inter-molecular hydrogen bonding between the amide groups (C=O ··· H–N) forms during the phase transition. In the case of PNIPAM hydrogel, the intra- and inter-molecular hydrogen bonding between the amide groups (C=O ··· H–N) also forms in the shrinking state. Therefore, the slower swelling of PNIPAM gel results from the increase in hydrophobicity resulting from hydrogen bonding formation. On the other hand, a poly (*N, N*-dialkylacrylamide) gel does not have amide protons, and neither intra- and inter-molecular hydrogen bonding between the amide groups is present in the shrinking state. Thus, slowing of the swelling response does not occur, instead a rapid swelling takes place as in the shrinking process.

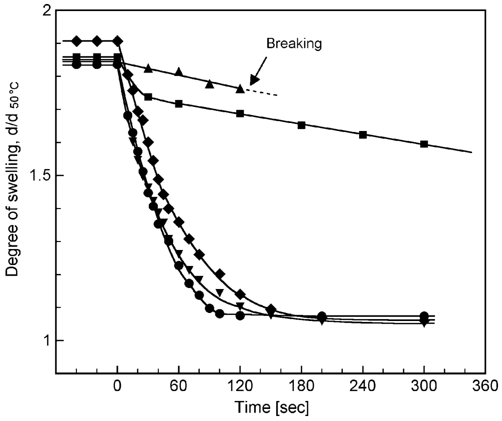

Fig. 3 Time profiles of the shrinking of gels for temperature change from 10 to 40 °C. PDEAMG-25 (*filled square*), PDEAMG-30 (*filled triangle*), PDEAMG-35 (*filled circle*), PDEAMG-40 (*inverted filled triangle*), PDEAMG-50 (*filled diamond*)

In contrast, the PDEAM gels prepared below and around the LCST showed different volume transitions from those prepared above the LCST. PDEAMG-25 shrank and swelled slowly compared to the porous gels, since the structure of the gel was non-porous and homogeneous. The relaxation times of shrinking and swelling were approximately 7 and 11 h, respectively. PDEAMG-30 also showed slow shrinkage in water at 40 °C; after 1 h, cracks appeared

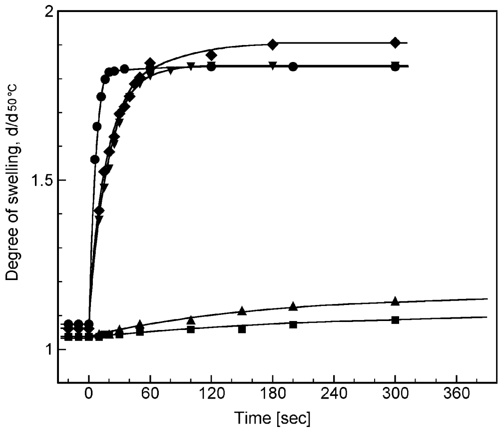

Fig. 4 Time profiles of the swelling of the gels for temperature change from 40 to 10 °C. PDEAMG-25 (*filled square*), PDEAMG-30 (*filled triangle*), PDEAMG-35 (*filled circle*), PDEAMG-40 (*inverted filled triangle*), PDEAMG-50 (*filled diamond*)

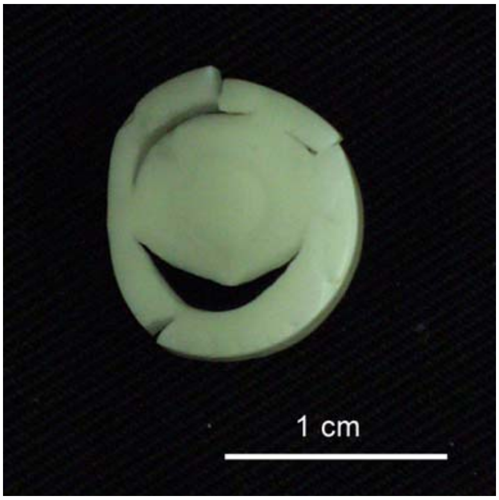

Fig. 5 Shrinking rupture of the PDEAMG-30 immersed in water at 40 °C

in the surface of the gel and grew gradually. About 5 min later, the growth of a crack led to rupture of the gel, shown in Fig. 5. We have already discussed the many depressions in the surface of PDEAMG-30 (see Fig. 2b). Many depressions in the surface increase the gel's surface area and therefore the shrinking speed of the surface seems to be faster than that of the interior of the gels. Furthermore, the pores inside the gel were discontinuous and independent making them unable to act as efficient water channels when the gel undergoes volume transitions; thus, the inside of the gel responded slowly to temperature changes. It appears, therefore, that the cracks are formed due to the difference in the rate of shrinking between the surface area and the inside of the gel. However, rupture of the PDEAMG-30 was not observed under the gradually temperature rising from 10 to 40 °C over 5 days. This gel also swelled slowly when the shrunken gel was re-immersed in water at 10 °C (Fig. 4); they completely recovered their original size and shape over 10 h.

Table 1 The deformation ratio and response time obtained by the exponential fittings of temperature-induced shrinking of PDEAM gels

Preparation temperature (°C)	Amount of deformation	Response time (s)
25	0.44[a]	820[a]
	0.28[b]	4,960[b]
30	–	–
35	0.83	41
40	0.78	46
50	0.91	59

[a] Fast mode
[b] Slow mode

Table 2 The deformation ratio and response time obtained by the exponential fittings of temperature-induced swelling of PDEAM gels

Preparation temperature (°C)	Amount of deformation	Response time (s)
25	0.24[a]	1,470[a]
	0.60[b]	10,000[b]
30	0.32[a]	1,330[a]
	0.45[b]	20,000[b]
35	0.76	6
40	0.78	20
50	0.81	21

[a] Fast mode
[b] Slow mode

Tables 1 and 2 show the deformation ratio and the response time obtained by the exponential fittings of temperature-induced shrinking and swelling of PDEAMG, respectively. The fitting equations are given by $R = \Delta R\exp(-t/\tau) + R_{\mathrm{fin}}$ for the single exponential curves and $R = \Delta R_{\mathrm{slow}}\exp(-t/\tau_{\mathrm{slow}}) + \Delta R_{\mathrm{fast}}\exp(-t/\tau_{\mathrm{fast}}) + R_{\mathrm{fin}}$ for the double exponential curves, where R is the deformation ratio $(d/d_{50\,^\circ\mathrm{C}})$, ΔR is the amount of deformation, and τ is the response time.

The shrinking and swelling processes of the porous gels showed a good fit to a single exponent. For example, the exponential fittings of PDEAMG-40 were shown in Fig. 6a and b. The volume transition effect is derived from their structures, made up of three-dimensional and continuous pores, which can behave as water channels when the gel undergoes volume transitions. Therefore, these gels responded quickly to a change in temperature. The response times of the porous hydrogels decreased with decreasing preparation temperature. We have described above their continuous porous structure observed from ESEM. The PDEAMG-50 is composed of interconnected microspheres, since its pore size is very small and 3.5 µm or less (Fig. 2e). The small pores inhibit water release and absorption during volume transition of the gel. On the other hand, the structures of PDEAMG-35 and PDEAMG-40 are the ordinary bi-continuous porous structures and their pore sizes are larger than that of the PDEAMG-50 (Fig. 2c); hence, these gels responded quickly to a change in temperature. In particular, PDEAMG-35 shows fast volume transitions on both shrinking and swelling processes (Tables 1 and 2).

In contrast, the shrinkage and swelling processes of the non-porous PDEAMG-25 exhibited better fits to double exponent as shown in Fig. 7a and b. The shrinkage occurred in the fast mode at the beginning of the process, but changed to slow mode at longer times (t>820 s). In the initial shrinking stage, the water contained in the gel was released from PDEAMG-25. Thus, the gels initially shrank

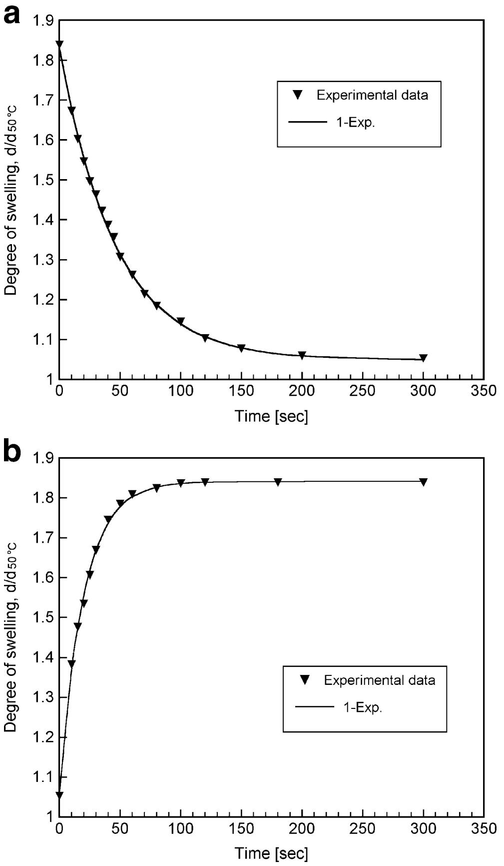

Fig. 6 Exponential fittings of temperature-induced shrinking and swelling of PDEAMG-40. **a** Shrinking process of PDEAMG-40, **b** swelling process of PDEAMG-40. Experimental data points (*inverted filled triangles* in Figs. 3 and 4) are also shown

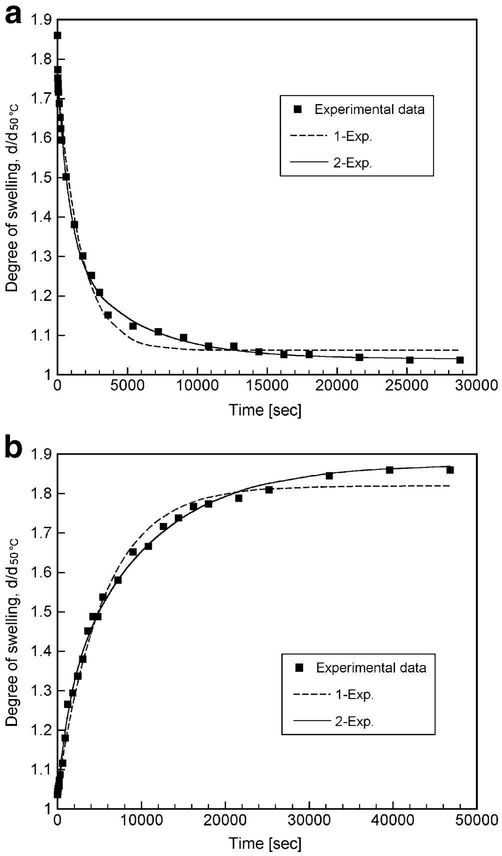

Fig. 7 Exponential fittings of temperature-induced shrinking and swelling of PDEAMG-25. **a** Shrinking process of PDEAMG-25, **b** swelling process of PDEAMG-25. Experimental data points (*filled squares* in Figs. 3 and 4) are also shown

quickly. However, since the network density of PDEAMG-25 was increased by the shrinking with water release, the release of the water that remained inside the gel was inhibited. Therefore, the shrinking speed was reduced. In the swelling processes of PDEAMG-25 and PDEAMG-30, the lowering of swelling speed was also observed. These reduced thermal swellings might result from the difference in diffusion rates of the network between the surface area and the inside of the gel.

Conclusions

We have prepared polymer hydrogels by γ-ray irradiation of a DEAM aqueous solution under different temperatures above and below the LCST of PDEAM (30 °C). Below the LCST (25 °C), we obtained a transparent and homogeneous gel (PDEAMG-25). On the other hand, cloudy and heterogeneous gels (PDEAMG-30, PDEAMG-35, PDEAMG-40, and PDEAMG-50) were formed at temperatures near and above the LCST of the polymer (30, 35, 40, and 50 °C). From ESEM observations of the gels, the structures of the gels depended strongly on the temperature during γ-ray irradiation. In the case of gels prepared by the irradiation above the LCST, PDEAG-35 and PDEAG-40 had ordinary bi-continuous porous structures, and PDEAG-50 had a porous structure consisting of interconnected microspheres. These porous gels showed a rapid volume transition with times on the order of a minute in response to temperature changes between 10 and 40 °C. Particularly, PDEAMG-35 showed fast volume transitions on both shrinking and swelling. This effect is derived from their structures which contain continuous reticulated gels and pores, which can behave as water channels when the gel undergoes volume transitions. On the other hand, the structure of the PDEAG-25 prepared below the LCST was homogenous while PDEAG-30 prepared around the LCST was discontinuous and had an independent porous structure. These gels responded more slowly to temperature changes than PDEAMG-35, PDEAMG-40, and PDEAMG-50. This reduced thermal transition response resulted from homogenous or discontinuous porous structures which could not function as water channels in volume transitions.

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