Synthesis and Properties of the Semi-Interpenetrating Polymer Network–Like, Thermosensitive Poly(*N*-isopropylacrylamide) Hydrogel

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ABSTRACT: A new strategy was used to prepare a semi-interpenetrating polymer network (semi-IPN)–like poly(*N*-isopropylacrylamide) (PNIPAAm) polymeric hydrogel, consisting of either low (2300) or high (33,000) molecular weight linear PNIPAAm chains and the crosslinked PNIPAAm network. The properties of the resulting PNIPAAm hydrogels were characterized by DSC and SEM as well as their swelling ratios at various temperatures, the deswelling in hot water (48°C), and the oscillating shrinking–swelling properties within small temperature cycles. It was found that the deswelling rate of these semi-IPN–like PNIPAAm hydrogels was improved if the molecular weight and/or composition of the linear PNIPAAm chains within the semi-IPN–like PNIPAAm hydrogels were increased. This improved deswelling rate was attributed to the fast response nature of the linear PNIPAAm chains and the increased pore number in the matrix network, which provided numerous water channels for the water to diffuse out during the deswelling process at a temperature above the lower critical solution temperature. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1935–1941, 2003

Key words: hydrogels; interpenetrating networks (IPN); lower critical solution temperature

INTRODUCTION

Stimuli-responsive hydrogels have attracted great interest during the past decade. These materials can modulate their shapes and volumes in response to changes in environmental stimuli,[1] including temperature, pH, ionic composition, electric field, and light intensity. Since the report of Tanaka et al.[2] that poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogel can undergo temperature-induced volume changes at around 33°C, which is called the phase-transition temperature (T_{tr}) or lower critical solution temperature (LCST), there has been a surge of studies of the PNIPAAm hydrogel.

Compared with the conventional hydrophilic hydrogels, PNIPAAm hydrogels are well known for their phase separation around the LCST and exhibit sudden shrinkage in volume (i.e., collapse of hydrogel network) upon heating. This transition is mainly controlled by the hydrophobic interactions among the pendant groups along the PNIPAAm chains. This thermoreversible property of phase separation of PNIPAAm hydrogel has been widely used in many devices, for instance, on-off switches for controlled drug release,[3] immobilization of enzyme,[4] dewatering of protein solutions,[5] and gene carrier.[6]

The widespread use of this temperature-sensitive hydrogel, however, is limited in many high-performance applications, such as rapid actuators and artificial organs, because of the slow response rate to the changes in external temperatures. Recently, several strategies were proposed to improve the properties, especially the response rate of the temperature-sensitive hydrogels. Kabra et al.[7] and Hoffman et al.[8,9] used the phase-separation technique to produce fast responsive PNIPAAm hydrogels resulting from the heterogeneous matrix structure created during the polymerization and crosslinking process. Okano et al.[10–12] suggested that introducing the freely mobile and grafted chains to the network of PNIPAAm hydrogel could greatly improve its deswelling property. Several strategies were also reported in previous studies conducted by Zhang et al.,[13–17] that the improved response rate of the hydrogels could be obtained through incorporating siloxane linkage, cold polymerization, vacuum synthesis, and using the pore-forming agent.

In this study a novel method was developed to prepare PNIPAAm hydrogels with a semi-interpenetrating polymer network (semi-IPN)–like structure. The properties of the resulting semi-IPN–like PNIPAAm hydrogels were investigated by measuring the swelling ratio at various temperatures, the de-

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TABLE I
Feed Compositions of the Semi-IPN–like PNIPAAm Hydrogels

	Sample ID						
	LG0	LG1	LG2	LG3	MG1	MG2	MG3
NIPAAm (mg)	100	100	100	100	100	100	100
PNIPAAm (mg)	0	10 (M_n: 2300)	20 (M_n: 2300)	30 (M_n: 2300)	10 (M_n: 33,000)	20 (M_n: 33,000)	30 (M_n: 33,000)
BIS (mg)	2.0	2.0	2.0	2.0	2.0	2.0	2.0
H_2O (mL)	1.2	1.2	1.2	1.2	1.2	1.2	1.2
10 wt % APS (μl)	20	20	20	20	20	20	20
TEMED (μl)	5	5	5	5	5	5	5

swelling, and the oscillating shrinking–swelling properties to temperature cycles. Furthermore, DSC and SEM were also used to investigate the LCST behavior and interior morphology of these semi-IPN–like PNIPAAm hydrogels, respectively.

EXPERIMENTAL

Materials

N-Isopropylacrylamide (NIPAAm; Aldrich Chemical, Milwaukee, WI) was further purified from benzene/*n*-hexane by recrystallization.[4] 2-Aminoethanethiol hydrochloride (AET·HCl; Aldrich), benzoyl peroxide (BPO; Aldrich), *N,N′*-methylenebisacrylamide (MBAAm; Bio-Rad Laboratories, Hercules, CA), ammonium persulfate (APS; Bio-Rad), and *N,N,N′,N′*-tetramethylethylenediamine (TEMED; Bio-Rad) were used as received.

Synthesis of PNIPAAm

PNIPAAms of different molecular weights were synthesized according to published procedures.[11,18] In brief, PNIPAAm of low molecular weight (designated as oligo-NIPAAm) was prepared by radical polymerization using AET·HCl as a chain-transfer agent. NIPAAm (5.65 g, 50 mmol), AET·HCl (0.452 g, 4.0 mmol), and BPO (0.242 g, 1.0 mmol) were dissolved in methanol (20 mL). Polymerization was carried out at 70°C for 24 h. After cooling to room temperature, the polymer was precipitated three times in an excess of diethyl ether and then dried *in vacuo*. The high molecular weight PNIPAAm (designated as macro-NIPAAm) was prepared by the same reaction conditions as the oligo-NIPAAm, except no chain-transfer agent (AET·HCl) was used during the radical polymerization. The molecular weights of the linear PNIPAAm polymer were determined by gel permeation chromatography (GPC; Waters 2690, Milford, MA). The samples for GPC measurement were prepared by dissolving the polymer synthesized in tetrahydrofuran (THF) at a concentration of 0.2% (w/v) followed by filtration of the solution at a flow rate of 1 mL/min. Based on the calibration curve of a series of polystyrene standards (Polymer Laboratories, Amherst, MA), the number-average molecular weights (M_n) of the oligo- and macro-NIPAAm were 2300 and 33,000, respectively.

Synthesis of the PNIPAAm hydrogel

Semi-IPN–like poly(*N*-isopropylacrylamide)/poly(*N*-isopropylacrylamide) networks were synthesized by incorporating various amounts of the linear PNIPAAm chains of different molecular weights into the aqueous solution of NIPAAm monomer (Table I). After 1.5 h stirring of the mixture at room temperature (22°C), TEMED and APS as the redox initiators, and MBAAm as a crosslinker were added to initiate the polymerization/crosslinking of the NIPAAm monomer. The reaction was carried out for 3 h at room temperature. Thereafter, a network structure consisting of the linear PNIPAAm chains and the newly crosslinked PNIPAAm network was formed, in which the linear PNIPAAm polymeric chains were physically entangled with the crosslinked PNIPAAm network. The resulting network structure was similar to the semi-IPN.

These semi-IPN–like PNIPAAm hydrogels were immersed in deionized water at room temperature for at least 72 h to extract any unreacted monomers and the free linear PNIPAAm chains. The water was refreshed every several hours during this treatment. The semi-IPN–like PNIPAAm hydrogels were then carefully cut into small discs (10 mm in diameter and 3 mm in thickness). The feed compositions and sample ID of the reaction are summarized in Table I, in which LG stands for the semi-IPN–like hydrogel series that had oligo-PNIPAAm and MG stands for the semi-IPN–like hydrogel series that had macro-PNIPAAm.

Thermobehavior of semi-IPN–like PNIPAAm hydrogels

The LCST behavior of the hydrogel samples was determined using a Perkin–Elmer 7-Series differential

scanning calorimeter (DSC, Model DSC 4; Perkin Elmer Cetus Instruments, Norwalk, CT). All samples were immersed in deionized water at room temperature and allowed to swell to reach the equilibrium state before DSC measurement. This swollen sample along with its water was placed in a hermetic sample pan and sealed. The thermal analyses were performed from 25 to 45°C (3°C/min) on the swollen hydrogels under a dry nitrogen atmosphere (flow rate of 40 mL/min). Deionized water was used as the reference in the DSC measurement.

Interior morphology of semi-IPN–like PNIPA hydrogels

The hydrogel samples were first equilibrated in deionized water at room temperature and the equilibrated hydrogel samples were quickly frozen in liquid nitrogen and then freeze-dried (−48°C, 38×10^{-3} mbar) for at least 24 h until all the solvent was sublimed. The freeze-dried hydrogel was fractured carefully and the interior morphology of the hydrogels was studied by use of a scanning electron microscope (XL Series-30; Philips, Hillsboro, OR) after gold coating for 40 s (JFC-1200 Fine Coater, Japan).

Measurement of equilibrium swelling ratio of semi-IPN–like PNIPAAm hydrogels

For the equilibrium swelling ratio studies, semi-IPN–like PNIPAAm hydrogels were swollen in deionized water within a temperature range from 22 to 45°C, which covered the expected LCST range of the hydrogels. The gravimetric method was employed to study the hydrogel's swelling ratio. After immersion in deionized water at a predetermined temperature, the hydrogels were removed from the water and blotted with wet filter paper to remove excess water on the hydrogels' surface. The swollen sample weight was recorded at each immersion temperature and the average values among three measurements were taken for each sample. The equilibrium swelling ratio was calculated as follows:

$$\text{Swelling ratio} = W_s/W_d \qquad (1)$$

where W_s is the weight of water in the swollen hydrogel at each temperature and W_d is the dry weight of the hydrogel. After the weight measurement, the hydrogels were immersed in deionized water at another predetermined temperature, reequilibrated, and weight measured as before.

Measurement of deswelling kinetics of semi-IPN–like PNIPAAm hydrogels

A fixed amount semi-IPN–like PNIPAAm hydrogel sample was immersed in deionized water at room temperature to reach equilibrium. After the establishment of equilibrium at room temperature, the sample was quickly transferred to a water bath of 48 ± 0.1°C. The deswelling kinetics of hydrogels were measured gravimetrically by removing the sample at a predetermined period and wiping off the excessive surface water with a moistened filter paper, after which its weight was determined by a balance. The 48°C was selected for this deswelling study because it is above the LCST of the hydrogel, and a significant change in volume or water loss could be attained rather easily within a short time frame. Water retention is defined as follows:

$$\text{Water retention} = \frac{W_t - W_d}{W_s} \times 100 \qquad (2)$$

where W_t is the total weight of hydrogel and the other symbols are the same as defined above.

RESULTS AND DISCUSSION

During the crosslinking process of the NIPAAm monomer in the solvent mixture of NIPAAm monomer and the linear PNIPAAm polymeric chains (oligo- or macro-NIPAAm), the growing PNIPAAm polymer chains will interact with these oligo- or macro-NIPAAm chains to form a structure like that of a semi-IPN network (i.e., semi-IPN–like) of the resulting PNIPAAm hydrogel through the molecular interactions such as hydrogen bonding.[19,20]

Thermal behaviors of semi-IPN–like PNIPAAm hydrogels

DSC thermograms of these semi-IPN–like PNIPAAm hydrogels in the temperature range from 25 to 45°C are shown in Figure 1; the LCST is referred to as the onset temperature of the endothermic peak.[16,21] The data in Figure 1 illustrate that all the semi-IPN–like PNIPAAm hydrogels exhibited virtually similar LCST at around 35.0°C.

There is a hydrophilic/hydrophobic balance[21–24] in the PNIPAAm chains and these polymer chains have many interactions, such as hydrogen-bonding interactions, which lead to the good water solubility of the PNIPAAm hydrogel at room temperatures. During the heating process in the DSC studies of semi-IPN–like PNIPAAm hydrogels, these interactions were broken and phase separation occurred at their LCST. The lack of change in LCST among the semi-IPN–like PNIPAAm hydrogels in this study is believed to be attributed to the fact that LCST depends mainly on the chemical structure of the hydrogel components; and all semi-IPN–like PNIPAAm hydrogels have the same chemical structure, except their molecular weights,

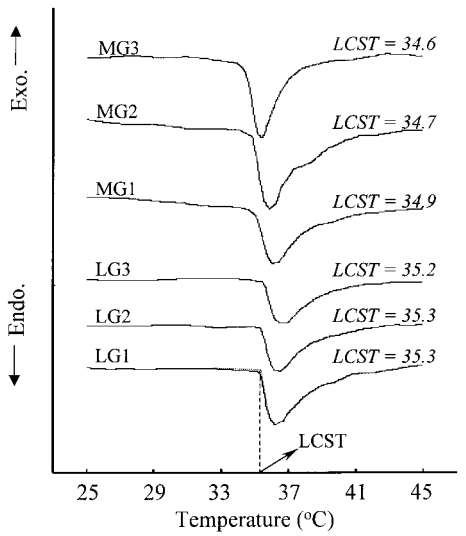

Figure 1 DSC thermograms of the semi-IPN–like PNIPAAm gels at a heating rate of 3°C/min from 25 to 45°C.

and hence similar hydrophilic/hydrophobic balance (i.e., similar LCST).

Interior morphology of semi-IPN–like PNIPAAm hydrogels

The interior matrix structure of the semi-IPN–like network is shown in the SEM micrographs (Fig. 2). The SEM data illustrate that, with the increase of the molecular weight and the amount of the linear PNIPAAm chains, the pore size of the hydrogel was reduced, whereas the number of pores in the network matrix was substantially increased. Although pore sizes were found irregularly within a single PNIPAAm hydrogel, as evident by the large standard deviation, the average pore size of the conventional PNIPAAm hydrogel (LG0) was the largest (8.0 $\pm$ 3.0 μm in diameter) and became smaller with an increase in the molecular weight or/and the amount of the linear PNIPAAm chains. MP3 samples had the smallest pore size (2.0 $\pm$ 1.0 μm in diameter). The number of pores per unit area, however, was opposite to the relationship of pore size. LG0 showed the smallest number of pores per unit area (1.5 per 100 μm^2), whereas the MG3 appeared to have the largest number of pores (25 per 100 μm^2).

As discussed above, the existence of the hydrophilic/hydrophobic balance in the PNIPAAm hydrogel network structure leads to its phase separation when the external temperature cycled around its LCST. When the temperature reaches the hydrogel's LCST or higher, the hydrophobic interactions among the hydrophobic groups become dominant and the hydrogel tends to collapse in volume. During this shrinking or deswelling process at a temperature above the LCST, the water molecules entrapped within the hydrogel network are freed as a result of the broken hydrogen bondings between the water and the hydrophilic groups in PNIPAAm. The response rate of the hydrogel during deswelling is usually determined by the rate of water loss or volume shrinkage. If the diffusion of freed water molecules is not quick and timely, the response rate will be greatly slowed down.

One of the main factors that control the rate of water diffusion during deswelling is the matrix structure of the PNIPAAm hydrogel. That is to say, if the matrix network could provide enough pores as the water-diffusing channels,[11,12,25,26] the freed water (from broken hydrogen bonds) will diffuse out quickly without the retarding effect of the dense, collapsed skin layer.[3,27,28] The resulting network would then exhibit a faster response rate to the temperature change across LCST. Based on the above discussion, the MG3 sample would have been, and indeed was, found to have the fastest response rate because of its numerous small pores, which would result in enhanced water diffusion during the deswelling process. On the other hand, the LG0 sample would exhibit a slower response rate for a similar reason.

Swelling ratio, deswelling, and oscillating deswelling/swelling kinetics of semi-IPN–like PNIPAAm hydrogels

Equilibrated swelling studies were performed on the semi-IPN–like PNIPAAm hydrogels to determine their temperature sensitivity as well as the temperature dependency of the swelling and collapse processes. Figure 3 shows the dependency of the swelling ratios of the conventional PNIPAAm hydrogels (LG0) and semi-IPN–like PNIPAAm hydrogels (LGs and MGs) on solution temperature. The data of the LG series in this figure show that all the samples have similar temperature-dependent swelling profiles (i.e., shrinking dramatically in volume as temperature increased), and the phase-transition temperatures (i.e., LCSTs) of these hydrogels are about 35–36°C, which is in agreement with the thermal data from the DSC study. The LG0 or the conventional PNIPAAm hydrogel, however, had the lowest swelling ratio among the group tested and its rate of deswelling near its LCST was the slowest. Obviously, at a temperature below the LCST, the swelling ratio of corresponding hydrogels increased with an increase in the composition of the linear PNIPAAm chains, from LG0 to LG3. Based on the swelling data, the MG series also exhibited a similar trend, although the difference among them is not as large as that of the LG series. Irrespective of the series, whether LG or MG, all hydrogels collapsed to the same swelling ratio level at temperatures above 35°C.

The deswelling kinetics of the hydrogels at 48°C is shown in Figure 4. The data clearly demonstrate that

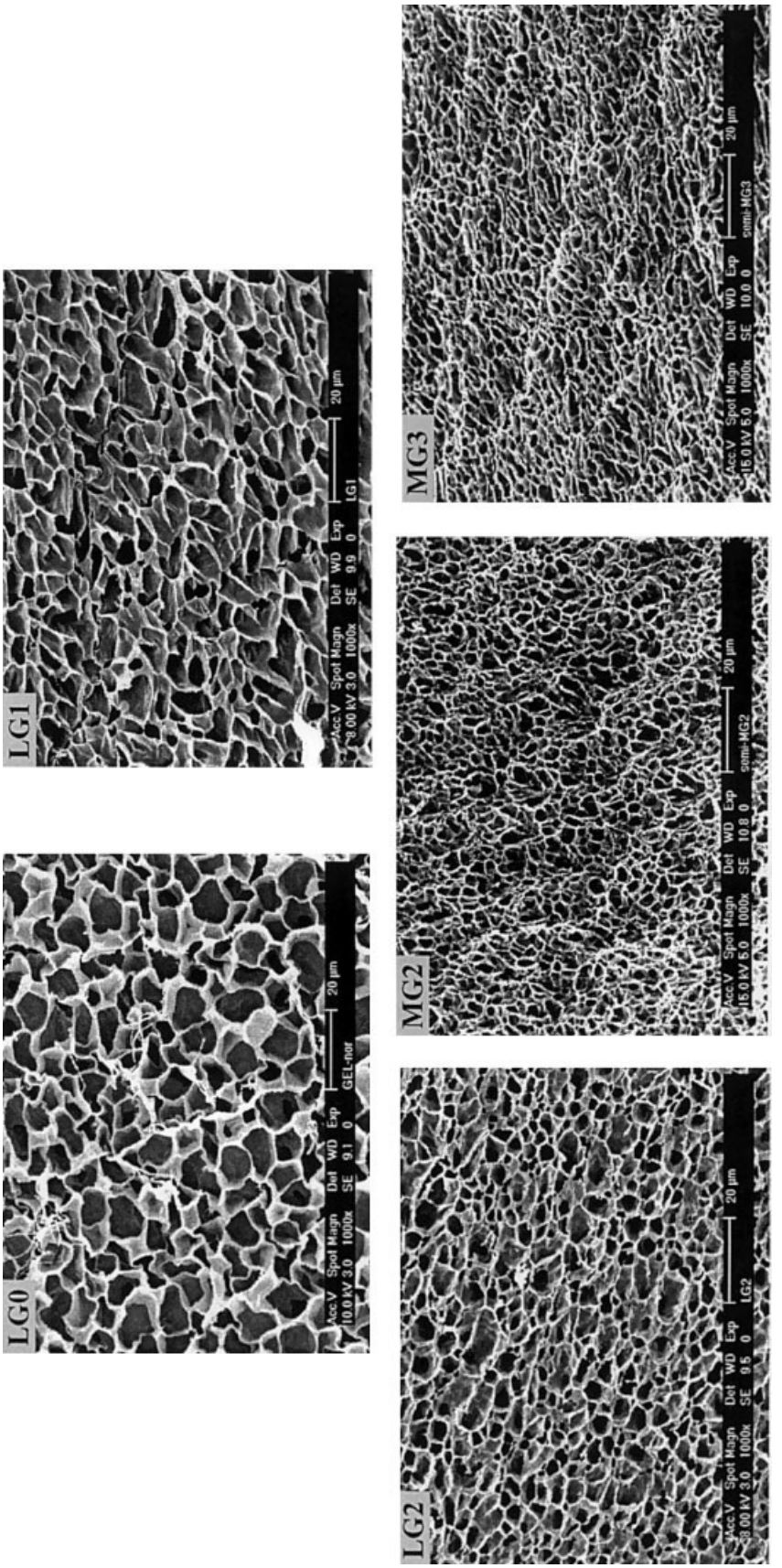

Figure 2 SEM micrographs of the interior of the swollen semi-IPN–like PNIPAAm hydrogels.

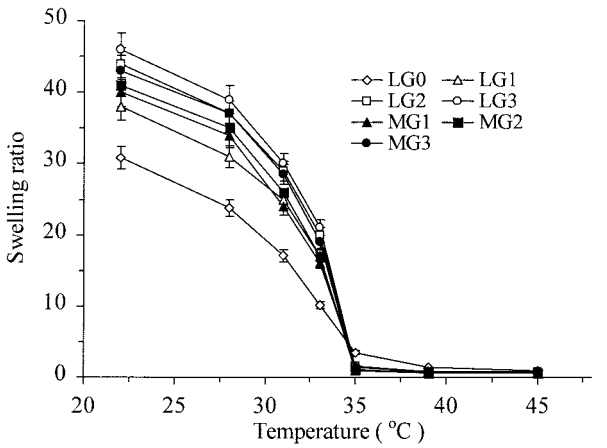

Figure 3 Equilibrium swelling ratios of the semi-IPN–like PNIPAAm hydrogels in the temperature range from 22 to 45°C.

the deswelling response rates were accelerated from LG0 < LG1 < LG2 < LG3 < MG1 < MG2 < MG3. For example, MG3 reached the constant water retention (lost >98% water) in less than 18 min, whereas LG3 lost about 80% within 38 min. The LG0 sample (the PNIPAAm hydrogel without linear PNIPAAm incorporated) had the slowest deswelling kinetics and lost only about 52% within 38 min.

The observed accelerated deswelling response rates from LG0 to LG1, LG2, LG3 to MG1, MG2, and MG3 hydrogels were attributed to the increase in the number of pores from LG0 to LG3 to MG3 observed and discussed in the morphology section (Fig. 2). This increase in hydrogel pores would improve water-diffusing channels. On the other hand, it is well known that the response time of a temperature-sensitive hydrogel is controlled by the square of its smallest linear dimension, and a bulk hydrogel with a three-dimensional network responds very slowly to external temperature changes compared against linear NIPAAm chains.[29–31] Because of this fast response nature, the linear PNIPAAm chains will undergo an abrupt response and precipitate suddenly from the solution as the temperature is increased above its LCST. Because of the strong molecular interlocking and interactions between the linear PNIPAAm chains and the crosslinked PNIPAAm network inside a semi-IPN–like network,[19,20] the inherently fast response characteristic of the linear PNIPAAm chains would influence the nearby PNIPAAm crosslinked network and hence force the network to respond and collapse faster than the conventional PNIPAAm hydrogel [i.e., the crosslinked network without the presence of linear PNIPAAm chains (LG0)]. As a result, the whole semi-IPN–like network exhibits a faster response rate, as observed. Because of the lower molecular weight of the linear oligo-NIPAAm chains, the molecular interlocking and interactions are much less than that of the linear macro-NIPAAm chains, and hence the linear oligo-NIPAAm chains cannot make the crosslinked network respond or shrink as quickly as that of the macro-NIPAAm could; that is, the MG series had a faster response rate than the LG series, as shown in Figure 4. In addition, an increase in the amounts of the linear chains will also improve the molecular interactions between the crosslinked network and the linear chains, which forces the whole network to respond to the shrinking process at a faster rate.

The above studies provide us with the information about the relationship between deswelling rate and the composition of the semi-IPN–like PNIPAAm hydrogels. However, from the viewpoint of applications, the response kinetics of the oscillating shrinking–swelling properties to the small temperature cycles (e.g., cycled around the physiologic temperature) of the hydrogel is important. For this purpose, LG1, which responds to temperature changes more slowly, and MG3, which responds to the temperature changes more quickly, were chosen as the model compounds to compare their oscillating shrinking–swelling properties. Figure 5 shows the kinetics of these two hydrogels over the 2-min temperature cycles between 35 and 40°C in deionized water. All swelling–shrinking cycles are accompanied by a slight decrease of the swelling ratio because of the slow reswelling kinetics and faster deswelling kinetics of the hydrogels. In addition, rapid and larger magnitude of swelling–shrinking was achieved for the MG series (MG3) compared to that of the LG series (LG1). The swelling ratio of MG3 decreased about 3.0 for each 2-min deswelling process at 40°C and increased about 1.8 for each 2-min swelling process at 35°C, whereas the corresponding data for LG1 reduced to 1.6 and 0.8. That is to say, the deswelling magnitude of the MG3 in the deswelling/swelling cycle is about 1.9 times that of LG1, whereas the swelling magnitude of the MG3 in the cycle is about

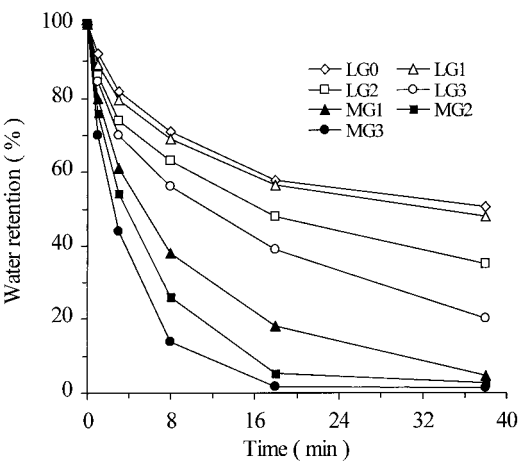

Figure 4 Deswelling kinetics of the semi-IPN–like PNIPAAm hydrogels at 48°C.

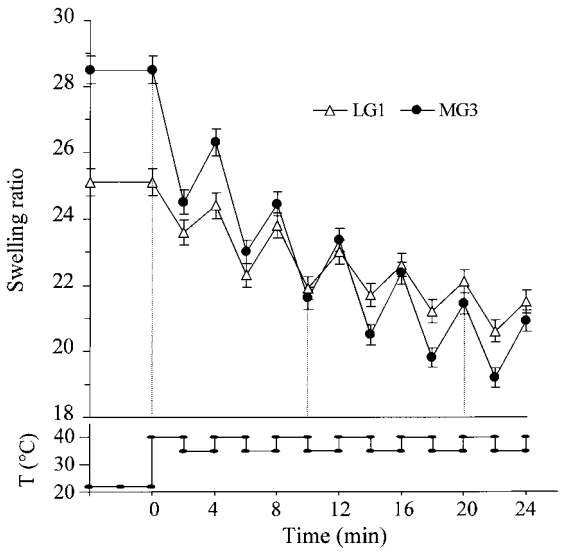

Figure 5 Oscillating shrinking–swelling kinetics of the semi-IPN–like PNIPAAm hydrogels over the 2-min temperature cycles between 35 and 40°C.

2.1 times that of LG1. This fast oscillating swelling–shrinking property, accompanied by a large magnitude of volume changes of MG3, would be more favorable for applications in many devices, such as rapid actuators, artificial organs, and drug delivery devices. After the first two cycles, the deswelling/swelling cycle of both LG1 and MG3 hydrogels became stable.

CONCLUSIONS

In this study, linear PNIPAAm chains of different molecular weights (M_n 2300 and 33,000) were synthesized. These linear PNIPAAm chains were incorporated into the NIPPAAm monomer solution to prepare the semi-IPN–like PNIPAAm hydrogels. The DSC data show the LCSTs of the semi-IPN–like hydrogels were almost the same, whereas the scanning electron microscopic micrographs revealed that the pore number in the semi-IPN network was significantly increased with an increase in the amount or the molecular weight of the linear PNIPAAm chains. These semi-IPN–like PNIPAAm hydrogels exhibited controllable, improved response rate to external temperature changes during the deswelling processes. The improved dynamic properties of these semi-IPN–like hydrogels were attributed to the fast response nature of the linear PNIPAAm chains and the numerous pores in the matrix network, which provided numerous water channels for the freed water during the deswelling process at a temperature above the LCST. These semi-IPN–like PNIPAAm hydrogels with controllable dynamic properties may have great potential applications in both biomedical and biotechnology fields.

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