Reentrant Phase Transition and Fast Responsive Behaviors of Poly{*N*-[3-(dimethylaminopropyl)] Methacrylamide} Hydrogels Prepared in Poly(ethylene glycol) Solutions

Gökçen Birlik Demirel, Tuncer Çaykara

Department of Chemistry, Faculty of Art and Science, Gazi University, Besevler, Ankara 06500, Turkey

ABSTRACT: Macroporous temperature-sensitive poly{*N*-[3-(dimethylaminopropyl)] methacrylamide} hydrogels were synthesized by free-radical crosslinking polymerization of the monomer *N*-[3-(dimethylaminopropyl)] methacrylamide and the crosslinker *N,N'*-methylenebisacrylamide in aqueous solutions at 22°C. Poly(ethylene glycol) (PEG) with a molecular weight of 1000 g/mol was used as the pore-forming agent during the polymerization reaction. The concentration of PEG in the polymerization solutions was varied between 0 and 18 wt %, whereas the crosslinker (*N,N'*-methylenebisacrylamide) concentration was fixed at 2 wt % (with respect to the monomer). The effects of the PEG concentration on the thermo-induced phase-transition behavior and the chemical structure, interior morphology, and swelling/deswelling kinetics were investigated. Normal-type hydrogels were also prepared under the same conditions without PEG. An interesting feature of the swelling behavior of both the normal-type and macroporous hydrogels was the reentrant phase transition, in which the hydrogels collapsed once and reswelled as the temperature was continuously increased. Scanning electron micrographs revealed that the interior network structure of the hydrogels prepared in PEG solutions became more porous with an increase in the PEG concentration in the polymerization solution. This more porous matrix provided numerous water channels for water diffusion in or out of the matrix and, therefore, an improved responsive rate to external temperature changes during the deswelling and swelling processes. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 547–552, 2009

Key words: hydrogels; phase behavior; stimuli-sensitive polymers; swelling

INTRODUCTION

A number of acrylamide-derivative hydrogels have come to attract much attention for their reversible discontinuous large change in volume caused by a small change in temperature. This phenomenon, known as the *volume phase transition,* has been studied experimentally and theoretically by many researchers.[1–3] The phase-transition phenomenon is associated with the temperature dependence of hydrogen bonding and hydrophobic interactions.[4,5] At lower temperatures, water molecules in the vicinity of hydrophobic polymer chains are highly hydrogen bonded. Hence, the polymer chains dissolve or swell in water at low temperatures. At higher temperatures, the hydrogen bonds weaken; the contact between water and hydrophobic surfaces, that is, the hydrophobic interaction, increases.[6] As a result, when a temperature-sensitive hydrogel is heated, a transition from a swollen to a collapsed state occurs at a critical temperature. Recently, a phenomenon called *reentrant conformational phase transition* (RCPT)

was observed in hydrophobically modified acrylamide-derivative hydrogels in water,[7] water/organic solvent mixtures,[8] and linear polymer solutions.[9,10] In such a transition, the hydrogel first collapses then reswells if a particular external parameter, such as temperature, organic solvent, or linear polymer concentration, is continuously changed. Because the reentrant phenomenon is not observable in acrylamide-derivative hydrogels with high hydrophilic characteristics, hydrophobic interactions are mainly responsible for the RCPT behavior of the hydrogels.[8]

On the other hand, the swelling and deswelling of normal-type homogeneous hydrogels proceed by solvent diffusion and are a slow process. Moreover, the so-called skin effect significantly decelerates the deswelling of hydrogels: a surface layer on the hydrogel surface deswells, becomes less permeable for solvent transport (skin), and thus additionally hinders further deswelling.

An interconnecting porous structure is known to be a key solution for preventing the skin effect in hydrogels and for promoting their fast volume changes in response to environmental stimuli. Channels of open-celled pore structures allow the solvent to be expelled or absorbed by convection, a much faster process than diffusion. Many methods have

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Correspondence to: T. Çaykara (caykara@gazi.edu.tr).

been used to prepare macroporous hydrogels.[11–15] A widely used method involves the use of the phase-separation technique[11,12] to prepare a heterogeneous structure of the resulting hydrogel. In this technique, a polymerization temperature above the volume phase-transition temperature is necessary for the formation of a heterogeneous matrix in the phase-separation system. The other commonly used method is the porosigen technique.[13–15] With the presence of a porosigen or pore-forming agents, macroporous hydrogels, which exhibit a fast response upon heating, can be obtained.

This article presents the results of the observation of normal-type and macroporous poly{N-[3-(dimethylaminopropyl)] methacrylamide} [P(DMAPMA)] hydrogels prepared in deionized water and in poly (ethylene glycol) (PEG) solutions, respectively. An unusual feature of the swelling behavior of normal-type and macroporous P(DMAPMA) hydrogels is a reentrant phenomenon where the hydrogels collapse once and reswell as the temperature is increased. Moreover, the response rate to external temperature changes of the normal type P(DMAPMA) hydrogel is slow, which restricts its applications; a fast response rate is needed for some potential applications, such as on–off switches. Therefore, to increase the response rate of the normal-type P(DMAPMA) hydrogel, its macroporous forms were prepared with PEG aqueous solution as the polymerization solvent. The resulting hydrogels were characterized with attenuated total reflectance/Fourier transform infrared (ATR–FTIR) spectroscopy and scanning electron microscopy (SEM) to investigate the chemical structure, interior morphology, and temperature dependence of the equilibrium swelling ratio and the deswelling and swelling kinetics.

EXPERIMENTAL

Materials

N-[3-(Dimethylaminopropyl)] methacrylamide (DMA-PMA), N,N-methylenebisacrylamide, ammonium persulfate, N,N,N′,N′-tetramethylethylenediamine, and PEG (weight-average molecular weight = 1000 g/mol) were purchased from Aldrich Chemical Co. (Milwaukee, WI). The chemicals were used as received. All aqueous solutions were prepared with deionized water.

Hydrogel preparation

The hydrogels, designated as Gel0, Gel4, Gel8, Gel15, and Gel18, were prepared in aqueous PEG solutions with different concentrations (0, 4, 8, 15, and 18 wt %, respectively). Another fabrication procedure was used as follows: 1.0 mL of the monomer DMAPMA, 0.02 g of the crosslinker N,N′-methylenebi-

sacrylamide, and 0.5 mL (0.056M) of the initiator ammonium persulfate were dissolved in 4 mL of aqueous PEG solution with a certain concentration and purged with nitrogen gas for 10 min. Then, 0.5 mL (0.32M) of N,N,N′,N′-tetramethylethylenediamine was added and used as the catalyst to accelerate the polymerization. The solution was placed in poly (vinyl chloride) straws 4 mm in diameter and about 20 cm long. The poly(vinyl chloride) straws were sealed and placed in a thermostated water bath. The polymerization was carried out at 22°C for 24 h. The resulting hydrogel was purified by immersion in deionized water for 1 week to remove the unreacted chemicals and PEG. The water was replaced three to four times every day, and the purified hydrogel was stored in deionized water for characterization. The normal-type hydrogel (Gel0) was prepared in pure water with the same recipe and fabrication conditions. All of the purified hydrogels were cut into disklike pieces approximately 10 mm in length for further study.

ATR–FTIR measurements

The ATR–FTIR spectra of the hydrogels were taken with a Nicolet (Madison, WI) 6700 FTIR spectrometer equipped with a smart orbit accessory in the range 2000–500 cm^{-1}. Before the measurements, the originally swollen hydrogels were freeze-dried in a Virtis freeze drier (Lobconco, Kansas City, MO) for 2 days to completely remove water.

Internal morphology observation

An SEM instrument (Jeol JSM-6360 LV; Tokyo, Japan) was used to study the internal or cross-sectional morphology of the P(DMAPMA) hydrogels. To prepare samples for SEM, the swollen hydrogels at 10°C were first freeze-dried and than fractured and sputter-coated with gold.

Measurement of the equilibrium swelling/deswelling ratio

We measured the equilibrium swelling/deswelling ratio of hydrogels gravimetrically after carefully blotting the surface water with moistened filter paper in the temperature range from 10 to 60°C. Hydrogel samples were immersed in deionized water for at least 24 h at each predetermined temperature. The average value of three measurements was taken for each sample, and the equilibrium swelling/deswelling ratio was defined as follows:

$$\text{Equilibrium swelling/deswelling ratio} = \frac{m_s - m_d}{m_d}$$

(1)

where m_s is the mass of the swollen hydrogel at a particular temperature and m_d is the mass of hydrogel dried at 60°C in a vacuum oven.

Measurement of the deswelling kinetics

The deswelling kinetics of the hydrogels were measured gravimetrically at 38°C. The hydrogel samples were first immersed in deionized water at 10°C until equilibrium was reached. Then, the equilibrated hydrogels were quickly transferred to a water bath at a temperature of 38°C. At specified time intervals, the samples were removed from the hot water and weighed after the excess surface water was wiped off with moistened filter paper. The average value of three measurements was taken for each sample, and the normalized deswelling ratio was defined as follows:

$$\text{Normalized deswelling ratio} = \frac{m_t - m_d}{m_s - m_d} \qquad (2)$$

where m_t is the mass of the hydrogel at regular time intervals and m_s is the mass of the swollen hydrogel at 10°C.

Measurement of the swelling kinetics

After they were dried at 60°C in a vacuum oven, the samples were then placed in deionized water at 22°C and removed from the water at regular time intervals. After the water on the surfaces of the samples was wiped off with moistened filter paper, the masses of the hydrogels were recorded. The swelling ratio was defined as follows:

$$\text{Swelling ratio} = \frac{m_t - m_d}{m_d} \qquad (3)$$

RESULTS AND DISCUSSION

ATR–FTIR spectra of the hydrogels

The ATR–FTIR spectra of the macroporous and normal-type P(DMAPMA) hydrogels, which were freeze-dried, are displaced in Figure 1(a,b), respectively. The spectra of the macroporous and normal-type hydrogels were similar. There existed a typical amide I band (~ 1633 cm^{-1}), which consisted of the C=O stretch of P(DMAPMA), and an amide II band (~ 1521 cm^{-1}), which included a N—H vibration in each spectrum. On the other hand, if PEG existed in the macroporous hydrogels, a typical and strong band positioned around 1093 cm^{-1}, which belonged to the C—O stretch of PEG, appeared [Fig. 1(c)]. For this purpose, the spectrum subtraction of Gel0 from Gel18 was made to compensate for the C—O stretching band of the PEG at 1093 cm^{-1} [Fig. 1(d)]. However, there was no typical absorbent band of PEG (~ 1093 cm^{-1}) in the spectra shown Figure 1(d), which indicated that the PEG was totally
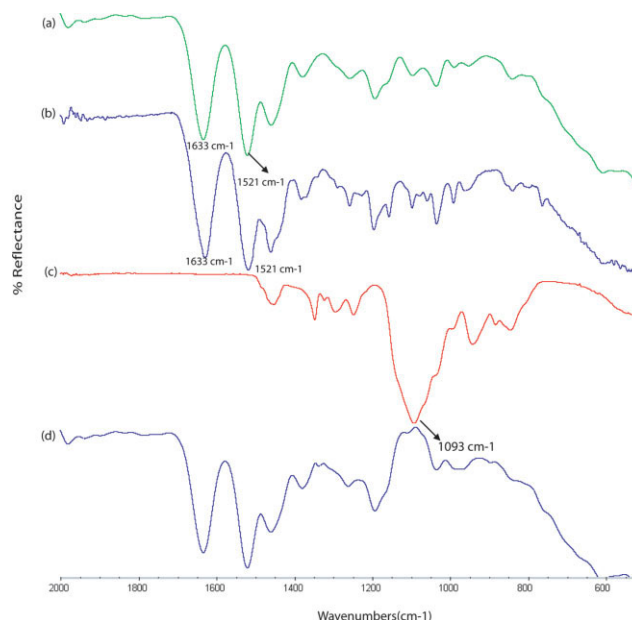
Figure 1 ATR–FTIR spectra of the P(DMAPMA) hydrogels prepared in (a) an 18 wt % PEG aqueous solution (Gel18), (b) pure water (Gel0), and (c) PEG. (d) A difference spectrum (panel a − panel b) is also shown. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

removed or that the amount of residual PEG was too small to be detected after the purification.

Interior morphology of the hydrogels

Figure 2 shows the cross-sectional views of the internal structures of the freeze-dried normal-type and macroporous hydrogels. When these micrographs are compared, one can see that the macroporous hydrogels had a more porous structure than the normal-type hydrogels. In this case, there were two possible reasons. First, the hydration and thus exclusion volume of PEG may have provided spatial hindrance during the polymerization and crosslinking process. Thus, a more porous structure was formed with the hydrogels prepared in the PEG solutions. Second, because of the presence of PEG, the phase separation of the formed P(DMAPMA) chains occurred during the polymerization, which led to macroporous and heterogeneous structures.

On the other hand, the PEG concentration in the reaction mixture affected the pore structure and increased the pore numbers of the matrix, which in turn, affected the swelling and deswelling behavior of the hydrogels. Although the geometry and size of the pores of the macroporous hydrogels prepared in this study were quite irregular, one can obtain from Figure 2 the regular assembly of polyhedral pores. This type of a microstructure is completely different from the macroporous matrices prepared by the
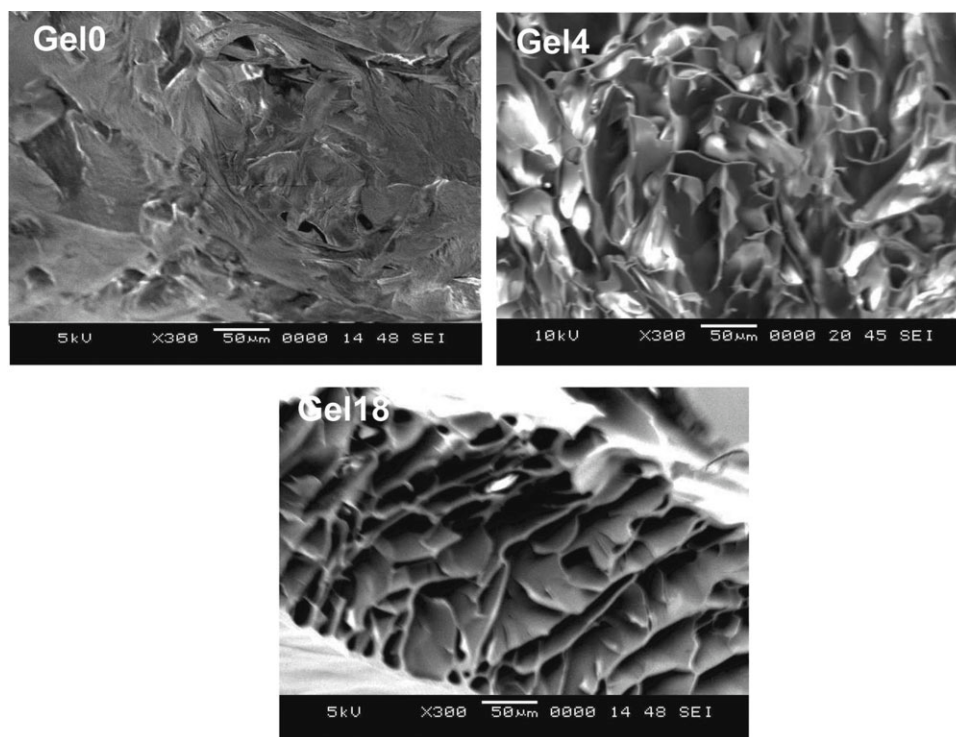
Figure 2 Internal morphologies of the P(DMAPMA) hydrogels prepared in pure water (Gel0) and in PEG aqueous solutions with concentrations of 4 (Gel4) and 18 wt % (Gel18) The magnification was 300×.

reaction-induced phase-separation mechanism, where the structure looked like cauliflower and was composed of segregates of different sizes.[16,17] All of the hydrogels prepared in the PEG solutions had a porous structure with pore diameters of 47–83 μm depending on the PEG concentration, whereas the normal-type hydrogels exhibited a morphology consisting of aggregates of various sizes.

Equilibrium swelling/deswelling ratio of the hydrogels

Figure 3 shows the equilibrium swelling/deswelling ratios of the hydrogels in the temperature range from 10 to 60°C. At all of the temperatures, the equilibrium swelling ratio of the normal-type hydrogel (Gel0) was lower than those of the macroporous hydrogels. For example, at 10°C, the equilibrium swelling ratio of Gel0 was around 16, whereas those of Gel4, Gel8, Gel15, and Gel18 were around 18, 18, 19, and 20, respectively.

Upon heating, all of the hydrogels exhibited an RCPT at 38°C. This is, the equilibrium swelling ratio of the hydrogels first decreased drastically up to 38°C (deswelling), then increased sharply up to 44°C (reswelling), and finally, remained almost constant in the range 44–60°C. As the temperature was increased in the range below reentrant conformational phase transition temperature (RCPT-T), the much strengthened hydrophobic interactions between the hydrophobic groups of the P(DMAPMA) chains overwhelmed

the hydrogen bonding interactions, and the hydrogels exhibited a dramatic decrease in the swelling ratios. However, with a further increase in the temperature above RCPT-T, the driving force for network expansion resulting from the formation of the hydrogen bonds overwhelmed the driving force for breakdown of the hydrophobic interactions between the dimethylaminopropyl groups of the P(DMAPMA) chains, and
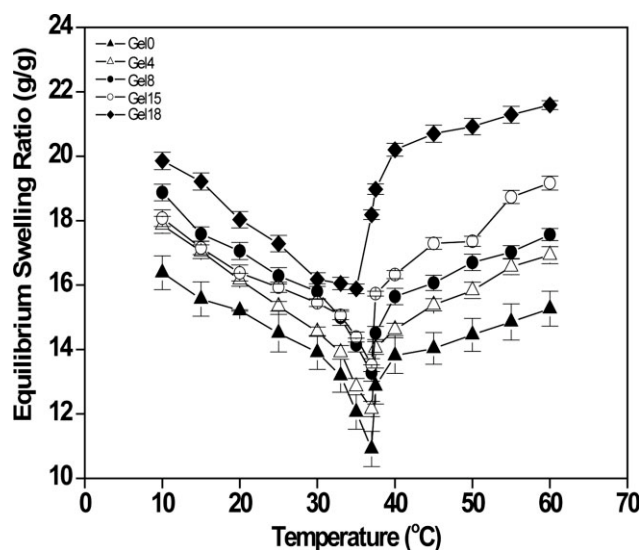
Figure 3 Temperature dependence of the equilibrium swelling/deswelling ratio of the P(DMAPMA) hydrogels in the temperature range of 10–60°C.
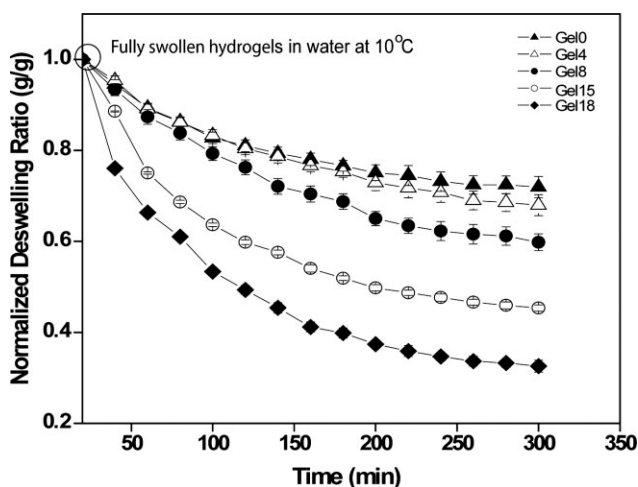
Figure 4 Deswelling kinetics of the P(DMAPMA) hydrogels upon a temperature jump from 10 to 38°C.

the hydrogels showed a dramatic increase in the swelling ratios. The experimental evidence of hydrogen bonding and hydrophobic interactions in acrylamide-derivative hydrogels has been reported before with a variety of techniques.[18–20] The results of FTIR studies have shown that most of the carbonyl groups of poly (N,N-diethylacrylamide) in water are associated with water through hydrogen bonds, even above the lower critical solution temperature.[20] Although the ethyl groups of poly(N,N-diethylacrylamide) are also hydrated below the lower critical solution temperature, upon phase transition, most of these groups are dehydrated and associate though hydrophobic interaction.[20] Orakdogen and Okay[8] showed that poly (N,N-dimethylacrylamide) [P(DMAAm)] hydrogels have a tendency toward RCPT in an aqueous solution of acetone, dioxane, and tetrahydrofuran; that is, the hydrogel first collapses and then reswells if the organic solvent concentration is continuously varied. They also determined the relative magnitude of the intermolecular forces responsible for the RCPT in P(DMAAm) hydrogels in water/organic solvent mixtures. In this respect, the results of our study indicate attractive interactions between water and P(DMAPMA), which were responsible for the observed RCPT behavior.

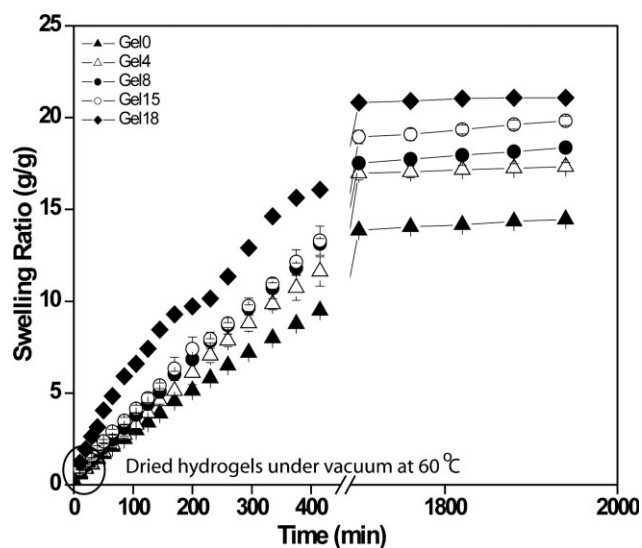### Deswelling kinetics of the hydrogels

The response rate upon external temperature changes is a critical factor for hydrogel applications. Improved equilibrium swelling/deswelling ratios of the hydrogels prepared in PEG solutions were shown. In this respect, the deswelling kinetics of the hydrogels upon temperature jumping from 10°C (below the RCPT-T) to 38°C (at RCPT-T) were studied further, and the data are shown in Figure 4. It was obvious that Gel18 exhibited the fastest shrink-

ing rate and lost water dramatically, and the normalized deswelling ratio decreased from 1.0 to about 0.7 within 50 min and to 0.5 within 100 min. Gel15 also showed a faster deswelling rate. However, Gel0, Gel4, and Gel8 exhibited almost the same slow deswelling rate, which decreased from 1.0 to about 0.9 within 50 min and to 0.8 within 100 min.

With respect to the deswelling kinetics, the normal-type hydrogel with an expanded network demonstrated an improved deswelling rate when transferred into hot water. When the Gel0 hydrogel was transferred into hot water, the surface layer of the hydrogel was the first region to be affected, and a dense skin layer was generated because of hydrophobic interactions among the dimethylaminopropyl groups of the P(DMAPMA) chains. Such a dense skin layer would greatly restrict the outward permeation of water from the hydrogel interior. However, in this study, the expanded P(DMAPMA) network prepared in the PEG solutions retarded the formation of such a dense skin layer during the deswelling process, and the freed water might have diffused out quickly. As a result, the macroporous hydrogels, such as Gel15 and Gel18, exhibited higher deswelling rates than the normal-type hydrogel at RCPT-T.

Swelling kinetics of the hydrogels

Figure 5 displays the swelling behaviors of the normal-type and macroporous hydrogels after drying in a vacuum oven at 60°C for 24 h. The data show that the macroporous hydrogels swelling rate increased with an increase in the pore-forming agent content, as from Gel4 to Gel18. Gel4 had a swelling ratio of

Figure 5 Swelling kinetics of the vacuum-dried P(DMAPMA) hydrogels at 22°C.

about 3.2 within 100 min or 12.4 within 450 min, whereas Gel18 had swelling ratios of about 6.5 and 17.2, respectively, within the same time frames. This results show also that all of the macroporous hydrogels absorbed water more quickly than the normal-type hydrogel (Gel0) because their macroporous structures made the transfer of water molecules easier between the hydrogel matrix and the external aqueous phase. The increase of the pore numbers caused by the increase of the PEG concentration affected their swelling ratios. Thus, the Gel18 hydrogel had the highest swelling rate among the macroporous hydrogels because of its highly porous structure.

CONCLUSIONS

In this study, the effects of the PEG concentration on the properties of P(DMAPMA) hydrogels, particularly, the RCPT-T behavior and response dynamics, were investigated. The addition of PEG did not change the chemical composition and RCPT-T of the P(DMAPMA) hydrogels. However, the morphological data from SEM revealed that interior network structure of the hydrogels became more porous with an increase of PEG concentration. This more porous matrix provided numerous water channels for water diffusion and, therefore, an improved response rate to the external temperature changes during the deswelling and swelling processes. The data obtained in this study are useful to us for the optimization of a macroporous P(DMAPMA) hydrogel for a particular application through the changing of the PEG concentration.

References

1. Tanaka, T. Phys Rev Lett 1978, 40, 820.
2. Katayama, S.; Ohta, A. Macromolecules 1985, 18, 2782.
3. Inomata, H.; Goto, S.; Saito, S. Macromolecules 1987, 23, 4887.
4. Feil, H.; Bae, Y. H.; Feijen, J.; Kim, S. W. Macromolecules 1993, 26, 2416.
5. Inomata, H.; Goto, S.; Saito, S. Macromolecules 1990, 23, 4887.
6. Zhang, X. Z.; Wu, D. O.; Chu, C. C. J Polym Sci Part B: Polym Phys 2003, 41, 582.
7. Caykara, T.; Birlik, G.; Izol, D. Eur Polym J 2007, 43, 514.
8. Orakdogen, N.; Okay, O. Polymer 2006, 47, 561.
9. Vasilevskaya, V. V.; Khokhlov, A. R. Macromolecules 1992, 25, 384.
10. Katayama, S.; Hirokawa, Y.; Tanaka, T. Macromolecules 1984, 17, 2641.
11. Kabra, B. G.; Gehrke, S. H. Polym Commun 1991, 32, 322.
12. Wu, X. S.; Hoffman, A. S.; Yager, P. J Polym Sci Part A: Polym Chem 1992, 30, 2121.
13. Zhang, X. Z.; Yang, Y. Y.; Chung, T. S.; Ma, K. X. Langmuir 2001, 17, 6094.
14. Zhuo, R. X.; Li, W. J Polym Sci Part A: Polym Chem 2003, 41, 152.
15. Zhang, X. Z.; Chu, C. C. Polymer 2005, 46, 9664.
16. Okay, O. Prog Polym 2000, 25, 711.
17. Dinu, M. V.; Ozmen, M. M.; Dragan, E. S.; Okay, O. Polymer 2007, 48, 195.
18. Wang, Y.; Morawetz, H. Macromolecules 1989, 22, 164.
19. Maeda, Y.; Higuchi, T.; Ikeda, I. Langmuir 2000, 16, 7503.
20. Maeda, Y.; Nakamura, T.; Ikeda, I. Macromolecules 2002, 35, 10172.