

# Swelling Characteristics of Poly(*N*-isopropylmethacrylamide-*co*-itaconic acid) Gels Prepared in Various Conditions

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**ABSTRACT:** Thermo- and pH-sensitive gels composed of *N*-isopropylmethacrylamide (NIPMA) and itaconic acid (IA) were prepared by free-radical crosslinking copolymerization in poly(ethylene glycol) (PEG) solution at 22°C and in water at -22°C and at 22°C, which were called as the macroporous gel (MGel), the cryogel (CGel), and the conventional gel (NGel), respectively. The gels were characterized by the equilibrium swelling, interior morphology, and deswelling kinetics. With increasing temperature in water, the gels exhibit reentrant conformational phase transition. During this transition, the gels first deswell in the range of temperature between 5 and 29°C, then drastically reswell if temperature is monotonically increased. The reswelling of the collapsed gels occurs above 45°C. It was shown that the

reentrant transition in poly(*N*-isopropylmethacrylamide-*co*-itaconic acid) [poly(NIPMA-*co*-IA)] gels requires moderate temperature, so that the hydrophobic interactions between chains dominate the swelling process. Scanning electron micrographs revealed that the interior network structure of MGel is more porous compared with those of CGel and NGel. This more porous structure provided numerous water channels for water diffusion out of the matrix and, therefore, an improved response rate to the external temperature and pH changes during the deswelling process. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 817–823, 2010

**Key words:** poly(*N*-isopropylmethacrylamide-*co*-itaconic acid); hydrogels; cryogels; macroporous gels

## INTRODUCTION

Responsive gels, a new-style polymer material, able to change their volume and properties in response to environmental stimuli such as temperature,<sup>1,2</sup> pH,<sup>3,4</sup> and certain chemicals,<sup>5–7</sup> have attracted significant attention from both academia and industry. Based on their dramatic swelling and deswelling behaviors, these gels are being utilized for new potential applications in numerous fields including chemical transducers,<sup>8</sup> chemical separations,<sup>9,10</sup> drug deliveries,<sup>11,12</sup> and artificial organs.<sup>13</sup>

From an application point of view, gels would be much favorable if they could respond to several stimuli simultaneously. Among these lines, temperature- and pH-sensitive gels have been commonly investigated during the last decade, because both parameters are important environmental factors in biomedical and other systems.<sup>14–20</sup> Thermo- and pH-responsive gels prepared by combining a temperature-sensitive component (e.g., *N*-isopropylacrylamide, *N*-isopropylmethacrylamide, etc.) with a

pH-sensitive component (e.g., acrylic acid, maleic acid, itaconic acid, etc.) are a common method used to make such compounds. However, the gels prepared by conventional methods are often restricted in their application because of very slow rates of swelling/deswelling in response to an external stimulus. In this regard, several strategies have been proposed to increase the response rate for gels.<sup>21</sup> These include (i) forming a heterogeneous network structure of the gel through a phase separation method,<sup>22,23</sup> (ii) graft-copolymerization, where the free ends of the grafts act to accelerate the hydration rate;<sup>24–26</sup> rapid deswelling has also achieved by using comb-type grafted gels,<sup>27</sup> silane containing crosslinking agents,<sup>28,29</sup> cold polymerization methods<sup>30,31</sup> and hydroxypropyl cellulose<sup>32</sup> as a pore-forming agent during the polymerization.

In this study, we compared the swelling properties of thermo- and pH-responsive poly(*N*-isopropylmethacrylamide-*co*-itaconic acid) [poly(NIPMA-*co*-IA)] gels formed in PEG solution at 22°C (MGel) and in water at two different temperatures, namely at -22°C (CGel) and at 22°C (NGel). The gels were synthesized by free-radical crosslinking polymerization of *N*-isopropylmethacrylamide (NIPMA) and *N,N'*-methylenebisacrylamide (MBAAm) at an initial monomer concentration of 5 wt %. Itaconic acid (IA)

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was used as the ionic comonomer in the gel preparation. As will be shown later, the swelling/dswelling rate of the MGel prepared in PEG solution are much higher than that for the same type of gels prepared in water at  $-22^{\circ}\text{C}$  (CGel) and at  $22^{\circ}\text{C}$  (NGel).

## EXPERIMENTAL

### Materials

NIPMA (Aldrich Chemical, Milwaukee, WI) was recrystallized in benzene/hexane. IA (Aldrich Chemical), *N,N*-methylenebis(acrylamide) (MBAAm, Aldrich Chemical), ammonium persulfate (APS, Aldrich Chemical), *N,N,N',N'*-tetramethylethylenediamine (TEMED, Aldrich Chemical) poly(ethylene glycol) (PEG, Aldrich Chemical) with molecular weight of  $100\text{ g mol}^{-1}$  were used as received. Glacial acetic acid, phosphoric acid, boric acid, and standardized sodium hydroxide were used to prepare Britton-Robinson (B-R) buffers. The stock B-R buffer solution was prepared by using 2.5 mL of glacial acetic acid, 2.7 mL of phosphoric acid, 2.47 g of boric acid and its dilution with deionized water to 1000 mL. Stock solution (50 mL) were taken, and the pH of the solutions was adjusted between 2.0 and 9.0 by addition of an appropriate amount of 2.0M sodium hydroxide solution.

### Preparation of gels

Gels were prepared by free-radical crosslinking copolymerization of NIPMA and IA with a small amount of MBAAm as the crosslinker (Fig. 1). For MGel, the purified NIPMA (0.2 g) and IA (0.07 g) were dissolved in deionized water (6.0 mL). Then, MBAAm (0.05 g, crosslinker), APS (0.06M, 2.0 mL, initiator), and TEMED (0.064M, 1.0 mL, accelerator) and PEG (0.75 g, pore-forming agent) were added to the solution. After nitrogen bubbling for 5 min, the solution was placed in poly(vinyl chloride) straws 4 mm in diameters and about 20 cm long. The poly(vinyl chloride) straws were sealed and placed in a thermostated water bath (Thermo Haake K10, USA). Polymerization was conducted at  $22^{\circ}\text{C}$  for 24 h. The CGel and NGel were prepared simultaneously at  $-22^{\circ}\text{C}$  and at  $22^{\circ}\text{C}$ , respectively, without PEG. After polymerization, the resulting gels were purified by immersing in deionized water for 1 week to remove PEG and unreacted chemicals. The water was replaced 3–4 times every day. The removal of PEG was confirmed by ATR-FTIR spectrometer at  $1100\text{ cm}^{-1}$  (the C–O stretch of PEG). However, there is no typical absorbent band at  $1100\text{ cm}^{-1}$ , indicating the PEG was totally removed or the amount of residual PEG was too little to be

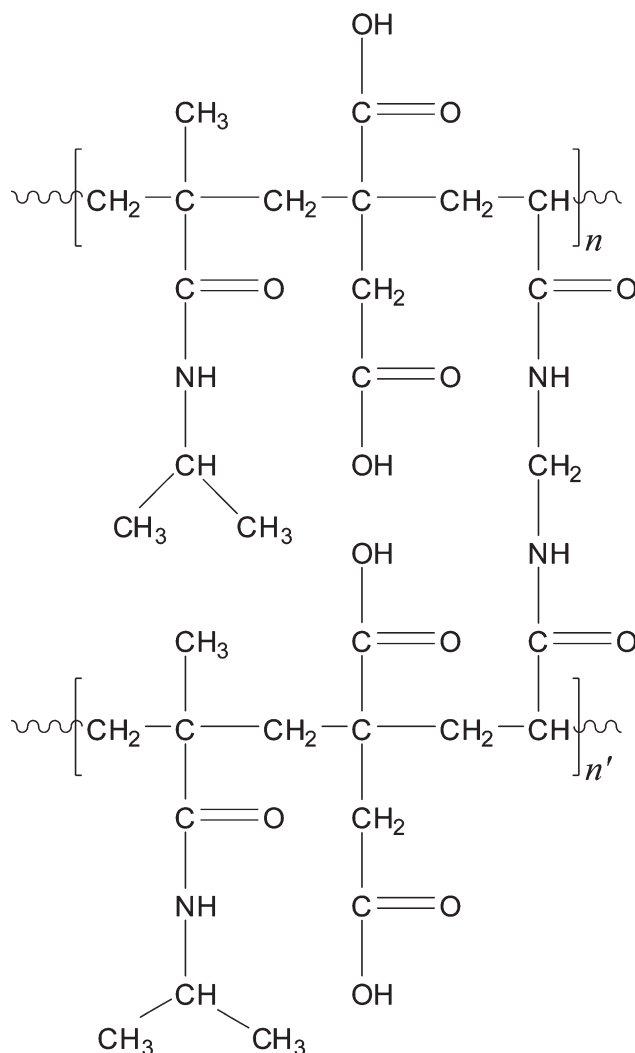


Figure 1 Chemical structure of poly(NIPMA-co-IA) gel.

detected after the purification. All the purified gels were cut into disk-like pieces  $\sim 10$  mm in length and freeze-dried in a Virtis freeze drier (Labconco Company, Kansas City, MO) for 2 days to completely remove water for further studies.

### Characterization of gels

ATR-FTIR measurements of the freeze-dried gels were taken by using a Nicolet 6700 (Madison, WI) FTIR spectrometer equipped with a smart orbit accessory in the range of  $4000\text{--}525\text{ cm}^{-1}$ . The internal or cross-sectional morphologies of the freeze-dried gels were determined by a scanning electron microscope (SEM) (JEOL, JSM-6360 LV, Tokyo, Japan). The freeze-dried gels were firstly fractured and then coated with a thin layer of gold in vacuum and photographed in the electron microscope  $100\times$  magnifications.

### Measurements of equilibrium swelling ratio

A gravimetric method was used to measure the equilibrium swelling ratio. The equilibrium swelling weights were measured at 22°C for the gel samples in water or in buffer solutions after wiping excess water from the gel surface with moistened filter paper. The effect of temperature on the equilibrium swelling ratio was measured in the temperature range from 5 to 60°C. At each particular temperature, gel samples were incubated in deionized water for 24 h, wiped with moistened filter paper to remove excess water from the gel surface, weighed. The weight data presented is an average of three samples. The swelling ratio (SR) was defined as follows:

$$SR = \frac{m_s - m_d}{m_d} \quad (1)$$

where  $m_s$  is the mass of swollen gel and  $m_d$  is the dry mass of gel.

### Measurements of deswelling kinetics

The deswelling ratio of gels was measured gravimetrically after the sample surfaces had been wiped with moistened filter paper to remove water in different conditions designed for the measurements. The gel samples were allowed to reach equilibrium in deionized water at 60°C or in pH 9.0 buffer solution at 22°C and were then transferred to a given condition. At regular time intervals, gel samples were retrieved and weighed. The weight data was an average of three samples. The normalized deswelling ratio (NDR) was defined as follows:

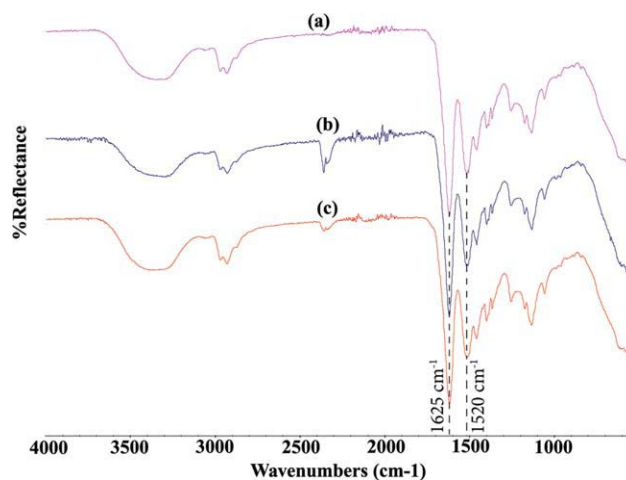
$$NDR = \frac{m_t - m_d}{m_s - m_d} \quad (2)$$

where  $m_t$  is the mass of gel at time  $t$  and the other symbols are the same as those described earlier.

## RESULTS AND DISCUSSION

### ATR-FTIR spectra of gels

The ATR-FTIR spectra of NGel, CGel, and MGel samples, which have been freeze-dried, are shown in Figure 2. The spectra of all the gels are similar. There exists a typical amide I band ( $\sim 1644 \text{ cm}^{-1}$ ), consisting of the C=O stretch of poly(NIPMA-co-IA) and the amide II band ( $\sim 1538 \text{ cm}^{-1}$ ), including N-H vibration in each spectrum. On the other hand, if there were PEG in the MGel, a typical and strong band positioned at around  $1093 \text{ cm}^{-1}$ , which belongs to the C-O stretch of PEG, would appear. From Figure 2(c), there is no obvious peak appearing



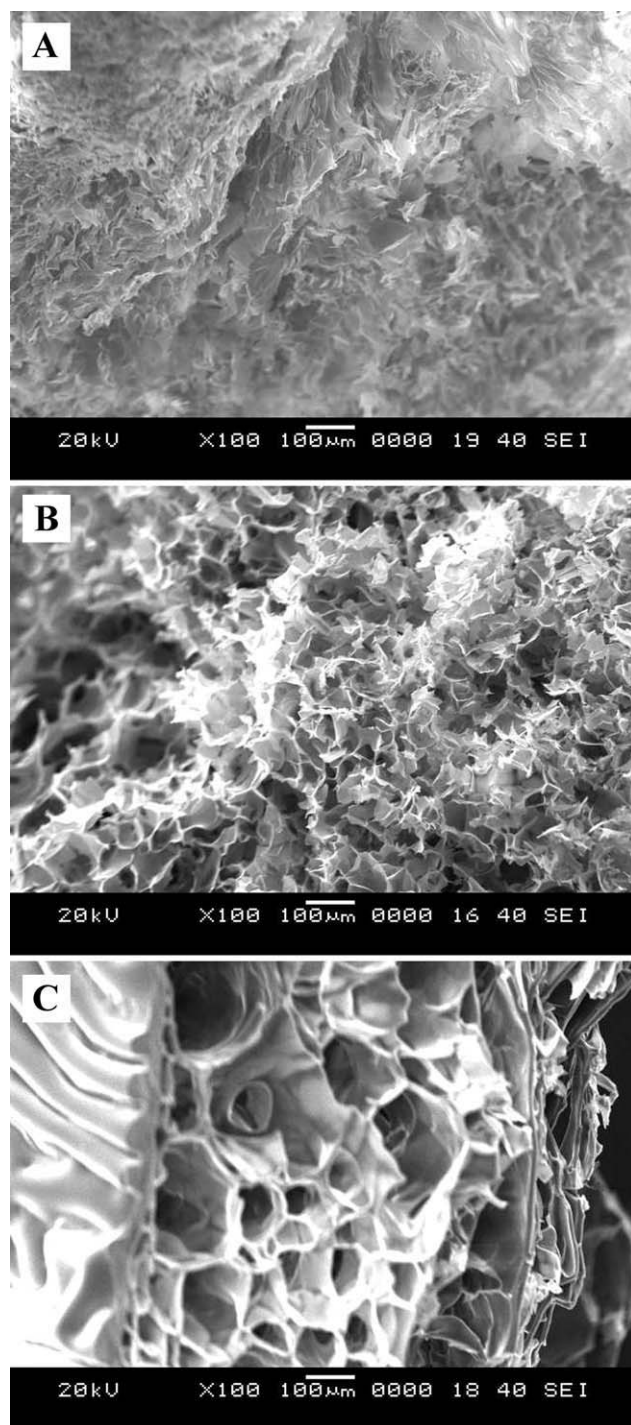
**Figure 2** ATR-FTIR spectra of poly(NIPMA-co-IA) gels. (a) NGel, (b) CGel, and (c) MGel. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

around  $1100 \text{ cm}^{-1}$  in the spectrum of MGel. These results show that the MGel has the chemical composition as the NGel [Fig. 2(a)] and the CGel [Fig. 2(b)], and PEG does not exist in the MGel after it is extensively washed. PEG acts as a pore-forming agent and does not participate with the polymerization.

### Interior morphology of gels

Figure 3 shows the cross-sectional views of the internal structures of the freeze-dried NGel, CGel, and MGel samples. The NGel (A) consist of large polymer domains, whereas the CGel (B) and the MGel (C) exhibit a discontinuous morphology with a two-phase structure, consisting of polymer phase separated by irregular pores. The porous structure of CGel is due to the action of ice crystals as a pore-forming agent during polymerization. Thus, during freezing of the monomer solution at  $-22^\circ\text{C}$ , an unfrozen phase containing a high concentration of dissolved monomers is formed as water is separated from the solution in the form of ice crystals. After polymerization and thawing, the voids left from the ice crystals constitute the pore structure of CGel.<sup>33</sup> Moreover, in comparison of these micrographs, it can also be noticed that compared with the NGel and the CGel, the MGel shows more porous network structure. There are two possible reasons. First, the hydration and thus exclusion volume of PEG may provide spatial hindrance during the polymerization and crosslinking process. Thus, a more porous structure is formed with the PEG-modified gel. Second, due to the presence of PEG, phase separation of formed poly(NIPMA-co-IA) chains occurs during the





**Figure 3** Internal morphologies of the gels (Magnification:  $\times 100$ ). (A) NGel, (B) CGel, and (C) MGel.

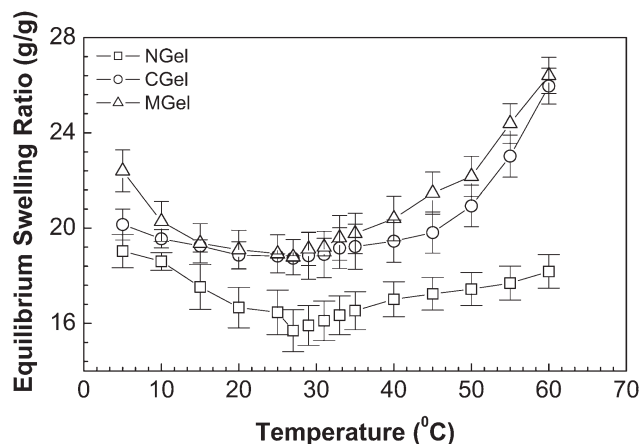
polymerization, leading to macroporous and heterogeneous structures.

#### Temperature dependence of the equilibrium swelling ratio in deionized water

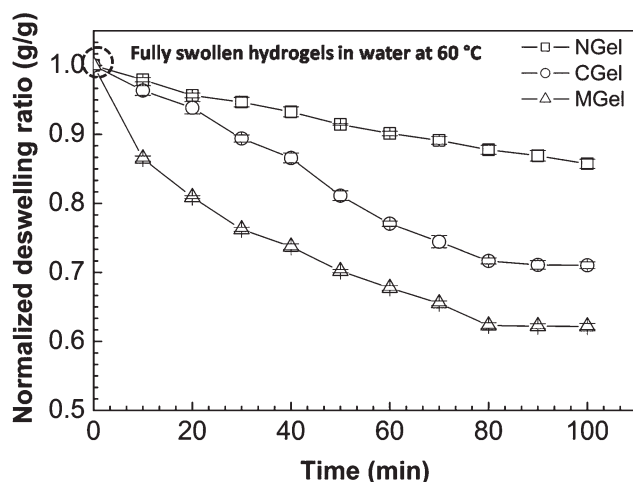
Figure 4 demonstrates the temperature dependence of the equilibrium swelling ratio of the freeze-dried NGel, CGel, and MGel samples in deionized water.

The data show that all the samples, regardless of the preparation condition, had similar swelling behaviors as a function of temperature and a reentrant conformational phase transition temperature (RCPT-T) at  $29^{\circ}\text{C}$ . Compared with conventional gels (e.g., poly(*N*-isopropylacrylamide) [poly(NIPAM)] is the best known temperature-sensitive material, exhibiting a lower critical solution temperature (LCST) at about  $33^{\circ}\text{C}$ .<sup>34,35</sup> The poly(NIPMA-*co*-IA) gels exhibited the reentrant phase transition at about  $29^{\circ}\text{C}$ , where the gels first collapse then reswell if temperature is increased. As the temperature is increased in the range below RCPT-T, the much strengthened hydrophobic interactions between the hydrophobic groups of poly(NIPMA-*co*-IA) chains overwhelmed the hydrogen bonding interactions and the gels 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 destruction of the hydrogen bonds overwhelmed the driving force for breakdown of the hydrophobic interactions between the isopropyl pendant groups of the poly(NIPMA-*co*-IA) chains and gels showed a dramatic increase in the swelling ratios.

Even though the RCPT-T of the poly(NIPMA-*co*-IA) gels was virtually not affected by the preparation conditions, the data in Figure 4 also clearly show that, at a temperature below the transition temperature (e.g.,  $5^{\circ}\text{C}$ ), the equilibrium swelling ratios of these gels were significantly reduced from MGel to NGel, and the magnitude of the negative swelling slope below the RCT-T decreased from MGel to NGel. For example, at  $5^{\circ}\text{C}$ , the equilibrium swelling ratio of NGel is around 19, whereas those of CGel and MGel are around 20 and 22, respectively. This may be explainable by various porous



**Figure 4** Temperature dependence of the equilibrium swelling ratio of poly(NIPMA-*co*-IA) gels in the temperature range from  $5^{\circ}\text{C}$  to  $60^{\circ}\text{C}$ . The type of gels was indicated in the figure.



**Figure 5** Deswelling kinetics of the gels at 29°C as measured from an equilibrium swelling condition at 60°C in deionized water. The type of gels was indicated in the figure.

structures that PEG and ice crystals create during the gelation process. As revealed in the SEM micrographs (Fig. 3), an increase of the pore size from NGel to MGel led to the increase of the water holding capacity because of the increased pore volume. This behavior shows that the equilibrium swelling ratio of these gels can be controlled by the phase transition at temperatures in the vicinity of their RCPT-T.

On the other hand, the MGel has the highest temperature sensitivity and undergoes the fastest phase separation when temperature increases to the RCPT-T. This phenomenon may be due to the fact that a more porous network structure makes water easier to diffuse in or out of the matrix, and thus the effect of temperature variation on phase separation is rapidly manifested.

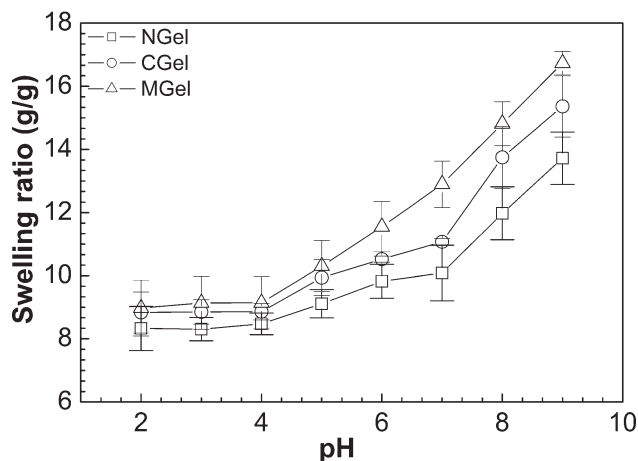
#### Deswelling kinetics of gels in deionized water with temperature changes

Figure 5 shows the deswelling kinetics of the gels after a temperature jump from the equilibrium state in deionized water at 60°C to the RCPT-T at 29°C. The CGel and MGel shrunk rapidly on the time scale and entrapped water was rapidly squeezed out from the gels interior for the experiment, and the quick response was ranked in the order of the pore size of gel in response to temperature changes. In contrast, shrinking of the NGel was much slower and hardly shrunk at all after 60 min. In this process, the diffusion rate of the freed water through the macroporous network determines the deswelling rates of the gel. The diffusion rate is controlled by collective diffusion coefficient and gel morphology. When a conventional gel (NGel) is immersed into the deionized water with a temperature at about

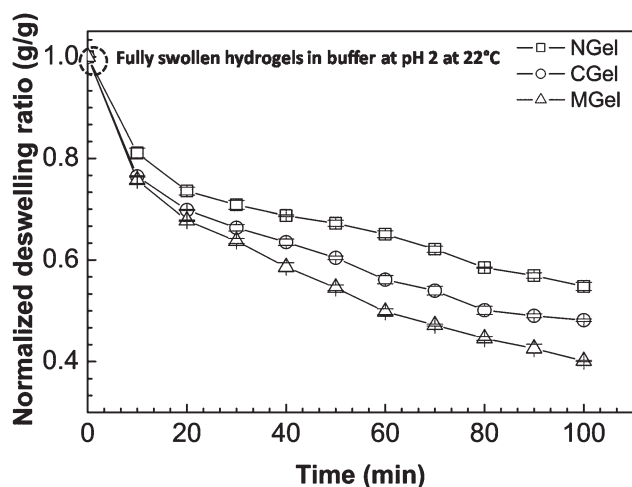
RCPT-T, the gel may start the phase transition and shrink in the utmost surface region, resulting in a thick and dense skin layer at the beginning of the shrinking process. The resultant dense skin layer acts as a barrier for further water permeation and prevents the freed water diffusion out of from the gel matrix. However, the macroporous gels (CGel and MGel) have more even heat release and mass transfers because of their macroporous structures. Heat release from the innermost gel matrix to the water at 29°C occur rapidly, which result in a rapid phase separation throughout the matrix. Thus, a large amount of the freed water can diffuse out quickly once the gels are immersed in deionized water at 29°C. From Figure 5, it can be seen that the MGel shrinks with the fastest rate because of its most porous structure.

#### pH dependence of the equilibrium swelling ratio in pH buffers at 22°C

pH-sensitive gels usually exhibit a variation of their equilibrium swelling ratio as a function of pH according to the acid–base equilibrium for a weak acid: in acidic solution, most of the acidic units remain in the protonated form while they are ionized under basic conditions. In this respect, the equilibrium swelling ratios of poly(NIPMA-co-IA) gels were measured in pH buffer solutions at 22°C and represented in Figure 6. Because of the effects of ionic strength, the equilibrium swelling ratio of gels in pH buffer solutions were universally smaller than those in deionized water.<sup>36</sup> In pH range 2.0–4.0, the network chains shrank because the electrostatic repulsive force between the protonated carboxylic acid groups of IA vanished, towing the whole polymer network to collapsed state. At pH range 4.0–9.0, the swelling ratio of hydrogels drastically increased



**Figure 6** pH dependence of the equilibrium swelling ratio of poly(NIPMA-co-IA) gels in pH buffer solutions at 22°C. The type of gels was indicated in the figure.



**Figure 7** Deswelling kinetics of the gels in buffer at pH 2.0 as measured from an equilibrium swelling condition in buffer at 9.0 at 22°C. The type of gels was indicated in the figure.

with increasing pH. This is mainly attributed to the carboxylic acid groups of IA in the hydrogel, in which the  $pK_{a1}$  and  $pK_{a2}$  of IA are 3.85 and 5.44, respectively. Above pH 6, the hydration of hydrophilic units are stronger and the electrostatic repulsive forces operating between the charged carboxylic acid groups of IA made the hydrophilic chains more extended, which towed the whole networks to a more swollen state. Thus, all of gels were swollen in pH > 6 buffer and were shrunk in pH < 4 buffer. As expected, the MGel and CGel samples showed the highest swelling ratio in all pH buffer solutions because of their porous structures.

#### Deswelling kinetics of gels in pH buffers at 22°C with pH changes

Figure 7 shows the deswelling behavior of the gels from a swollen equilibrium in a pH 9.0 buffer solution at 22°C to a pH 2.0 buffer solution. The deswelling occurred because of the pH sensitivity of the IA incorporated in the backbone of gels.<sup>37,38</sup> In the buffer solution of pH 9.0, the gels are negatively charged, and therefore the electrostatic repulsion between  $-\text{COO}^-$  groups causes the gel to swell. In the buffer solution of pH 2.0, the gels shrank and aggregated with each other because of the disappearance of electrostatic repulsion and the generation of hydrophobic interactions owing to hydrogen bond formation between carboxylic acid of IA and isopropylamide amide pendant groups of NIPMA in the backbone of gel. As presented in the previous paragraphs, all the porous gels (CGel and MGel) adsorb water or shrink more quickly than the conventional gel (NGel) because their macroporous

structures make transfer of water molecules easier between gel matrix and external aqueous phase. However, the MGel leads the highest deswelling rate according to both the CGel and NGel samples because of its highly porous structure.

#### CONCLUSIONS

In this study, thermo- and pH-sensitive poly (NIPMA-*co*-IA) gels were prepared by free-radical crosslinking copolymerization in PEG solution at 22°C and in water at -22°C and at 22°C, which were called as the macroporous gel (MGel), the cryogel (CGel), and the conventional gel (NGel), respectively. Swelling behavior of the gels prepared in various conditions was investigated as functions of temperature and pH. The results showed that all poly(NIPMA-*co*-IA) gels have a tendency to re-entrant transition in deionized water at about 29°C; that is, the gels first collapse then reswell if the temperature is continuously varied. The morphological data from SEM revealed that the interior network structure of MGel is more porous compared with those of NGel and CGel. This more porous matrix provided numerous water channels for the water diffusion and, therefore, an improved response rate to the external temperature and pH changes during the deswelling process. Thermo- and pH-responsive MGel may be useful in controlled release of macromolecular active agents.

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