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Fast synthesis of temperature-sensitive PNIPAAm hydrogels by microwave irradiation

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Abstract

A novel method, microwave irradiation synthesis, is proposed for the preparation of thermo-sensitive poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogels. The PNIPAAm hydrogels were separately synthesized by using microwave irradiation method and water-bath heating method. Chemical groups, lower critical solution temperature (LCST) and surface morphology of these PNIPAAm hydrogels were characterized by FT-IR, DSC and SEM. Swelling ratios of the gels were measured gravimetrically in the temperature range from 10.0 to 60.0 °C. Results showed that (1) the use of microwave irradiation can greatly shorten the reaction time required for PNIPAAm hydrogel synthesis from several hours to several minutes in comparison with water-bath heating method, and obviously improve the yields of the PNIPAAm gels, which were up to 99% after a short reaction time; (2) SEM micrographs and textural measurement revealed that the gels synthesized using microwave irradiation had more porous structure, and their average pore sizes and specific surface areas were larger than those of the gels synthesized using water-bath heating method; and (3) the PNIPAAm hydrogels synthesized using microwave irradiation had much higher swelling ratios at 10.0 °C below the LCST, and had lower swelling ratio at 60.0 °C above the LCST compared to the hydrogels synthesized by water-bath method.

Keywords: PNIPAAm hydrogels; Microwave irradiation; Swelling ratio; Porous structure

1. Introduction

Recently, temperature-sensitive hydrogels have gained considerable attention due to their abilities to swell or/and deswell as a result of changes in temperature of the surrounding fluid [1], offering great potential applications in the bioengineering and biotechnological fields [2]. The poly *N*-isopropylacrylamide (PNIPAAm) hydrogel is one of the temperature-sensitive hydrogels. It has a lower critical solution temperature (LCST) at around 32 °C in aqueous solution, and is usually synthesized from the monomer *N*-isopropylacrylamide, with a proper cross-linker and initiator, by chemical crosslinking [3,4].

PNIPAAm is synthesized by conventional hydrothermal method, such as water-bath heating, in general [5], which usually takes a long time with very slow synthesis rate, low yield [6] and non-uniform properties [7]. Frisken synthesized PNIPAAm gels

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at 70 °C for 4 h by thermal heating [8]. Zhang and co-worker Ciszkowska [9] prepared PNIPAAm copolymer at 22 °C for 20 h. To improve the synthesis of PNIPAAm hydrogel as well as its properties, many researchers tried to use some novel methods, including e-beam radiation, photo-initiated polymerization and plasma-induced grafting. Eder et al. [10] prepared the PNIPAAm gels by e-beam irradiation, and found that its swelling degree was up to four times as high as the gels prepared by conventional thermal heating. Wang [11] used plasma-induced polymerization technique to graft PNIPAAm gels into tubular-type porous polyethylene membranes, and found that the grafted PNIPAAm could respond instantly to environmental temperature changes and showed a sharp change around the LCST.

As we all know that microwave irradiation is a special heating energy, and it has some significant advantages over the conventional thermal methods in preparation of colloid particles. Omprakash [12] used microwave irradiation followed by hydrothermal method for synthesizing ZSM-5 type of zeolite, and found that zeolite synthesized by microwave irradiation method only took half the time for ZSM-5 crystallization of 100% crystallinity to that of conventional hydrothermal heating method. Hence, microwave treatment method is economic and time saving. Yi [13] reviewed the application of microwave irradiation in polymer synthesis, and pointed out that microwave irradiation had excellent advantages over the conventional thermal method in improving yields of the polymer synthesis and its properties. Gao and co-worker [14] first reported the use of microwave irradiation to prepare narrowly distributed surfactant-free stable polystyrene nanospheres. In comparison with the conventional heating method, microwave irradiation could greatly shorten the synthesis time and control the size of the nanoshperes by varying the macroscopic monomer-to-initiator weight ratio as well. Liu and co-worker [15] synthesized porous poly (*N*-isopropylacrylamide) (PNIPAAm)-based hydrogels with poly (ethylene oxide)-600 by the microwave irradiation, and found that microwave could accelerate the reaction rate and increase the yield of PNIPAAm hydrogels. The hydrogels obtained by microwave irradiation exhibited an excellent property in pore size, the equilibrium swelling ratios and the swelling/deswelling rates. Ma et al. [16] used microwave low temperature plasma to initiate synthesis of dualistic intelligent hydrogel and found that the synthesized hydrogel had three-dimension crosslinked network, and thus it could absorb water and swell greatly.

In this work, a novel synthesis method, microwave irradiation method, will be proposed for PNIPAAm hydrogels synthesis. Then, the PNIPAAm hydrogels will be synthesized respectively by microwave irradiation method and conventional hydrothermal method, and Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) would be used to investigate the chemical group, LCST behavior, and morphology, respectively, of the resulting PNIPAAm hydrogels. We will compare the porous structures of the hydrogels synthesized using two different methods, and discuss the effects of the hydrogel structures on its swelling ratio.

2. Experimental

2.1. Materials

Chemical reagents: *N*-isopropylacrylamide (NIPAAm, 97% pure) as monomer and *N*,*N*′-methylenebisacrylamide (Bis, 99% pure) were obtained from Aldrich, USA. 2,2′-azobis (isobutyronitrile) (AIBN) was purchased from YiNeng Chromatogram. Acetone was purchased from Shantou chemical reagent factory. The last two were analytical grade. Water was deionized before use.

2.2. Hydrogels synthesis

Normal water-bath heating method [17,18]: Firstly, the monomer (*N*-Isopropylacrylamide, 1.50 g), cross-linker (*N*,*N*′-methylenebisacrylamide, 150 mg), and initiator [azobis (isobutyronitrile), 164 mg] were dissolved in 15 mL-degassed acetone and then injected into a rockered flask. After that, the flask was kept under N_2 atmosphere, and then the degassed acetone solution was evenly transferred into four mini-reactors (Ø10 mm × 150 mm). The polymerization took place separately at different water-bath temperatures (70 °C, 80 °C and 90 °C). After 24 h gelation, the prepared PNIPAAm hydrogels were removed from the mini-reactors and immersed in pure water for 48 h to remove all non-reactive materials. After drying overnight under the vacuum oven, the samples of the PNIPAAm hydrogels were obtained and respectively denoted as PN-70-24 h, PN-80-24 h and PN-90-24 h according to

their reaction temperature and reaction time, as shown in Table 1.

Microwave irradiation method: Firstly, the reaction mixture with the same weight ratios as the water-bath heating method were dissolved in 15 mL-degassed acetone and bubbled N_2 for 60 min at room temperature. After that, the solution was transferred to the mini-reactors, and then they were put into a bigger special microwave reactor. The polymerization reaction was carried out in Mars-5 microwave accelerator purchased from the USA CEM Company with adjustable and controllable temperature system. Reaction temperature was measurable and controllable with a deviation of ±0.05 °C. The maximum power output was set at 300 W. The reaction duration was designed from 5 to 30 min. Finally, the samples of the PNIPAAm hydrogels were obtained and respectively denoted as PM-70-20 min, PM-80-20 min, PM-90-20 min, PM-80-30 min, PM-80-10 min and PM-80-5 min according to the reaction temperatures and times of the microwave irradiation, as shown in Table 1.

2.3. Characterization

2.3.1. FT-IR and LCST

The FTIR spectra of PNIPAAm were analyzed by using SP2000 FT-IR spectrometer (Pye Unicam Ltd., from England) at room temperature in the region of 4000 and 500 cm^{-1}, with a resolution of 2 cm^{-1} and 20 scans [19]. Powder samples were prepared by dispersing the samples in KBr and compressing the mixture to form disks. Before measurement, the PNIPAAm hydrogels were dried at 60 °C under vacuum oven over 24 h.

Table 1
Reaction temperature and reaction time of the PNIPAAm hydrogels

Samples	Reaction temperature (°C)	Reaction time (min)
Water-bath heating		
PN-70-24 h	70	1440
PN-80-24 h	80	1440
PN-90-24 h	90	1440
Microwave irradiation (300 W)		
PM-70-20 min	70	20
PM-80-20 min	80	20
PM-90-20 min	90	20
PM-80-30 min	80	30
PM-80-10 min	80	10
PM-80-5 min	80	5

Differential scanning calorimetry (DSC) was used to measure the lower critical solution temperatures (LCST) of the PNIPAAm hydrogels by means of DSC/TGA (Netz-DSC/TGA STA409) [17]. Firstly, the samples were degassed at 25.0 °C for 20 min. Then DSC thermograms were measured under He flow from 25.0 °C to 60.0 °C (heating rate: 2.0 °C/min).

2.3.2. Measurement of porous and morphological properties [18]

The accelerated surface area and porosimetry apparatus (ASAP 2010, Micromeritics Ins. Corp.) was used to measure the texture of the synthesized gels.

The morphology of synthesized gels was characterized by scanning electron microscopy (SEM) (JSM-6300, JEOL). The samples characterized by SEM were prepared as follows: the surface of dried gels was directly deposited with gold under vacuum; and the swollen gel was quickly frozen with liquid nitrogen and then freeze-dried for at least 24 h prior to SEM observation.

2.3.3. Yield and swelling

Yield of PNIPAAm hydrogel was calculated by the following equation [6]:

$$\text{Yield } (\%) = [m_d/(m_{NIPAAm} + m_{Bis})] \times 100 \quad (1)$$

where m_{NIPAAm} is the weight of NIPAAm; m_{Bis} is the weight of cross-linker and m_d is the weight of the dried hydrogels.

The swelling of hydrogels were characterized by measuring their equilibrium swelling degree, which was suggested by Jun [8]. The equilibrium swelling ratio SR% was measured using gravimetric method, and then calculated according to following equation:

$$\text{SR } (\%) = [(m_s - m_d)/m_d] \times 100 \quad (2)$$

where m_d is the weight of dried gels, and m_s is the weight of gels immersed in water for 24 h at different temperatures.

3. Results and discussion

3.1. FT-IR spectra of the PNIPAAm hydrogels

Fig. 1 shows the FTIR spectra of NIPAAm as monomer and the PNIPAAm hydrogels synthesized respectively by microwave irradiation and water-bath heating methods. It can be seen that there

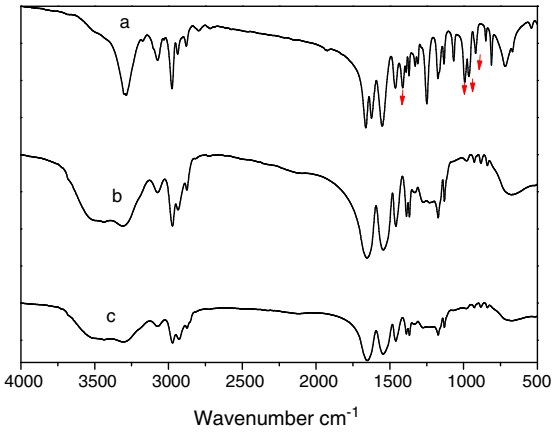

Fig. 1. FT-IR spectrum of PNIPAAm hydrogels prepared by different methods. (a) NIPAAm, (b) PM-80-20 min and (c) PN-80-24 h.

existed characteristic peaks of NIPAAm monomer at 1618 cm^{-1} (C═C), at 1407 cm^{-1} (CH_2═) and between 986 and 913 cm^{-1} for the vinyl group peaks in NIPAAm monomer spectrum, while these characteristic peaks of the NIPAAm monomer disappeared in the PNIPAAm polymer spectra. It implied that the polymerization reaction had taken place. At the same time, it could be clearly seen that the FTIR spectra shapes of the hydrogels PM-80-20 min and PN-80-24 h were similar. Both of their spectra showed the typical amide I band (1645 cm^{-1}) consisting of C═O stretch of PNIPAAm and an amide II band (1547 cm^{-1}), including N–H vibration. These bands were characteristic peaks of the PNIPAAm hydrogels [20]. The FTIR spectra of the PNIPAAm gels synthesized were consistent with that reported previously by Liang [21]. It suggested that the use of microwave irradiation method could synthesize the PNIPAAm hydrogels.

3.2. LCST and yield of PNIPAAm hydrogels

Fig. 2 shows the DSC thermograms of PM-90-20 min and PN-90-24 h in the temperature range from 25.0 to 60.0 °C. It can be clearly seen that their DSC thermogram shapes were similar. Temperatures corresponding to these exothermic peaks were the LCSTs of the synthesized PNIPAAm gels. Table 2 lists the LCSTs of the PNIPAAm gels synthesized separately by microwave irradiation and water-bath heating. It indicated that the LCSTs of these PNIPAAm hydrogels were around 32 °C with a tiny change as previously reported [19].

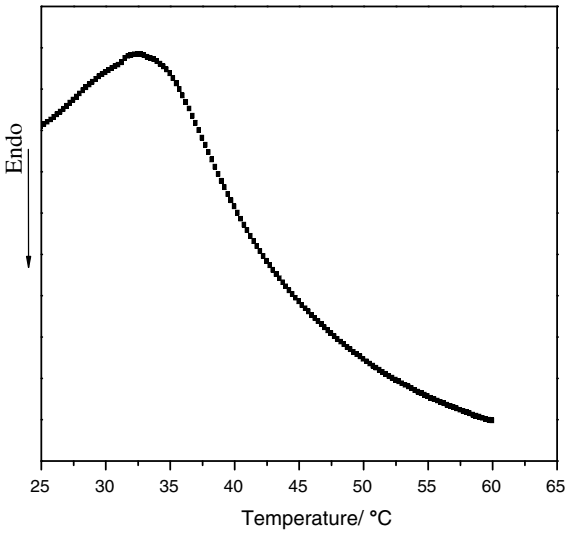

Fig. 2a. DSC thermogram of the PN-90-24 h hydrogel.

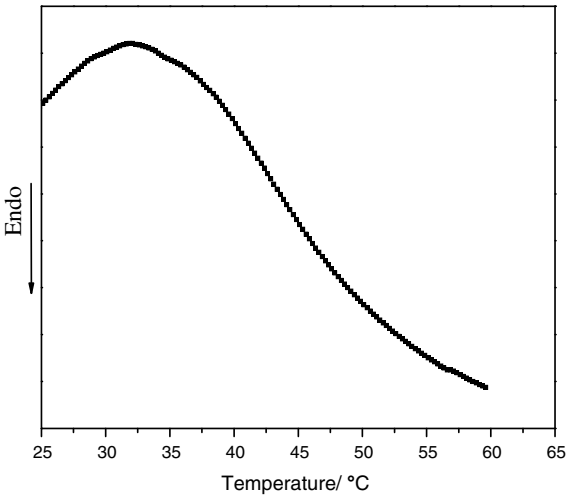

Fig. 2b. DSC thermogram of the PM-90-20 min hydrogel.

Table 2 lists the obtained yields of the PNIPAAm hydrogels synthesized separately by microwave irradiation and water-bath heating methods. It indicated that the use of the water-bath heating method resulted in the formation of the hydrogels with yields between 72.11% and 75.33% in 24 h, while the application of the microwave irradiation method made the formation of the hydrogels with yields between 87.36% and 99.43% in less than half an hour. The microwave irradiation method did have the significant advantages over the conventional hydrothermal method in aspect of preparation of thermo-sensitive polymers [14]. It made the formation of hydrogels not only rapid, but also with higher yield. Obviously,

Table 2
Effect of reaction temperature on the conversion efficiency and LCST of the PNIPAAm hydrogels

Synthesis methods	Samples	Yield (%)	LCST (°C)
Normal water-bath heating	PN-70-24 h	72.11	31.49
	PN-80-24 h	73.35	32.07
	PN-90-24 h	75.33	32.14
Microwave irradiation (300 W)	PM-70-20 min	97.69	31.12
	PM-80-20 min	98.09	31.25
	PM-90-20 min	99.43	32.02
	PM-80-30 min	98.99	32.05
	PM-80-10 min	92.35	31.79
	PM-80-5 min	87.36	32.11

it was an available, rapid and effective method to prepare PNIPAAm hydrogels.

3.3. Textural properties of the PNIPAAm hydrogels

Table 3 lists the specific surface area, pore volume and average pore size of the samples. It indicated that the specific surface areas, the pore volumes and average pore sizes of the gels synthesized by microwave irradiation were obviously larger than those synthesized by water-bath heating. The specific surface area S_{BET} (BET surface area) of the PM gels ranged from 6.8 to 10.3 m^2/g, while S_{BET} of the PN gels only ranged from 0.7 to 1.1 m^2/g. The pore volume of the PM gel was up to 4.5×10^{-3}–2.7×10^{-2} cm^3/g, whilst the pore volume of the PN was just 5.2×10^{-4}–1.5×10^{-3} cm^3/g. It meant that the PM gels were much more porous in comparison with the PN gels.

3.4. Morphologies of the swollen and dried PNIPAAm hydrogels

SEM topography measurement on air-dried PNIPAAm was performed under atmospheric conditions. Fig. 3 shows SEM micrographs of surfaces of the air-dried gels PN-80-24 h and PM-80-20 min. It can be seen that the surface of gel PN-80-24 h was very dense and rather smooth except for small spherically shaped protrusions and light cavities, while the surface of the gel PM-80-20 min had a rougher surface with some deep and interconnected pores. Compared to the gel PN-80-24 h, the gel PM-80-20 min had more porous network structures, which would allow water to diffuse more easily within the gel matrix during the swelling process.

Fig. 4 shows SEM micrographs of the surfaces of the gels PN-80-24 h and PM-80-20 min, which were in the fully swollen state. It can be seen from Fig. 4 that gels PN-80-24 h and PM-80-20 min exhibited a characteristic three-dimensional coral-like pattern. However, the gel PM-80-20 min has more uniform and deep pores in comparison with the gel PN-80-24 h. Smaller cavities were confined by the thin and alveolate wall of the polymer matrix. Figs. 4c and 4d gave a closer inspection and revealed a

Table 3
The parameter of the porous structure of the PNIPAAm hydrogels

Sample	BET[a] (m^2/g)	BJH[b] (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)
PN-70-24 h	0.73	0.341	5.2×10^{-4}	2.10
PN-80-24 h	1.01	0.918	1.5×10^{-3}	2.37
PN-90-24 h	0.98	0.446	1.2×10^{-3}	2.55
PM-70-20 min	6.82	5.328	5.4×10^{-3}	3.19
PM-80-20 min	10.26	7.850	2.7×10^{-2}	2.91
PM-90-20 min	7.02	4.702	4.4×10^{-3}	3.14

[a] BET: the Brunauer–Emmett–Teller, which is one of the models to calculate the surface area of the materials [22].

[b] BJH: the Barrett–Joyner–Halenda, which is one of the models to calculate the mesopore of the material [22].

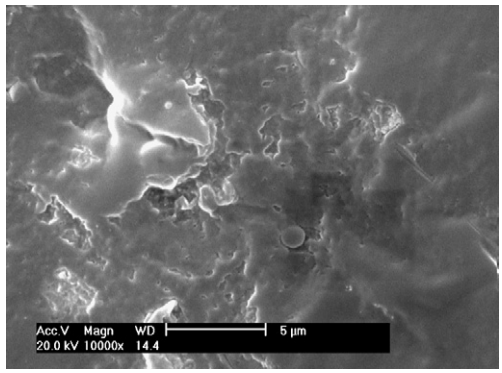

Fig. 3a. SEM micrograph of the air-dried PN-80-24 h gel surface (10 000× magnification).

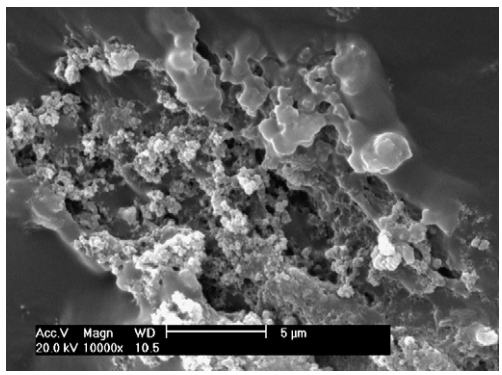

Fig. 3b. SEM micrograph of the air-dried PM-80-20 min gel surface (10 000× magnification).

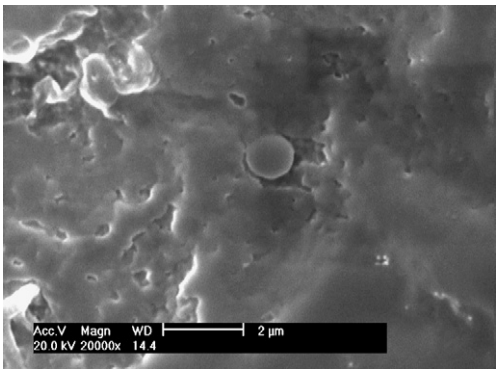

Fig. 3c. SEM micrograph of the air-dried PN-80-24 h gel surface (20000× magnification).

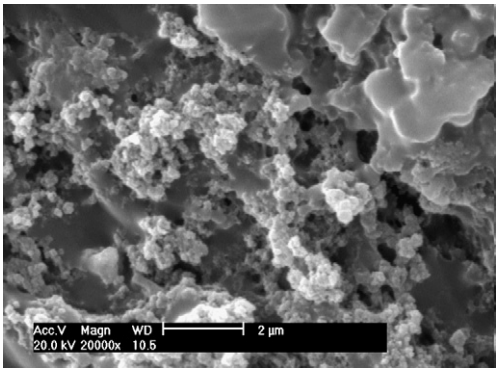

Fig. 3d. SEM micrograph of the air-dried PM-80-20 min gel surface (20000× magnification).

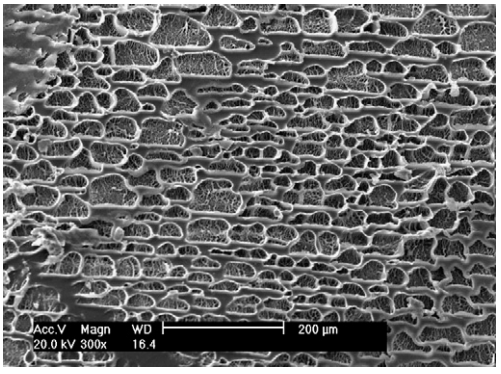

Fig. 4a. SEM micrograph of the PN-80-24 h gel surface in the swollen gel surface at 10 °C (300× magnification).

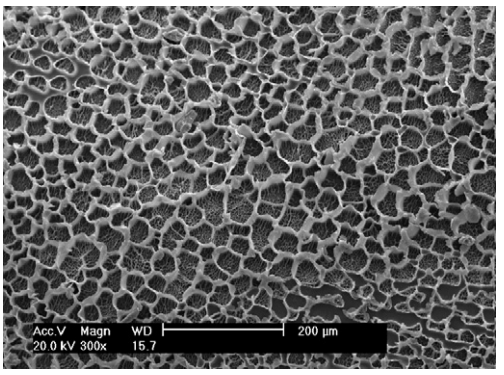

Fig. 4b. SEM micrograph of the PM-80-20 min gel surface in the swollen gel surface at 10 °C (300× magnification).

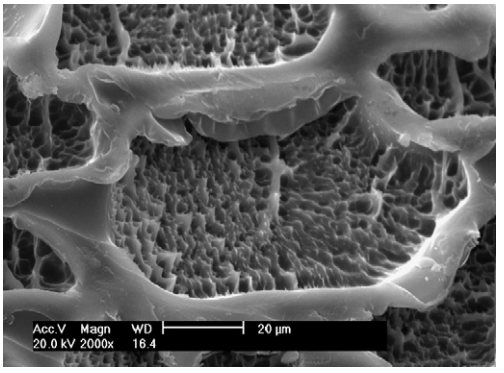

Fig. 4c. SEM micrograph of the PN-80-24 h gel surface in the swollen gel surface at 10 °C (2000× magnification).

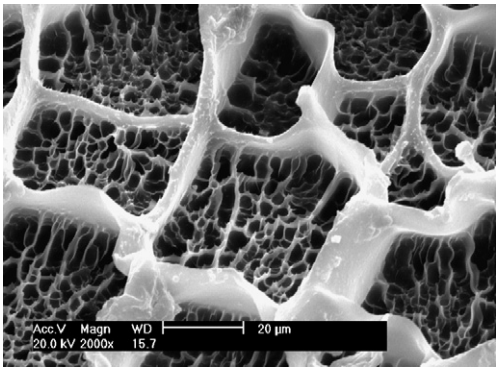

Fig. 4d. SEM micrograph of the PM-80-20 min gel surface in the swollen gel surface at 10 °C (2000× magnification).

noticeable difference in polymer matrix. It was clear that the pores of the gel PM-80-20 min were deeper and larger than that of the gel PN-80-24 h. In addition, the wall thickness of the gel PM-80-20 min was higher and thinner than that of the gel PN-80-24 h.

From forgoing discussion, it can be deduced that the application of microwave irradiation to prepare PNIPAAm gels made the gels have more porous structure than the gels synthesized by using water-bath heating method. Developed porous structure of the gels would make water diffusion into or out

of its network easier during the deswelling and reswelling process.

3.5. The swelling change of the PNIPAAm with temperature swings

Swelling ratios of the gels synthesized were measured gravimetrically in the temperature range from 10.0 to 60.0 °C. Figs. 5 and 6 show the swelling ratios SR% of the PM hydrogels and the PN hydrogels. It can be seen that the swelling ratios of the gels decreased as the temperature increased. When the temperature was above the LCST, the gels shrank dramatically in volume due to the occurrence of the phase transition. The sharp change in swelling ratio as a function of temperature variation around the LCST indicated that the temperature sensitivity of the gel synthesized. There are two kinds of functional groups in the NIPAAm monomer, a hydrophilic group and a hydrophobic group. At the temperatures above LCST, the non-polar carbon chains of the PNIPAAm hydrogel tended to expose outwards to envelop the polar amide groups in the shrinking state [23] with the collapsed hydrogel chains and weaker hydrogen bonding between C=O and N–H groups. As a result, the PNIPAAm hydrogel was hydrophobic in distilled water with a low SR%. Whereas, below the LCST, the PNIPAAm hydrogel converted inversely to the swelling state [25] and thus the PNIPAAm hydrogel had a moderate hydrophilic property with a large SR%.

It was observed that below LCST the SR% of the PM hydrogels were much higher than that of the PN hydrogels, whilst at 50.0 or 60.0 °C above the LCST their swelling ratios were lower than that of the PN hydrogels. When temperature of water was changed from 10.0 to 60.0 °C, the decrease magnitude of the swelling ratios (SR%) of the PM hydrogels were much larger than the PN hydrogels. For example, the SR% of the gel PM-80-20 min decreased sharply from 4013% to 50%, while the SR% of the gel PN-80-24 h varied from 1836% to 178%. Such a significant difference was mainly ascribed to the difference in texture of the synthesized hydrogels.

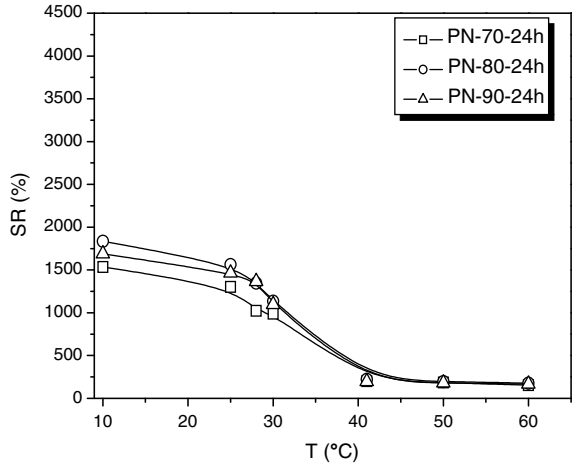

Fig. 5. The SR% of the PN hydrogels synthesized at different reaction temperatures.

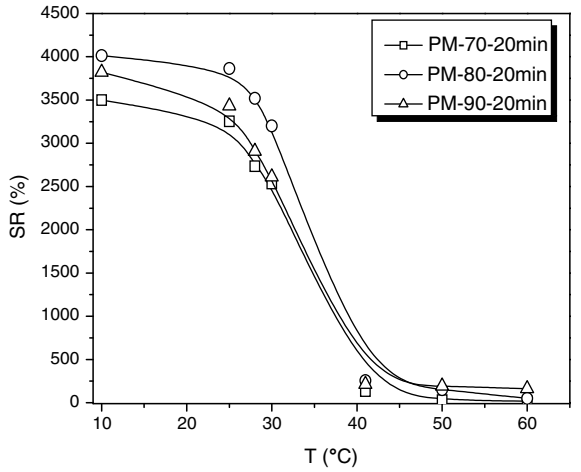

Fig. 6. The SR% of the PM hydrogels synthesized at different reaction temperatures.

Generally speaking, a more porous matrix provides more space to accommodate water [24]. As shown in Figs. 4c and 4d, the PM hydrogels had more developed porous structure than the PN hydrogels below LCST, and therefore, it would have higher water uptake. On the other hand, when temperature was above LCST, the hydrophilic property of the side groups in the network of the hydrogels was changed into hydrophobic property, and thus the hydrogels discharged water and shrunk. Since the average pore size of the PM hydrogels was larger than that of the PN hydrogels as indicated in Table 3, it resulted in equilibrium water retention of the PM hydrogels being smaller in comparison with that of the PN hydrogels because the larger the pore size was, the weaker its force of absorbing water [25].

4. Conclusions

Microwave irradiation can greatly shorten the reaction time required for hydrogel synthesis from

several hours to several minutes in comparison with the hydrothermal method, and obviously improve the yields of the PNIPAAm gels, which were up to 99%. The hydrogels synthesized by microwave irradiation have much developed porous structure in the gels matrix, which would facilitate the water diffusion into or out of the hydrogels network. Therefore, the PNIPAAm hydrogels synthesized by microwave irradiation method had much higher swelling ratios at 10.0 °C below LCST, and had lower swelling ratios at 60.0 °C above LCST in comparison with the hydrogels synthesized by water-bath method.

Acknowledgments

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