

# Preparation and Thermal Response Behavior of Poly(*N*-isopropylacrylamide-*co*-acrylic acid) Microgels via Soap-Free Emulsion Polymerization Based on AIBN Initiator

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**ABSTRACT:** Poly(*N*-isopropylacrylamide-*co*-acrylic acid) (poly(NIPAM-*co*-AA)) microgels with different copolymer compositions were prepared through soap-free emulsion polymerization at 80°C, and 2, 2'-azobisisobutyronitrile (AIBN) was used as initiator. Scanning electron microscope (SEM) characterization shows that the prepared microgels are regular and smooth and not easy to distort. Result of <sup>1</sup>H-NMR characterization shows that with increasing of the initial concentration of AA (AA in feed), the AA content in polymer chains increases. The thermal response of microgels latex was investigated by UV-3010 spectrophotometer through detecting the transmittance of the latex at different temperature in the range of 190–900 nm. The thermal response of the poly(NIPAM-*co*-AA)

microgels was tested by dynamic light scattering (DLS). The results show that with the increase of AA content in polymer chains, the low critical solution temperature (LCST) of microgels latex first decreases and then increases. Still, with increasing of AA in poly(NIPAM-*co*-AA) microgels, the LCST of microgels first increases and then decreases. The basic reasons causing the changes of LCST of microgels latex and microgels are interpreted clearly in this article from the perspective of hydrogen bonding interaction. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3322–3331, 2011

**Key words:** poly(NIPAM-*co*-AA) microgels; soap-free emulsion polymerization; AIBN; thermal response; LCST

## INTRODUCTION

Since Pelton and Chibante<sup>1</sup> reported the synthesis of the first temperature-sensitive microgels from *N*-isopropyl acrylamide and *N,N*-methylene-*bis*-acrylamide (MBA) in 1986, responsive microgels have attracted considerable attention to investigate the correlation between structure and properties and to explore their potential application.<sup>2</sup> Till now, the most extensively studied responsive microgels are thermosensitive poly(*N*-isopropyl acrylamide) microgels.<sup>3–6</sup>

Poly(*N*-isopropyl acrylamide) (PNIPAM) is one of the well-known thermosensitive polymers, which can have abrupt volume transition near the low critical solution temperature (LCST).<sup>7</sup> In aqueous solution, poly(*N*-isopropyl acrylamide) (PNIPAM) undergoes a reversible coil-to-globule transition to form inter- and intra-chain associations that results in an insoluble and hydrophobic aggregate above the lower critical solution temperature (LCST) around 30–34°C,<sup>8,9</sup> and the LCST could be adjusted

to 37°C by copolymerization with a more hydrophilic monomer.<sup>10</sup> When the environmental temperature is below the LCST, PNIPAM adsorbs much water and exhibits a swollen and hydrophilic state, while above the LCST, it becomes hydrophobic due to expelling of free water inside the polymer network and demonstrates abrupt volume shrinkage.<sup>7</sup> Because of their unique properties, PNIPAM microgels have numerous potential applications in various biomedical and biotechnological fields, including controlled drug delivery systems,<sup>11–15</sup> sensing,<sup>16</sup> catalysis,<sup>17</sup> and optical devices,<sup>18</sup> artificial organs,<sup>19</sup> “on-off” switches,<sup>20</sup> and so on.

Functionality of the microgels can be improved by introducing other monomers in the synthesis. Previous method of preparing pH- and temperature-sensitive microgels was generally based on a free radical emulsion copolymerization of temperature-sensitive monomers, such as *N*-isopropylacrylamide (NIPAM), and pH-sensitive monomers, such as acrylic acid (AA), methacrylic acid (MAA) and so on.<sup>21–25</sup> Compared with traditional emulsion polymerization, soap-free emulsion polymerization does not suffer from residual surfactant contamination and is easy to get narrow distribution of microgels latex, so this method has wider application prospect.<sup>26,27</sup>

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TABLE I  
Formulation and Polymerization Temperature for Preparing Poly(NIPAM-co-AA) Microgels Latex

Sample index	NIPAM (mmol)	AA (mmol)	AIBN (mmol)	KPS (mmol)	MBA (mmol)	H <sub>2</sub> O (g)	T (°C)
L-1	3.54	0	0.18	0	0.026	200	80
L-2	3.54	1.39	0.18	0	0.026	200	80
L-3	3.54	2.78	0.18	0	0.026	200	80
L-4	3.54	4.17	0.18	0	0.026	200	80
L-5	3.54	5.56	0.18	0	0.026	200	80
L-6	3.54	0	0	0.18	0.026	200	80

There are already a lot of researches on introducing different co-monomers to change the thermal response of PNIPAM microgels, and the possible affect factors of introducing co-monomers to the thermal response of PNIPAM were also discussed in some reports.<sup>8,28,29</sup> Usually, water-soluble initiator such as ammonium persulfate (APS) and potassium persulfate (KPS) are used in preparing PNIPAM microgels.<sup>8,24,28,29</sup>

In our research, we found an oil-soluble initiator was also effective to prepare PNIPAM microgels, and the obtained microgels were more smooth and stable than that using KPS as initiator. The reason may be the oil-soluble initiator can better prevent the microgels absorbing water than water-soluble initiator. In this article, 2, 2'-Azobisisobutyronitrile (AIBN) was used to prepare poly(NIPAM-co-AA) microgels with different copolymer compositions. The thermal response of the obtained microgels latex and microgels were investigated. The thermal response mechanism and the effect of AA on thermal response were deeply discussed from the perspective of hydrogen bonding interaction.

## EXPERIMENT

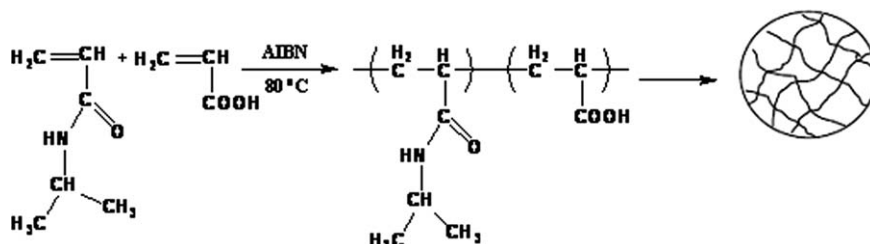
### Materials

*N*-isopropylmethacrylamide (NIPMA) (98%) was purchased from Sigma-Aldrich (Shanghai, China) and was recrystallized from hexane. 2, 2'-Azobisisobutyronitrile (isobutyronitrile; AIBN) was supplied by Kelong Chemical Reagents Factory (Chengdu, China) and was recrystallized twice from methanol. *N,N*-methylenebisacrylamide (MBA; Aldrich) (BIS) was analyt-

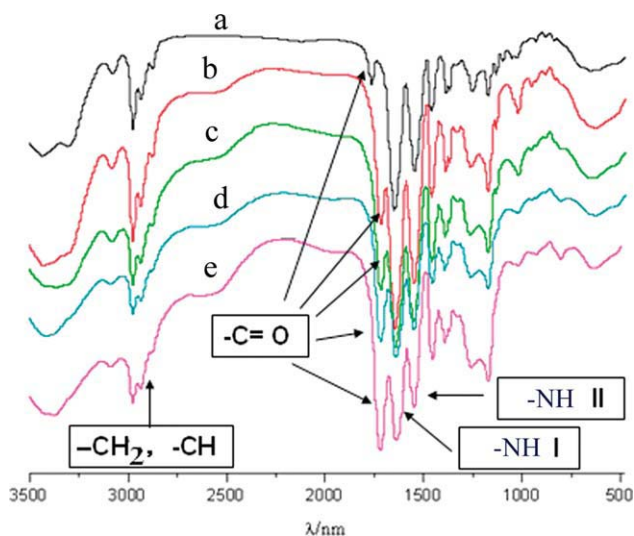
ical-reagent-grademand and supplied by Kelong Chemical Reagents Factory (Chengdu, China). Acrylic acid (AA) was obtained from Kelong Chemical Reagents Factory (Chengdu, China) and further purified by distillation under a reduced pressure before use. KPS also was purchased from Kelong Chemical Reagents Factory (Chengdu, China). Cellulose membrane tubings (CelluSepT4) with nominal molecular weight cut-off 8000–14,000 g/mol were used as membranes in microgel purification by dialysis.

### Preparation of poly(NIPAM-co-AA) microgels latex and microgels

A summary of the formulation for preparing poly(NIPAM-co-AA) microgels latex is shown in Table I. Polymerizations were carried out in a four-necked flask. In a typical synthesis, NIPAM (0.4 g, 3.54 mmol) and MBA (0.004 g, 0.026 mmol) were dissolved in distilled water (200 g) and transferred into the reaction flask, then an appropriate amount of AA (0–5.56 mmol) was added. The flask was sealed with a septum, and the solution was purged with nitrogen and stirred (400 rpm) at room temperature for 20 min. After that temperature was increased to 80°C and AIBN (0.18 mmol, 0.03 g) or KPS (0.18 mmol, 0.05 g) was added to initiate polymerization. The reaction was allowed to proceed in stirring for 4 h and then the product was cooled to room temperature, and the microgels latex was prepared. Certain of the microgels latex was purified by dialysis for 7 days against distilled water, which was refreshed daily (twice every day during the first 3 days) and the low molecular weight of



Scheme 1 The formation of the thermal responsive poly(NIPAM-co-AA) microgels prepared by soap-free emulsion polymerization using AIBN as initiator at 80°C.



**Figure 1** FTIR spectra of the homopolymer (PNIPAM) and the copolymer poly(NIPAM-*co*-AA) obtained by different mole ratios of AA : NIPAM in feed (a) 0 : 1, (b) 0.38 : 1, (c) 0.76 : 1, (d) 1.14 : 1, and (e) 1.52 : 1. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)].

homopolymer could be removed during the process. The purified microgels latex was freeze-dried and the microgels were obtained. The obtained microgels latex and microgels were stored at the room temperature for characterization.

## Measurement and characterization

### Morphology of poly(NIPAM-*co*-AA) microgels

The morphology of microgels was investigated using a scanning electron microscope (SEM: JEOL JSM-5900LV, Japan) operating at 20 kV. The original microgels latex was first heated to 80°C, and then quenched in liquid nitrogen for one day. After that the quenched microgels were freeze-dried for three days. The dried samples were coated with gold in vacuum before being viewed under SEM.

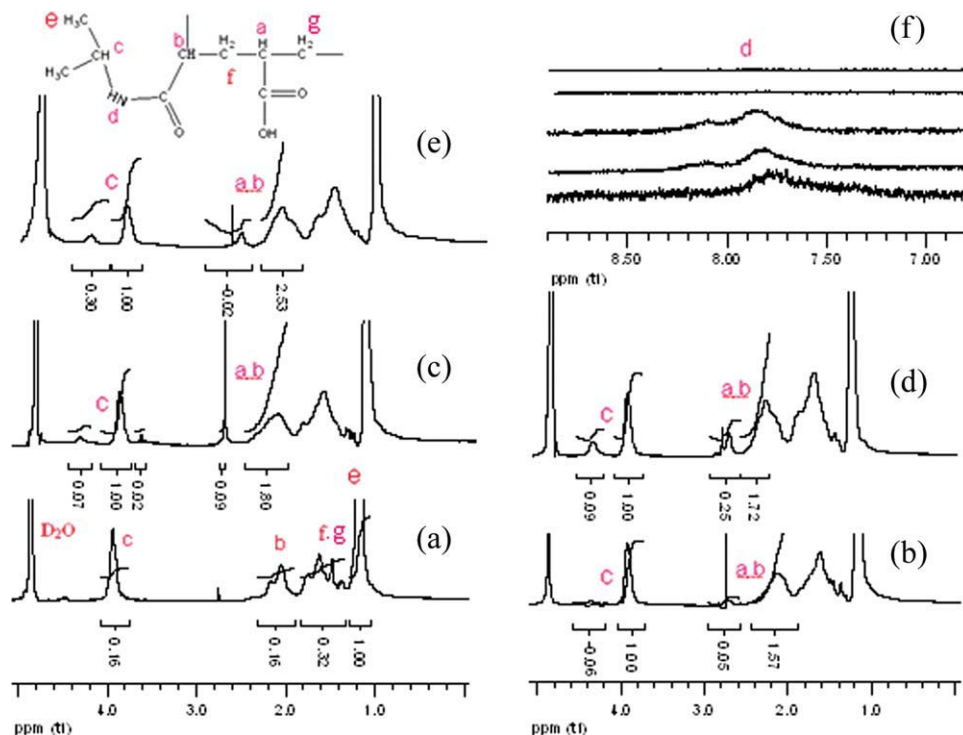
### Chemical structure of poly(NIPAM-*co*-AA) microgels

**FT-IR analyses.** FTIR measurements were carried out using purified microgels with various compositions. The samples were directly analyzed using a Fourier transform infrared spectroscope (FT-IR, Nicolet NEXUS-670) in a KBr flake.

**<sup>1</sup>H-NMR analyses.** <sup>1</sup>H-NMR spectra of the microgels were recorded with a VARIAN, 400 MHz spectrometer, and D<sub>2</sub>O was used as solvent.

### Thermal response of poly(NIPAM-*co*-AA) microgels latex and microgels

Thermal response of microgels latex was measured by UV-3010 spectrophotometer (Japan) with temperature controller equipment. The transmission of microgels latex with increasing temperature (23–49°C, 2°C



**Figure 2** <sup>1</sup>H-NMR spectra of PNIPAM and poly(NIPAM-*co*-AA) microgels with different mole ratios of AA : NIPAM in feed (a) 0 : 1, (b) 0.38 : 1, (c) 0.76 : 1, (d) 1.14 : 1, (e) 1.52 : 1, and (f) enlarged <sup>1</sup>H-NMR spectra of -NH. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)].

**TABLE II**  
Integral Area of  $\delta_1$ -CH: 2.0 ppm–3.0 ppm and  $\delta_2$ -CH: 3.5 ppm–4.8 ppm of Poly(NIPAM-co-AA) Microgels (M-1–M-5) and the Mole Ratios of NIPAM : AA in Copolymer

Chemical shift/ppm	Samples index				
	Integral area				
	(1)	(2)	(3)	(4)	(5)
$\delta_1$ -CH: 2.0–3.0	1.07	1.62	1.89	1.97	2.55
$\delta_2$ -CH: 3.5–4.8	1.07	1.06	1.09	1.09	1.30
Mole ratio of AA : NIPAM in feed	0 : 1	0.39 : 1	0.78 : 1	1.18 : 1	1.57 : 1
Mole ratio of AA : NIPAM in copolymer	0 : 1	0.53 : 1	0.65 : 1	0.81 : 1	0.95 : 1

interval) was directly measured on the UV-vis spectrophotometer in the range of 190–900 nm. At each temperature, the samples were stabilized for 10 min before measurements.

The mean diameter of microgels at various temperatures (20–50°C) were measured by dynamic light scattering (DLS) techniques through using the instrument of Bookhaven Instruments (BI-200SM goniometer, BI-9000AT digital correlator) equipped

with an argon laser at wavelength of 532 nm. Scattering was measured at 90° angle and the obtained time correlation functions were analyzed by CONTIN Laplace-inversion program. The polymer concentrations in the samples were 0.4 mg/mL obtained by diluting the dialyzed particle dispersions with distilled water. All samples were filtered through 0.45  $\mu\text{m}$  disposable filters (Whatman ANOTOP) before used.

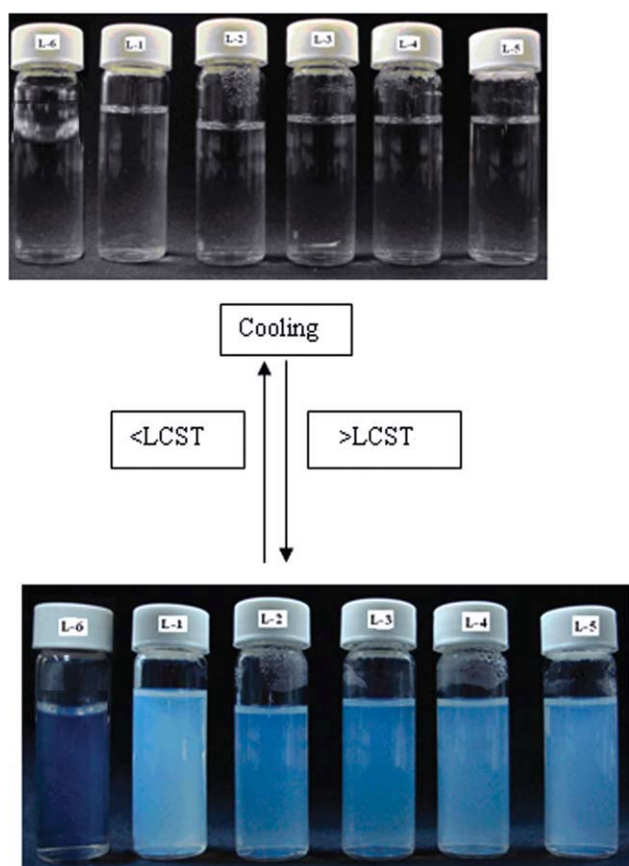
## RESULTS AND DISCUSSION

Thermal responsive poly(NIPAM-co-AA) microgels were successfully prepared through soap-free emulsion polymerization technique using AIBN as initiator. The formation scheme of the thermal response microgels is illustrated in Scheme 1.

### Copolymer compositions of poly(NIPAM-co-AA) microgels

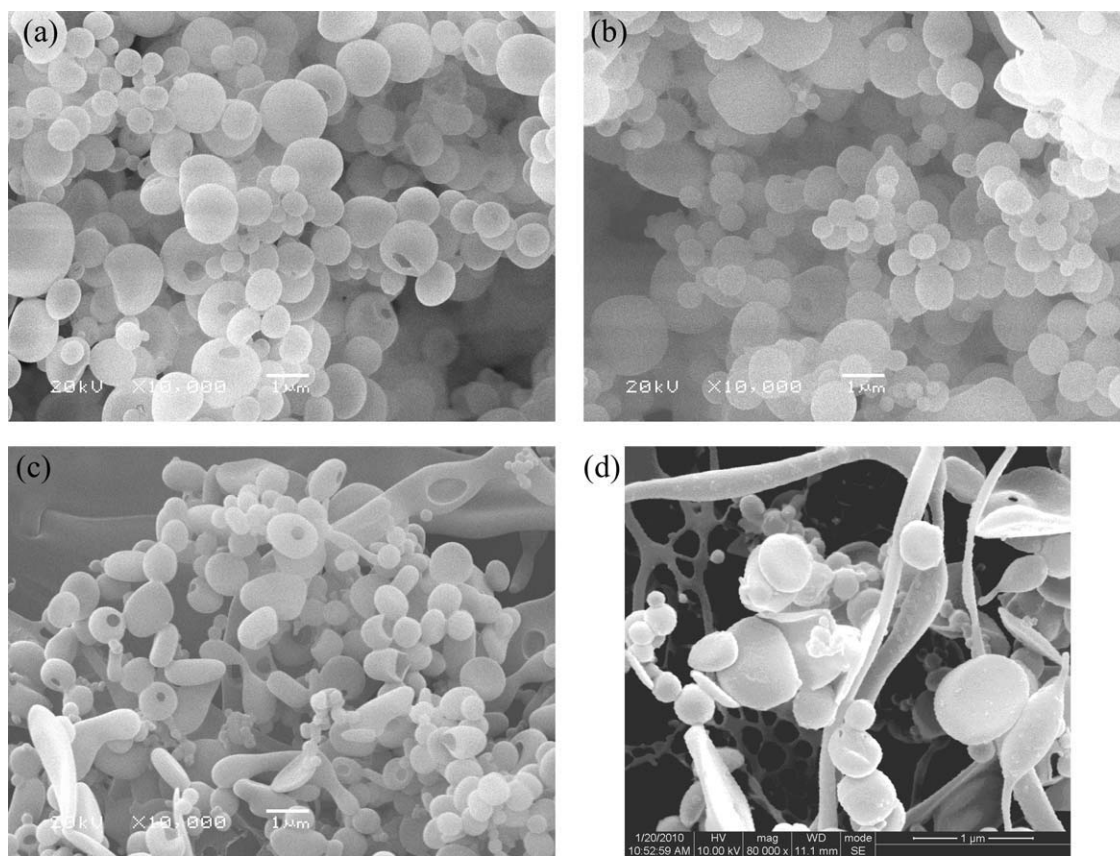
Figure 1 shows the infrared spectra of the homopolymer (PNIPAM, curve 1) and the copolymer (poly(NIPAM-co-AA), curve 2–curve 5). The infrared spectrum of PNIPAM shows that the carbonyl ( $\text{C}=\text{O}$ ) stretching vibration appears as strong absorption band at  $1764.2\text{ cm}^{-1}$  (curve 1). Amide I ( $\text{NH I}$ ) and Amide II ( $\text{NH II}$ ) peaks appear at  $1649$  and  $1546.8\text{ cm}^{-1}$ , respectively. When AA was introduced into polymer chain, the carbonyl ( $\text{C}=\text{O}$ ) stretching vibrations of poly(NIPAM-co-AA) copolymer move to  $1716\text{--}1719\text{ cm}^{-1}$  (curve 2–curve 5). With increasing of AA, the absorption of amide I moves to longer wavelength and the amide II absorption moves to shorter wavelength. The bands appearing at  $2973\text{--}2975\text{ cm}^{-1}$  can be attributed to stretching and bending vibrations of  $\text{CH}_2$  and  $\text{CH}$  groups, respectively.

As shown in Figure 2, the structure of the microgel was further supported by  $^1\text{H-NMR}$  ( $\text{D}_2\text{O}$ , 400 MHz). There are different chemical environments of  $\text{CH}$  groups shown in Figure 2. One is the  $\text{CH}$  backbone of polymer chain which links to carbonyl (a,  $\text{CH}$  comes from AA; b,  $\text{CH}$  comes from



**Figure 3** Appearance changes of poly(NIPAM-co-AA) microgels latex at the temperature below and above LCST, the numbers are corresponding to which of Table I, L-1–L-5 present microgels latex using AIBN as initiator, and L-6 presents PNIPAM microgels latex using KPS as initiator. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 4** SEM photographs of PNIPAM ((a), (d)) and poly(NIPAM-co-AA) ((b), (c)) molar ratio of AA : NIPAM in copolymer (b) 0.53 : 1, (c) 0.95 : 1, (a)–(c) using AIBN as initiator, (d) using KPS as initiator.

NIPAM), the other is  $-\text{CH}$  lone pair proton of isopropyl group (c,  $-\text{CH}$  comes from NIPAM only). Figure 2(a) indicates the structure information of PNIPAM:  $\delta$  3.938 ppm (c,  $-\text{CH}$  lone pair proton of isopropyl group),  $\delta$  2.052–2.763 ppm (b,  $-\text{CH}$  backbone of polymer chain which links to carbonyl),  $\delta$  1.187–1.956 ppm (e, f,  $-\text{CH}_2$ ,  $-\text{CH}_3$  of isopropyl group),  $\delta$  7.752 ppm (d,  $-\text{NH}$  of NIPAM and MBA). The mole ratio of signal integral area of the two kinds of  $-\text{CH}$  (b:  $\delta$  2.052–2.763 ppm and c:  $\delta$  3.938 ppm) is 1 : 1. There are not obvious new signals appear in the  $^1\text{H-NMR}$  spectrum of the copolymer [Fig. 2(b–d)], the reason is the signals come from AA are overlapped by NIPAM structure. But the mole ratio of the two kinds of  $-\text{CH}$  ((a, b): c) is not 1 : 1 any more in the  $^1\text{H-NMR}$  spectrum of copolymer. The reason is interpreted as follows. In the copolymer structure only the  $-\text{CH}$  (c) leads to a signal peak at the range of  $\delta$  3.8–4.0 ppm, and the mole concentration of  $-\text{CH}$  (c) is equal to the mole concentration of NIPAM. But the signals of  $-\text{CH}$  (a, b), coming from NIPAM and AA, are overlapped by each other because of the similar chemical environment. We already know that the mole ratio of signal integral area of  $-\text{CH}$  (b):  $-\text{CH}$  (c) is 1 : 1. So the result of signal integral area of  $-\text{CH}$  (a, b) deducts

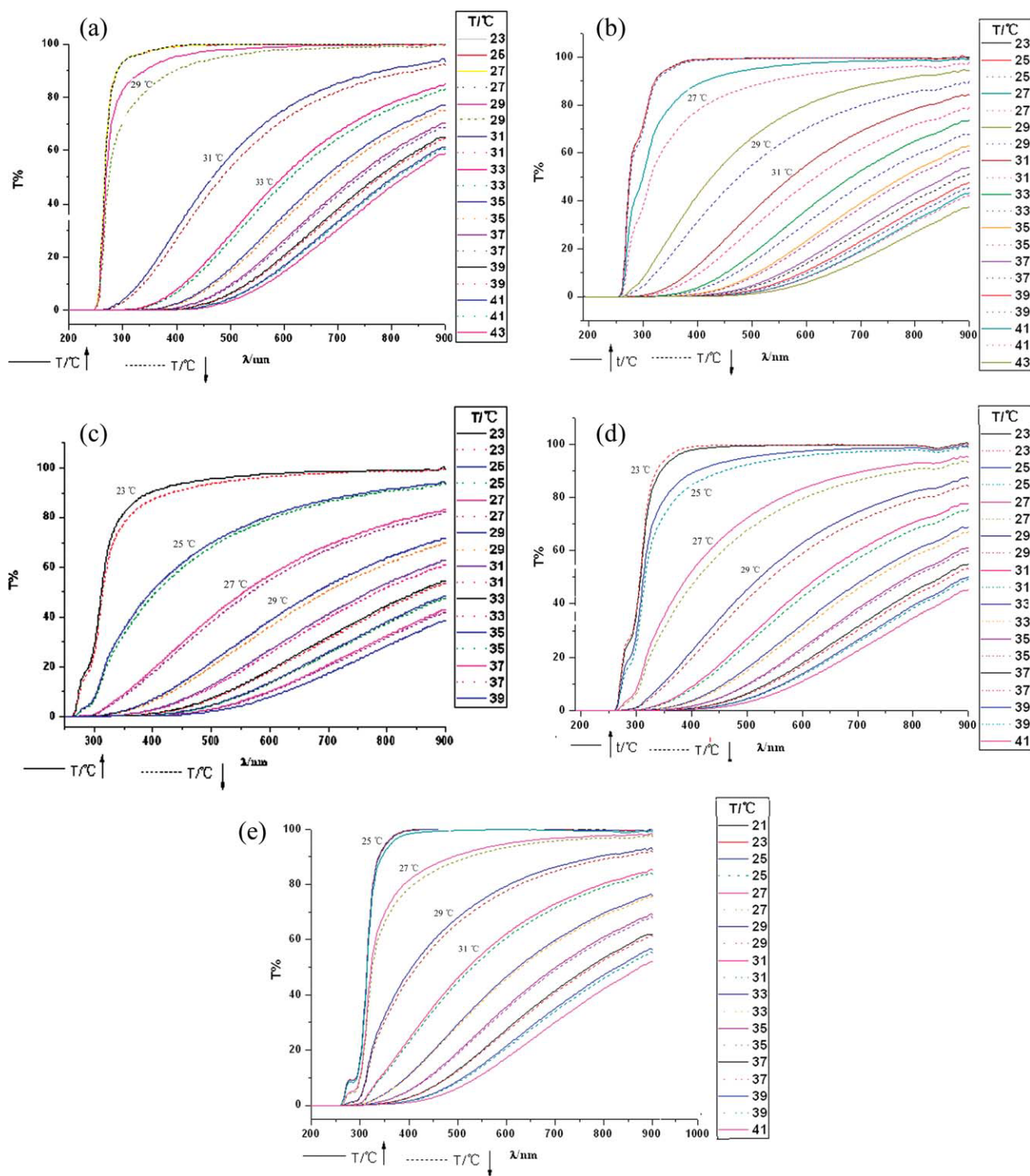
the signal integral area of  $-\text{CH}$  (c) is the signal integral area of  $-\text{CH}$  (a) only from AA unit. Finally the mole ratio of NIPAM: AA units in copolymer can be obtained.

From the analysis above, the mole ratio of NIPAM : AA units in copolymer can be formulated by

$$M_{\text{AA}} / M_{\text{NIPAM}} = (S_{\delta 1} - S_{\delta 2}) / S_{\delta 2}$$

$M_{\text{AA}}$  and  $M_{\text{NIPAM}}$  are the mole of AA and NIPAM units respectively in the copolymer;  $S_{\delta 1}$  is the integral area of  $-\text{CH}$  backbone of polymer chain which links to carbonyl (a, b);  $S_{\delta 2}$  is the integral area of  $-\text{CH}$  lone pair proton of isopropyl group (c). So from the result of  $^1\text{H-NMR}$ , the mole ratio of NIPAM : AA units in copolymer can be calculated and the results are presented in Table II.

With increasing of AA in feed, the mole percent of AA units in the copolymer structure increases, but it is not the same as that in feed. Actually the mole percent of AA units of copolymer is lower than that in feed AA. The possible reason may be that with increasing of AA in feed, the possibility of homopolymerization of AA increases. The PAA was removed before  $^1\text{H-NMR}$  test, so the calculated AA content in copolymer is lower than that in feed.

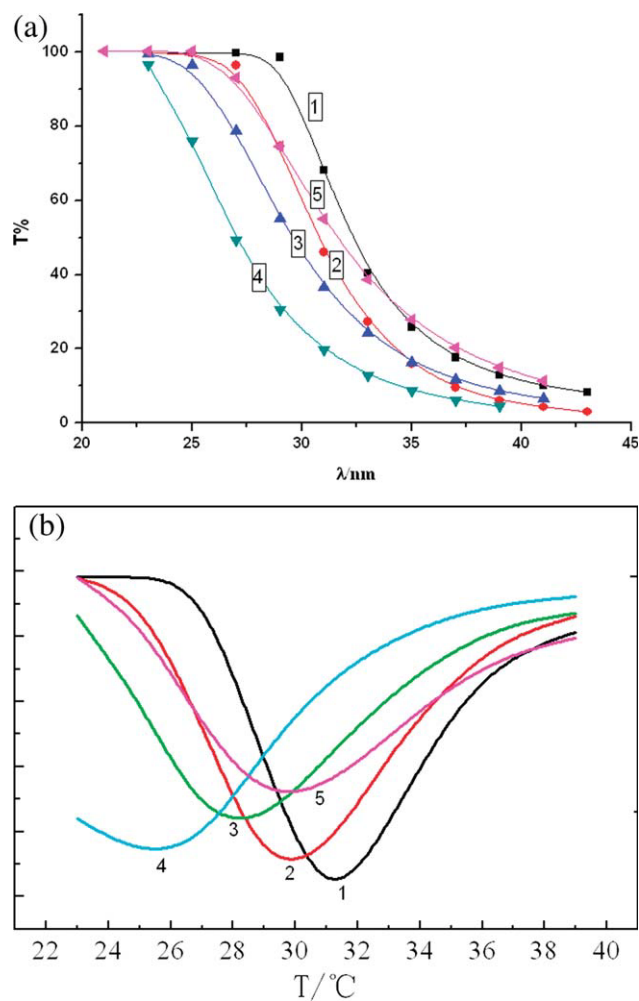


**Figure 5** Transmission change curves of poly(NIPAM-co-AA) microgels latex with increasing and decreasing temperature. The mole ratio of AA : NIPAM in feed (a) 0 : 1, (b) 0.38 : 1, (c) 0.76 : 1, (d) 1.14 : 1, and (e) 1.52 : 1 and in copolymer (a) 0 : 1, (b) 0.53 : 1, (c) 0.65 : 1, (d) 0.81 : 1, and (e) 0.95 : 1. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com)].

**Morphology of poly(NIPAM-co-AA) microgels latex**

Figure 3 shows the appearance changes of poly(NIPAM-co-AA) microgels latex with different composition above and below LCST. It can be observed that

when the temperature changes from below LCST to above LCST, the transmittance of microgels latex decreases and all microgels latex change from colorless transparent to bluing latex. The poly(NIPAM-co-AA) microgels latex L-1-L-5 all present bigger



**Figure 6** (a) Transmission change curves of poly(NIPAM-*co*-AA) microgels latex with increasing temperature at 552 nm and (b) the differential curves. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

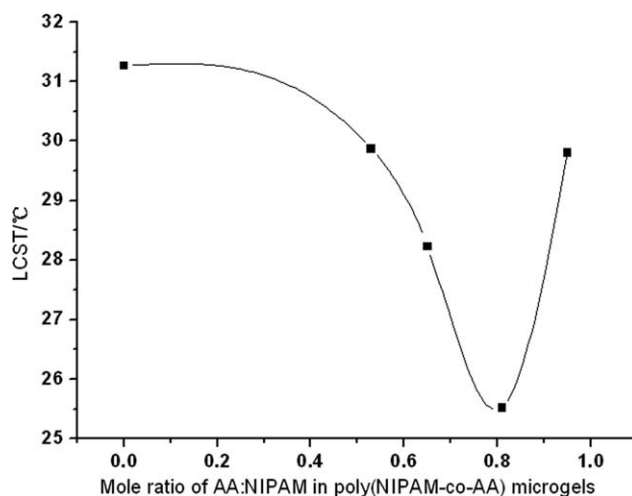
transmittance changes than L-6, which means that the AIBN-initiated microgels latex has more obvious phase transition than KPS-initiated one, so the AIBN-initiated microgels latex present more obvious thermal response than KPS-initiated microgels latex. Above LCST, the transmittance of L-1-L-5 increases with the increase of AA content. The reason is the increasing hydrophilic  $-\text{COOH}$  groups intend to enrich at surface of microgels and absorb water (Fig. 3).

Figure 4(a-d) are the SEM images of poly(NIPAM-*co*-AA) microgels. The AIBN-initiated PNIPAM microgels [Fig. 4(a)] are regular and smooth but not homogeneous and parts of the big microgels present an obvious hollow structure. The reason is that some water was contained in microgels during the quenching process by nitrogen from high temperature, and the water was cleared during the freeze-drying process, and finally led to the hollow structure of microgels. The wide distribution of PNIPAM

microgels can be attributed to the slower decomposition rate of AIBN. Figure 4(b,c) show the morphology of AIBN-initiated poly(NIPAM-*co*-AA) microgels with different composition. The two SEM images also indicate that the microgels become more irregular and easier to be distorted with increasing AA. The reason is the hydrophilic AA units are easy to absorb water and distort. Figure 4(d) is the SEM image of KPS-initiated PNIPAM microgels, these microgels are easier to absorb water and distort than other AIBN-initiated microgels. The possible reason is that the persulfate anion radical residues (residue of KPS) distribute at surface of microgels and results to the microgels are easy to absorb water and distort. Oppositely, residues of oil-soluble initiator AIBN can effectively prevent the absorption procedure and better stabilize the microgels.

#### Thermal response of AIBN-initiated poly(NIPAM-*co*-AA) microgels latex and poly(NIPAM-*co*-AA) microgels

Figure 5 indicates the transmittance change of AIBN-initiated poly(NIPAM-*co*-AA) microgels latex with the change of temperature. The series of solid and dotted lines are the transmittance curves of microgels latex in the heating and cooling process, respectively. Figure 5(a) indicates that the PNIPAM microgels latex has an obvious phase transition at the temperature range of 29–33°C. The solid curves and the dotted lines are almost coincident which indicates the thermal response time effectiveness of PNIPAM microgels latex is good. Further, from Figure 5 we get the phase transition temperature of poly(NIPAM-*co*-AA) microgels latex (2)–(5) are at range of 27–31°C, 25–29°C, 25–29°C, 27–31°C respectively. In order to determine the LCST, we draw the transmission change curves of poly(NIPAM-*co*-AA)



**Figure 7** LCST of poly(NIPAM-*co*-AA) microgels with different mole ratio of AA : NIPAM.



**TABLE III**  
**The Phase Transition of Poly(NIPAM-co-AA) Microgels Latex and the Poly(NIPAM-co-AA) Microgels**

Latex	L-1	L-2	L-3	L-4	L-5
Mole ratio of AA: NIPAM					
In feed	0 : 1	0.38 : 1	0.76 : 1	1.14 : 1	1.52 : 1
In poly(NIPAM-co-AA)	0 : 1	0.53 : 1	0.65 : 1	0.81 : 1	0.95 : 1
Temperature range of main phase transition taking place (°C)	29–33	27–31	25–29	25–29	27–31
$\Delta T$ of 552 nm in the temperature range of main phase transition taking place in heating process	59.4	50.5	47.4	41.3	25.6
LCST (°C)	31.27	29.87	28.22	25.52	29.80
Microgels	M-1	M-2	M-3	M-4	M-5
Mole ratio of AA : NIPAM in polymer	0 : 1	0.53 : 1	0.65 : 1	0.81 : 1	0.95 : 1
Phase transition temperature (°C)	25–29	29–33	35–37	23–25	27–29

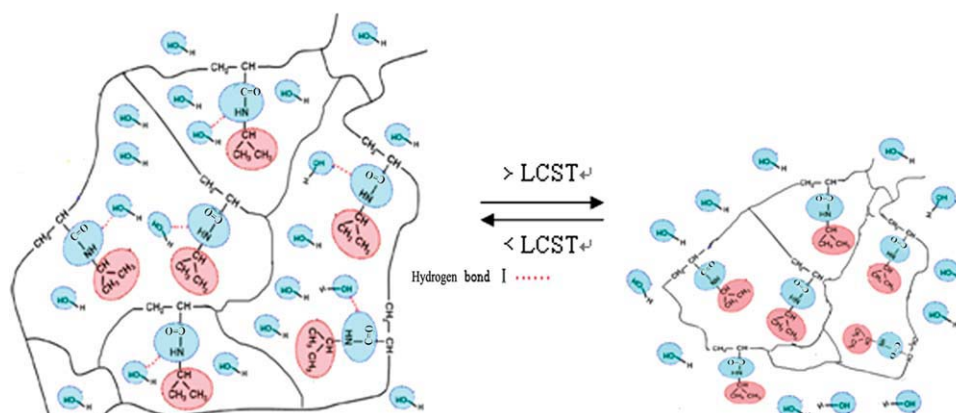
microgels latex with increasing temperature at 552 nm [Fig. 6(a)] and then made out the differential curves [Fig. 6(b)]. The inflection point temperature of differential curve is the LCST. With increasing of AA, the LCST of microgels latex first decreases and then increases (Fig. 7).

We compared the transmittance change degree ( $\Delta T$ ) of poly(NIPAM-co-AA) microgels latex at the phase transition temperature range at 552 nm, which can characterize the thermal sensitivity of poly(NIPAM-co-AA) microgels latex. The larger  $\Delta T$  means better thermal sensitivity (Table III). Table III shows that the  $\Delta T$  of PNIPAM microgels latex (L-1) is the largest which indicates that the PNIPAM microgels latex has better thermal sensitivity than other microgels latex. With increasing of AA in feed, the thermal sensitivity of the obtained microgels latex decreases. The reason is that with increasing mole percent of AA, the mole percent of thermal-responsive groups of NIPAM decreases in polymer chain, resulting in the decrease of thermal sensitivity.

From Figure 7, we can observe that with AA increasing, the LCST of microgels latex first decreases and then increases. In order to interpret the phenomenon clearly, we introduce two schematic diagrams (Schemes 2 and 3). The forming and

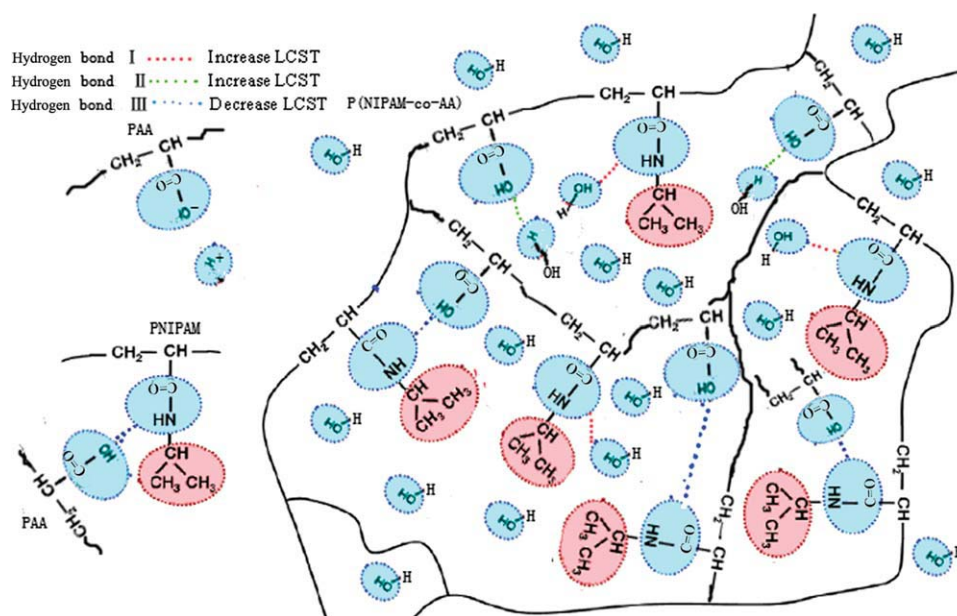
destroying of the hydrogen bonds between H<sub>2</sub>O molecules and –NH groups of NIPAM are the essential causes of thermal response of PNIPAM microgels. When temperature is below LCST, hydrogen bonds form between H<sub>2</sub>O molecules and –NH groups (Hydrogen bond I). Polymer chains are fully swelling to present water soluble at this situation. Oppositely, when temperature is above LCST, the hydrogen bonds are destroyed. Polymer chains become curling, and the water molecules are extruded from polymer chains because of the hydrophobicity of isopropyl groups. Finally, the polymers change from water soluble to oil soluble, and the phase transition happened.

In the poly(NIPAM-co-AA) microgels latex, there are not only poly(NIPAM-co-AA) copolymers but also homopolymers of PAA and PNIPAM. There are three kinds of hydrogen bonds, the hydrogen bonds I between –NH groups and H<sub>2</sub>O molecules, hydrogen bonds II between the –COOH groups and H<sub>2</sub>O molecules, and hydrogen bonds III between the –NH groups and –COOH groups (Scheme 3). Increasing of hydrogen bonds I and II would increase the phase transition temperature, but increasing of hydrogen bonds III would decrease that. When AA content is lower, the microgels is at



**Scheme 2** Schematic illustration of volume phase transition of PNIPAM microgels in aqueous solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com)].



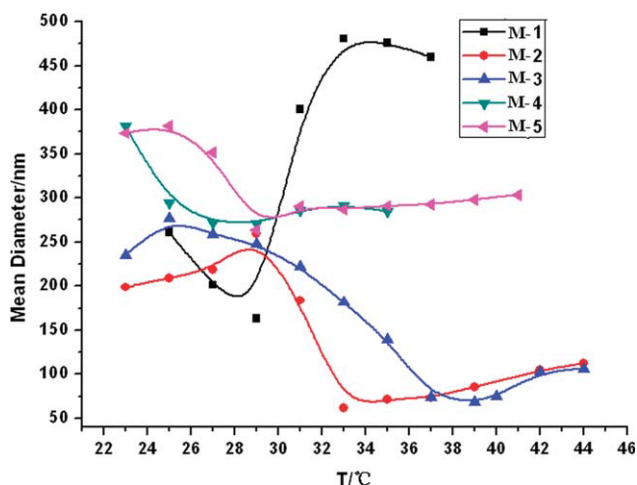


**Scheme 3** The hydrogen bonding interaction in poly (NIPAM-*co*-AA) microgels latex. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)].

a higher pH because of the existence of more  $-\text{NH}$  groups, and in this situation the  $-\text{COOH}$  groups are easy to be ionized to  $-\text{COO}^-$ , so there are less hydrogen bonds III in the microgels latex. With increasing of AA in feed, the content of PAA increases, and the pH decreases, which results in the decreases in hydrolysis degree of  $-\text{COOH}$ , so the number of hydrogen bonds III between the  $-\text{NH}$  groups and  $-\text{COOH}$  groups increases, finally the LCST of microgels latex decreases. On the other hand, with increasing AA, the number of hydrogen bonds II between  $-\text{COOH}$  and  $\text{H}_2\text{O}$  increases and LCST would increase. So with increasing of AA in feed, the two factors interact, and finally cause the LCST of microgels latex first decreases (L-1-L-4) and then increases (L-5).

Mean diameter changes of the poly(NIPAM-*co*-AA) microgels with increasing temperature were determined through DLS techniques. The samples were prepared by diluting purified and frozen-drying microgels to 0.05 g/L. From Figure 8, we can observe that the mean diameter of poly(NIPAM-*co*-AA) microgels (M-1-M-5) first decreases and then increases. The possible reason is that with increasing temperature, the polymer chains first become curling and shrinking, the mean diameter of microgels decreases. But the repellency between initiator AIBN fragment and  $-\text{NH}$  is always exist, so when polymer chains shrink to a certain extent, the repelling force would play a major role and the mean diameter of microgels increases. Figure 8 indicates that when the temperature is above  $29^\circ\text{C}$ , the mean diameter of PNIPAM microgels increases sharply, which means the effect of the repellency between

AIBN fragment and  $-\text{NH}$  groups is large to the mean diameter of PNIPAM microgels (1). When AA is introduced, the AA units can obstruct AIBN fragment and  $-\text{NH}$ , and weaken the repellency between them. So the more percent of AA means the less effect of the repellency, that's the explanation for why the mean diameter increase becomes less with increasing of AA. Figure 8 also shows that the poly (NIPAM-*co*-AA) microgels (M-2) have better thermal response sensitivity than other poly(NIPAM-*co*-AA) microgels (M-3, M-4, M-5). Same as the thermal response sensitivity change of microgels latex, with



**Figure 8** Mean diameter change curves of poly(NIPAM-*co*-AA) microgels with increasing temperature. The mole ratio of AA: NIPAM units in copolymer (M-1) 0 : 1, (M-2) 0.53 : 1, (M-3) 0.65 : 1, (M-4) 0.81 : 1, and (M-5) 0.95 : 1. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)].

increasing of mole percent of AA units, the thermal response sensitivity of microgels decreases.

It can be observed from Table III that with increasing AA units, the phase transition temperature of poly(NIPAM-co-AA) microgels first increases and then decreases. When AA content is lower (AA : NIPAM < 0.65 : 1), there are mainly exist hydrogen bonds I and hydrogen bonds II in microgels solution. First, the PAA and PNIPAM with lower molecular weight, which are the main sources of forming hydrogen bonds III, have been purified before test; Second, there are not enough AA units in polymer chains, so it is hard to form intermolecular hydrogen bonds III; These two factors cause that the phase transition temperature of microgels increase when increasing AA. Actually the result is the same as most work reported,<sup>1,2,21-25</sup> the phase transition temperature of poly(NIPAM-co-AA) increases rapidly with increasing AA, because AA is intrinsically more hydrophilic than NIPAM. But when the AA content increases to a certain range, there are more AA units in polymer chains, the possibility of forming intermolecular hydrogen bonds III increases. When the influence of hydrogen bonds III is greater than hydrogen bands I and II, the phase transition temperature decreases.

### CONCLUSION

AIBN-initiated poly(NIPAM-co-AA) microgels latex with different AA content were prepared through soap-free emulsion polymerization. With increasing of AA in feed, the mole percent of AA in copolymer structure increases, but the mole ratio of AA : NIPAM in copolymer structure is lower than that in feed. SEM photographs indicate the AIBN-initiated microgels are more smooth and stable than the KPS-initiated microgels. With the mole ratio of AA : NIPAM increasing from 0 : 1 to 1.52 : 1 in feed, the thermal response sensitivity of microgels latex decreases, and the LCST of microgels latex first decreases and then increases. Still, with increasing of AA in poly(NIPAM-co-AA) microgels, the LCST of microgels first increases and then decreases. The reasons of all the changes of LCST of microgel latex

and microgels can be attributed to the hydrogen bonding interaction as we have interpreted.

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