# Hydrogel Characteristics of a Novel Temperature-Sensitive Polymer, Poly(*N*-2-methoxyisopropylacrylamide)

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**ABSTRACT:** In this study, a novel temperature-sensitive polymer, poly(*N*-2-methoxyisopropylacrylamide), PNMIPA, in the crosslinked hydrogel form was obtained. The monomer, *N*-2-methoxyisopropylacrylamide (NMIPA) was synthesized by the nucleophilic substitution reactions of acryloyl chloride with 2-methoxyisopropylamine. Hydrogel matrix of PNMIPA was obtained by the bulk polymerization method. The bulk polymerization experiments were performed at +4°C, by using *N*,*N*-methylenebisacrylamide (MBA) as crosslinker, polyethyleneglycol (PEG) 4000 as diluent, and potassium persulfate (KPS) and tetramethylethylenediamine (TEMED) as the initiator and accelerator, respectively. The same polymerization procedures were applied by changing monomer, initiator, crosslinker and diluent concentrations in order to obtain crosslinked gel structures having different temperature–sensitivity properties. The equilibrium swelling ratio of PNIMPA gel matrices at constant temperature increased with increasing initiator concentration and decreasing monomer concentration. The use of PEG 4000 as diluent in the gel synthesis resulted in about two times increase in equilibrium swelling ratios in the low temperature region. A decrease in the equilibrium swelling ratios of gel matrices started at 30°C and the decrease became insignificant at 55°C. Temperature-sensitivities were determined in two different media. Distilled water medium was used in order to observe the temperature-sensitivity of the gel clearly and the phosphate buffer medium was used in order to represent the temperature-sensitive swelling behavior of the gel when it is used in biological media. Step effect was applied on ambient temperature in two opposite directions in order to examine the dynamic swelling and shrinking behaviors of the gels. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1461–1466, 2008

**Key words:** poly(*N*-2-methoxyisopropylacrylamide); *n*-isopropylacrylamide; thermo-responsive polymers; hydrogel; cross-linked gel; hydrophilic polymers; swelling

## INTRODUCTION

Hydrogel structures, which are defined as crosslinked hydrophilic three-dimensional polymer networks, can change their volumes abruptly in response to the changes of the external environmental factors such as temperature,[1,2] pH,[3,4] photo field,[5] antigen[6] and ions or other chemical species, electric or magnetic fields[7] by uptaking or releasing large amounts of water. An important factor for application is not only the maximum amount of water absorbed or released but also the rate of swelling and shrinking. Another important factor is response time. A gel may need minutes or hours before reaching equilibrium conditions after a change in external environmental factors.[8] However, it is known that reduction in response time is possible by using the gels composed of a porous structure.[9]

Hydrogels are widely used for so many applications such as drug delivery,[10] artificial organs[11] and enzyme immobilization[12,13] because of their high water contents and soft consistency that is similar to natural tissue.[14–21]

Among the family of temperature responsive hydrogels poly(*N*-isopropylacrylamide) (PNIPA) is the most extensively studied and investigated one. Because of the good balance between hydrophilic and hydrophobic interactions in the PNIPAm, it shows a sharp lower critical solution temperature (LCST) at 32°C.[22–26] PNIPAm or its copolymers have been studied and used as temperature-sensitive hydrogels for various applications such as drug delivery,[27–29] cell culture,[30,31] bioreactors[32] and diagnostics.[33] Recently, attention has also been paid for various poly(alkylacrylamide)s (i.e., poly(*N*,*N*-diethylacrylamide), poly(methylpropylacrylamide), poly (*N*-cyclopropylacrylamide), poly(propylacrylamide), poly(ethylpropylacrylamide), poly(*n*- and *tert*-butylacrylamide) and poly(ethoxyethylacrylamide), etc.), which become insoluble above their lower critical solution temperature (LCST) values. These alternative temperature sensitive polymers were synthesized to trigger the developments in the various applications

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of stimuli-responsive polymers.[34–49] In this context, synthesis and characterization of new alternative temperature sensitive polymeric structures was found useful. Thus, in this study, *N*-2-methoxyisopropylacrylamide (NMIPA) was synthesized for the first time by the nucleophilic substitution reaction of acryloyl chloride with 2-methoxyisopropylamine. Then, the novel thermosensitive polymer, poly(*N*-2-methoxyisopropylacrylamide), (PNMIPA), was obtained in its crosslinked hydrogel form. Hydrogel production conditions (i.e. the initiator, crosslinking agent, monomer and diluent concentrations) were changed to investigate the thermoresponsive swelling behavior of obtained crosslinked hydrogels in different media.

## EXPERIMENTAL

### Materials

The monomer, NMIPA, was synthesized by using acryloyl chloride (Aldrich Chemicals, Milwaukee, WI) and 2-methoxyisopropylamine (Aldrich Chemicals). *N*,*N*-methylenebisacrylamide (MBA) (Aldrich Chemicals, Germany), Potassium persulfate (KPS) (Aldrich Chemicals, Germany) and tetramethylethylenediamine (TEMED) (Aldrich Chemicals, Germany) were used in hydrogel matrix synthesis. Polyethyleneglycol (PEG 4000, BDH Chemicals, UK) was used as polymeric porogen. Acryloyl chloride, KPS, TEMED, MBA and PEG 4000 were used as received. All polymerizations and gel characterizations were performed in distilled water.

### Monomer synthesis

In the monomer synthesis, the same way as given in the literature for all *N*-alkylacrylamide monomers was used.[45,46,49,50] Typically, 2-methoxyisopropylamine, 23.5 g (0.25 mol), and *p*-benzoquinone (10 mg) were added to a solution of 27.24 g (0.25 mol) triethylamine in dichloromethane (200 mL). The mixture was cooled to 0°C in an ice bath. Acryloyl chloride, 25.12 g (0.25 mol), containing dichloromethane (100 mL) was added drop by drop into this solution at approximately 0°C in a duration of 4 h with constant magnetically stirring. The stirring procedure was continued for 24 h at +4°C. Then the organic phase was extracted with cold water and water was removed from the media. The organic phase was dried over $MgSO_4$ for 12 h in order to remove remained water completely. Finally, dichloromethane was evaporated *in vacuo* for the isolation of NMIPA. The monomer was characterized by H-NMR and FTIR spectroscopy. H-NMR was recorded on Bruker spectrometer in $CDCl_3$ as solvent. FTIR spectra was taken by using UNICAM Mattson 1000 spectrophotometer.

$^1$H-NMR characteristics: $\delta_H$ ($CDCl_3$, 400 MHz) = 1.11–1.12 (3H, d, J = 16,98 Hz, —C*H*$_3$), 3.27 (3H, s, —OC*H*$_3$), 3.29–3.3 (2H, d, J = 12,02 Hz, —C*H*$_2$), 4.13–4.18 (1H, m, —C*H*), 5.45–5.53 (1H, dd, J=5.04 and 24.96 Hz, —C*H*), 6.02–6.2 (2H, m, —C*H*$_2$) and 6.42 (1H, s, —N*H*).

FTIR characteristics: 3286 (N—H, amide), 3070–2831 (alkyl), 1661 (C=C), 1549 (amide II).

### Synthesis of hydrogels

The hydrogels investigated in this work were prepared by bulk polymerization. For this purpose, NMIPA (0.125 g) was added to 0.8 mL water in a glass tube with 8 mm inner diameter and 100 mm length. Monomer was solved completely in water by mixing with a rod in an ultrasonic bath. A 0.15 mL aqueous solution of the crosslinker MBA was added (50 mg/mL) and the tube was placed in a water–ice bath, and it was allowed to cool to +4°C. On this cooled solution, 0.15 mL of aqueous KPS solution (50 mg/mL) cooled in a water–ice bath and 0.15 mL aqueous solution of TEMED (10% v/v) were added as initiator and accelerator, respectively. Prepared polymerization medium was homogenized by mixing and washed with nitrogen for 3 min. Then the tube was sealed by a stopper plug. The tube was placed in a water bath at +4°C, and hydrogel formation occurs in the duration of 24 h. By this way, obtained hydrogels were of 8 mm diameter and almost 25 mm height. Then the obtained hydrogels were taken into a distilled water medium at +4°C (100 mL). The distilled water medium was replaced once at each 2 h. By this way, the polymer gel was rinsed and unconverted monomers and initiator system components were removed from the medium completely. After completing this rinsing procedure, the gel was kept in distilled water at +4°C. Hydrogel prepared according to above mentioned procedure had 100 mg/mL NMIPA, 6 mg/mL MBA, 6 mg/mL KPS and 13.9 mg/mL TEMED concentration. The same procedures were applied by changing initiator, monomer, diluent and crosslinker concentrations in order to obtain crosslinked gel structures having different temperature–sensitivity properties.

### Swelling studies

Swelling studies were performed in distilled water, phosphate buffer and different ionic strength media. Distilled water medium was used in order to observe the temperature–sensitivity of the gel clearly. The phosphate buffer medium was used in order to represent the temperature-sensitive swelling behavior of the gel when it is used in biological

media. Different ionic strength values were obtained by dissolving NaCl in distilled water at proper concentrations in order to determine the effect of ionic strength on the gel swelling ratio. To obtain pH 7 phosphate buffer, 0.05*N* $NaH_2PO_4$ and 0.05*N* $Na_2{\cdot}HPO_4$ solutions were mixed in appropriate quantities.

For all media, the determination of the equilibrium water contents of the crosslinked gels following experimental procedure was performed. For this purpose, a sample of rinsed gel having an approximate dry weight of 0.1 g was transferred to the medium in which the equilibrium water content of the gel was determined, and the gel was hold in this medium for 24 h at +4°C. Thus, the equilibrium swelling was reached at this temperature. The weight of the gel swelled at +4°C was determined. The gel in this medium was then placed in a shaker water bath and temperature was raised to 12°C. The gel was kept at this temperature for 6 h and its weight was determined again. By this way, swelled gel weights were determined at each definite temperature up to 80°C. Gel was kept at each definite temperature for 3 h. Each sample was measured for three times and the average value of three measurements was taken. After weighing the gel swelled at 80°C, the gel sample was dried by vacuum at 50°C in the duration of 48 h. The dry weight of the gel was determined after this drying. There was no change in weight of the hydrogels at the end of this time and dry weights of the hydrogels were constant. The equilibrium swelling ratio at each temperature was calculated by the expression:

$$Q = (W/W_0) \times 100 \quad (1)$$

where $Q$: g swelled gel/g dry gel, $W$ is the weight of the swelled gel at a definite temperature, and $W_0$ is the weight of the dried gel.

### Measurement of swelling and deswelling kinetics of hydrogels

Step effect was applied on ambient temperature in two opposite directions in order to examine the dynamic swelling and shrinking behaviors of the gels. In the first applications, gels were hold at +4°C for 24 h until they reach their equilibrium swelling values and then they were transferred into the distilled water media hold at 80°C. This moment was taken as the time of zero ($t = 0$), and hydrogel samples were measured gravimetrically and periodically in terms of water retention at 80°C. This experimental method was applied in order to observe the shrinking kinetics of the gel. In addition to this, the gel reached its equilibrium water content at 80°C was transferred into distilled water medium at +4°C for determining the swelling kinetics of the gel by the influence of higher temperature. By taking this moment as time of zero ($t = 0$), the change in equilibrium water content with time was determined by weighing the gel sample in definite time intervals.

## RESULTS AND DISCUSSIONS

NMIPA was synthesized by the nucleophilic substitution reaction given in Figure 1. The effects of polymerization conditions and media on the thermoresponsivity of crosslinked hydrogels is discussed below.

Firstly, the effect of the initiator concentration was investigated. As seen in Figure 2, the initiator concentration is not an effective factor on the temperature sensitive behavior of the synthesized hydrogels. The constant temperature equilibrium water contents of the gels synthesized with two different initiator concentrations were very close to each other and the observed change is in the probable error limits of the gravimetric method used to determine the equilibrium swelling ratios. As can be seen in Figure 2, the change in equilibrium swelling ratios with temperature gave an S-shaped graph just as in the case of commonly used temperature sensitive polymeric gels. PNIPA hydrogels exhibit an abrupt swelling ratio variation around 31–34°C[26,51,52] whereas PNMIPA hydrogels synthesized in this study show the same variation in a wide temperature interval between 30 and 55°C. This temperature interval also includes the physiological temperature and could provide an advantage to PNMIPA in biomedical applications. PNMIPA hydrogels show very similar phase transition temperature with poly(*N*-ethoxypropylacrylamide) (PNEPAM).[48] On the other hand, PNMIPA hydrogels have higher equilibrium/swelling ratio than that of PNEPAM. The completely shrunken gel situation was reached at 60°C. This behavior could be seen from Figure 2. Polymerization conditions for the experiments are given in the figure's legend.

The change with temperature in the equilibrium swelling ratios of the gels obtained with different monomer concentrations are shown in Figure 3. The equilibrium swelling ratio of the gel decreased significantly with increasing monomer concentration especially at lower temperatures. On the other hand, monomer concentration is not effective on the equi-

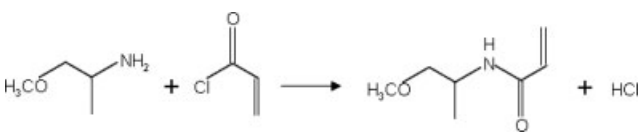


**Figure 1** Preparation of NMIPA monomer.

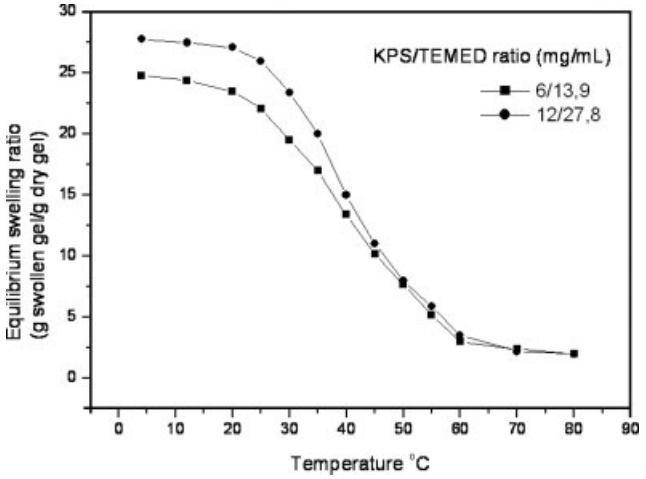


**Figure 2** The effect of initiator concentration on the variation of equilibrium swelling ratio with the temperature in distilled water medium. Gel synthesis conditions: NMIPA: 100 mg/mL, MBA: 6 mg/mL, +4°C, 24 h. Gel dimensions: 8 mm in diameter and 25 mm in length under production conditions.

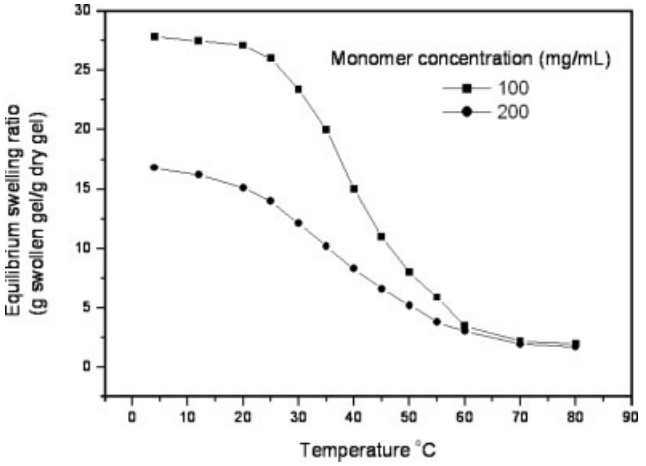


**Figure 3** The effect of monomer concentration on the variation of equilibrium swelling ratio with the temperature in distilled water medium. Gel synthesis conditions: MBA: 6 mg/mL, KPS: 12 mg/mL, TEMED: 27.8 mg/mL, +4°C, 24 h. Gel dimensions: 8 mm in diameter and 25 mm in length under production conditions.

librium swelling ratio at higher temperatures at which the gel shrinks.

For the investigation of crosslinker (MBA) concentration, three crosslinker concentration values were applied. The change in equilibrium swelling ratio of the gels with temperature is seen in Figure 4. Especially in the low temperature region, the equilibrium swelling ratio decreased with increasing crosslinker concentration. On the other hand, the equilibrium swelling ratios of the gels were not affected by changing the MBA concentration over 60°C. In other words, the effect of hydrophobic interactions on the equilibrium swelling ratio is more significant than that of the crosslinking concentration in the high temperature region. Similar behavior was also observed in PNIPAM based gels.[53]

More significant temperature sensitivity can be obtained by using a diluent in the synthesis of temperature sensitive hydrogels. In the study, polyethyleneglycol PEG-4000 ($M_n$ = 4000) was used as diluent. PEG-4000 was previously used in NIPA based hydrogels and provided an increase in the thermoresponsivity.[26] The effect of PEG-4000 concentration on the swelling behavior of PNMIPA hydrogels is shown in Figure 5. This effect was investigated for PNMIPA hydrogels in both an aqueous solution and 0.05*N* phosphate buffer at pH 7. Three different diluent concentrations were used in the experiments. The temperature response in the aqueous media was significantly affected by the use of diluent, and, at lower temperatures, the equilibrium swelling ratios increased definitely with increased diluent concentrations. On the other hand, the increase in diluent concentration in the phosphate buffer medium did not affect the equilibrium swelling ratio significantly at lower temperatures. Hydrophobic interactions are more effective in phosphate buffer medium than in distilled water at high temperatures.

The effect of ionic strength on the swelling behavior of PNMIPA hydrogels is shown in Figure 6. The aqueous media having different ionic strength values were prepared and the ionic strength values of the media were adjusted by using NaCl. In the gels of PNIPA[26] and PNEPAM,[48] a decrease was observed in the equilibrium swelling ratio by increasing ambient ionic strength under constant conditions. Figure 6 shows that the same behavior was also observed in PNMIPA gel. On the other hand, the equilibrium swelling ratio was not affected such significantly by

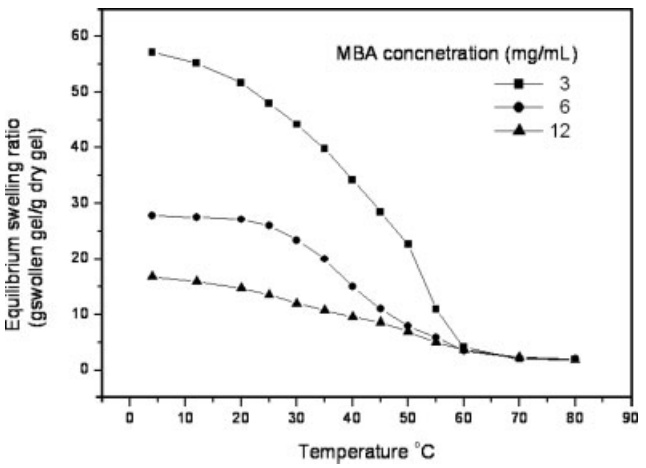


**Figure 4** The effect of cross-linking agent concentration on the variation of equilibrium swelling ratio with the temperature in distilled water medium. Gel synthesis conditions: NMIPA: 100 mg/mL, KPS: 12 mg/mL, TEMED: 27.8 mg/mL, +4°C, 24 h. Gel dimensions: 8 mm in diameter and 25 mm in length under production conditions.

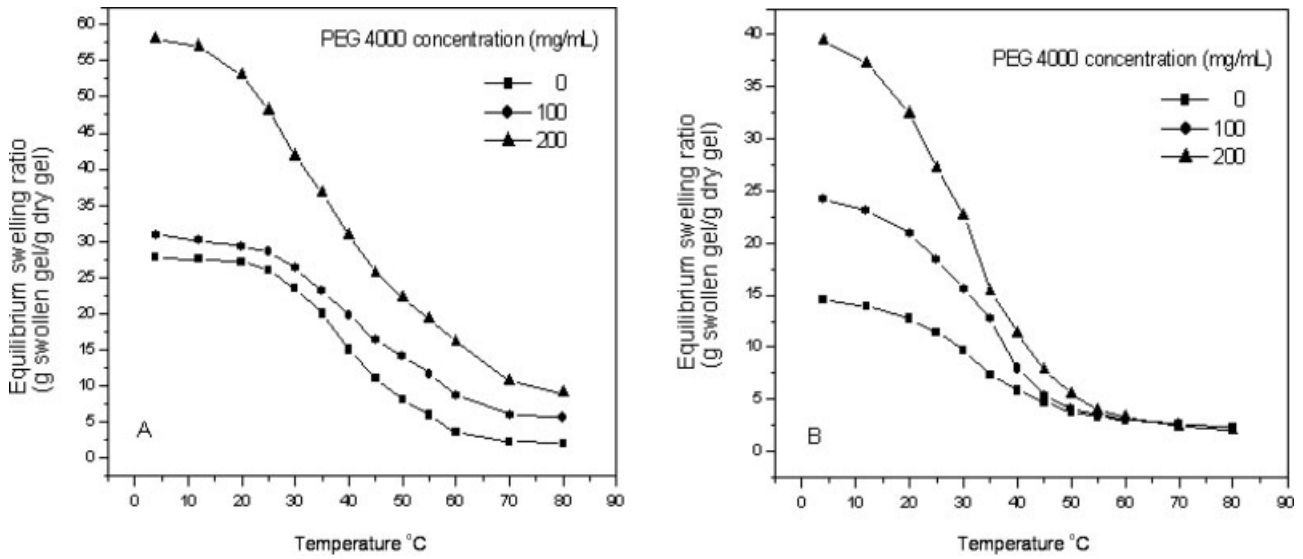


**Figure 5** The effect of PEG 4000 concentration on the variation of equilibrium swelling ratio with the temperature. Medium: (A) Distillated water, (B) Phosphate buffer at pH 7. Gel synthesis conditions: NMIPA: 100 mg/mL, MBA: 6 mg/mL, KPS: 12 mg/mL, TEMED: 27.8 mg/mL, +4°C, 24 h. Gel dimensions: 8 mm in diameter and 25 mm in length under production conditions.

the change in the ambient ionic strength at higher temperature region.

Dynamic swelling and shrinking experiments were performed by using a PNMIPA hydrogel disc sample 16 mm in diameter and 5 mm in length taken from the obtained gel 16 mm in diameter and 20 mm in length under production conditions. Dynamic swelling and shrinking behaviors of the crosslinked gels are seen in Figure 7. The general behavior observed in temperature-responsive gels is that the dynamic swelling is slow whereas dynamic shrinking is very fast. A typical example of this behavior is seen in Figure 7. The dynamic shrinking process is completed in about 0.5 h. On the other hand, dynamic swelling process is fast in the first 1.5 h and then it slows down significantly due to weak diffusion of water into the hydrogel. This behavior was also similar to that observed with PNIPA gels and should be explained by the convective diffusion of water induced by shrinking of crosslinked PNMIPA chains. In this case, the internal hydrodynamic pres-

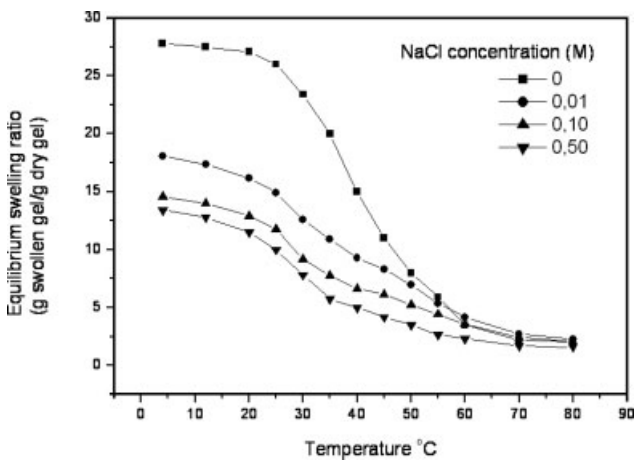


**Figure 6** The effect of ionic strenght on the variation of equilibrium swelling ratio with the temperature in ionic medium. Gel synthesis conditions: NMIPA: 100 mg/mL, MBA: 6 mg/mL, KPS: 12 mg/mL, TEMED: 27.8 mg/mL, +4°C, 24 h. Gel dimensions: 8 mm in diameter and 25 mm in length under production conditions.

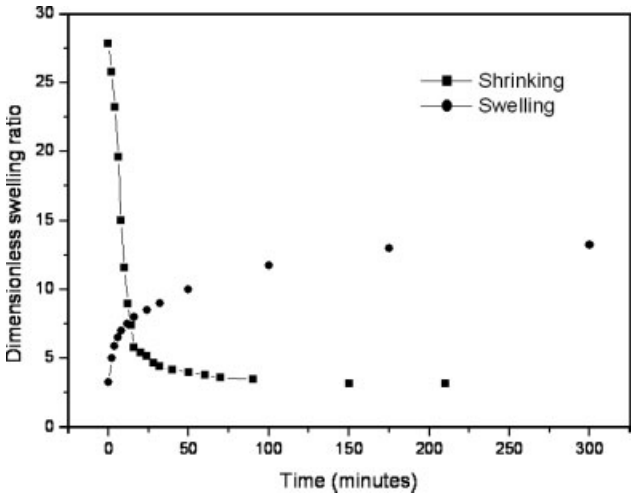


**Figure 7** The variation of swelling ratio with the time for the shrinking induced by the step change of temperature from +4 to 80°C and for the swelling induced by the step change of temperature from 80 to +4°C. Gel synthesis conditions: NMIPA: 100 mg/mL, MBA: 6 mg/mL, KPS: 12 mg/mL, TEMED: 27.8 mg/mL, +4°C, 24 h. Gel dimensions: 16 mm in diameter and 20 mm in length under production conditions.

sure inside the gel upon shrinking causes convective outflow of water from the gel interior.[13,26,54,55]

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