Journal of Applied Polymer Science

Effects of End Groups on the Thermal Response of Poly(*N*-isopropylacrylamide) Microgels

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ABSTRACT: Poly(*N*-isopropylacrylamide) (PNIPAM) microgels were prepared through soap-free emulsion polymerization using 2, 2′-azobisobutyronitrile and potassium persulfate as initiator respectively. The thermal response of microgels was researched by measuring the transmittance and the hydrodynamic diameter of the microgels at different temperatures. The result shows that the different structure of the end groups of polymer that come from residues of initiator result in the different thermal response of PNIPAM microgels. The LCST (lower critical solution temperature) of AIBN-initiator microgels is 5°C lower than that of the KPS-initiator microgels, whereas the AIBN-initiated PNIPAM microgels have better thermal response sensitivity. The scanning electron microscope characterization shows that the morphology of AIBN-initiated PNIPAM microgels is more regular than that of KPS-initiated. Furthermore, the T_g of the microgels was measured by differential scanning calorimeter and the result indicates that the end groups influences the T_g of microgels severely. This work demonstrated that the hydrophobic end group coming from initiators can decreases the LCST of PNIPAM microgels and increases the thermal response sensitivity, which providing a newly simple but effective method to regulate the thermal response of PNIPAM microgels. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 1164–1171, 2013

KEYWORDS: colloids; functionalization of polymers; microgels; phase behavior

Received 9 December 2012; accepted 18 March 2013; Published online 17 April 2013
DOI: 10.1002/app.39291

INTRODUCTION

Temperature sensitive materials have attracted significant interest of many researchers because of their ability of intelligent response to external temperature changes. Perhaps the most extensively investigated class of responsive polymers are temperature-sensitive poly(*N*-isopropylacrylamide) (PNIPAM), which exhibits a phase transition named lower critical solution temperature (LCST) around 32–34°C.[1–3] In aqueous solution, PNIPAM undergoes a reversible phase transition caused by the coil-to-globule transition close to its LCST. When the environmental temperature is below the LCST, PNIPAM adsorbs much water and exhibits a swollen and hydrophilic state, whereas above the LCST; it becomes hydrophobic because of expelling free water inside the polymer network and demonstrates abrupt volume shrinkage.[4,5] Because of their unique properties, PNIPAM microgels have numerous potential applications in various biomedical and biotechnological fields, including controlled drug delivery systems,[6–10] sensing,[11] catalysis,[12] optical devices,[13] artificial organs,[14] "on–off" switches,[15] and so on.

The LCST is important to thermal responsive materials, because it determines the application fields of the material. As the first thermal-sensitive microgel synthesized from *N*-isopropylacrylamide (NIPAM) and *N, N*-methylene-bis-acrylamide (MBA) was reported in 1986,[16] how to adjust the LCST and the thermal response sensitivity of the materials is always the focus of research. According to the reported work, there are mainly three methods to adjust the LCST of PNIPAM microgels. They are introducing the secondary copolymerization monomer,[17–24] modifying the end group of polymer chain,[25,26] and adding additive, respectively.[27–30] But these methods have their own fault. The former two methods both modify the polymer structure, the first one usually decreases the thermal sensitivity and widens the phase transition temperature range of microgels and the second method usually uses the organic solution and chain transfer agent in preparation process, which are expensive and not environmental protection, still, the preparation process is complicated. The microgels prepared through the third method usually inapplicable to some field that needs purified microgels. The question comes out that is how to modulate the LCST of PNIPAM microgels more simply and more effectively? At present, the water-soluble initiator such as ammonium persulfate (APS) and potassium persulfate (KPS) is mostly used to prepare the purified thermal response PNIPAM through soap-free emulsion polymerization[16,31–34]; the prepared polymers all have hydrophilic end groups, which possibly increase the LCST of microgels.[35,36] There is less work about using the oil-soluble initiator to prepare the thermal response material through

Table I. Formulation Temperature and Result for Preparing PNIPAM Microgels and Polymers

Sample index	NIPAM (mmol)	AIBN (mmol)	KPS (mmol)	MBA (mmol)	H_2O (g)	T (°C)	Result
L_p-0	1.77	0.18	0	0	200	75	No reaction
L_p-1	2.67	0.18	0	0	200	75	Stable latex
L_p-2	3.54	0.18	0	0	200	75	Stable latex
L_M-2	3.54	0.18	0	0.026	200	75	Stable latex
L_p-3	4.43	0.18	0	0	200	75	Stable latex
L_p-4	5.31	0.18	0	0	200	75	Unstable
L_p-5	3.54	0	0.18	0	200	75	Stable latex
L_M-5	3.54	0	0.18	0.026	200	75	Stable latex

soap-free emulsion polymerization. But according to our research,[5] using oil-initiator in soap-free emulsion polymerization can prepare the thermal response microspheres, which have better performance compared to the KPS-initiated PNIPAM microgels, it indicates that the hydrophobic end groups come from the initiators may change the thermal response of PNIPAM microgels. In other words, the polymer structure can be changed just through changing the initiator type, further to achieve the purpose of regulation and control of the property of functional microspheres and to expand the preparation method of the environmental response materials.

In our work, we prepared thermal response PNIPAM microgels microspheres through (soap-free) emulsion polymerization based on oil-initiator, and compared to the PNIPAM microgels based on KPS water-soluble initiator. The effect of initiator on the property of PNIPAM microgels was deeply discussed.

EXPERIMENTAL

Materials

NIPAM (98%) was purchased from Sigma-Aldrich (Shanghai, China) and was recrystallized from hexane. 2, 2′-azobisobutyronitrile (AIBN) was supplied by Kelong Chemical Reagents Factory (Chengdu, China) and was recrystallized twice from methanol. MBA(Aldrich) (BIS) was analytical-reagent-grade and supplied by Kelong Chemical Reagents Factory (Chengdu, China). KPS was purchased from Kelong Chemical Reagents Factory (AR, 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.

Synthesis of PNIPAM Microgels

Polymerizations were carried out in a four-necked flask. In a typical synthesis (L_M-2, L_M-5 in Table I) 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. 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 75°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 by stirring for 4 h and then the product was cooled to room temperature, at last, the PNIPAM latex containing PNIPAM microgels was obtained. The microgels were purified by dialysis for 7 days against distilled water, which was refreshed daily (twice every day during the first 3 days).The purified microgels were freeze-dried and then the microgels were obtained. The synthesis formulation of PNIPAM is shown in Table I and the schematic graph is shown in Scheme 1.

Chemical Structure of PNIPAM Microgels

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

^{1}H-NMR Analyses. ^{1}HNMR spectra of the microgels were recorded with a VARIAN, 400 MHz spectrometer, and D_2O was used as solvent.

Thermal Response of PNIPAM Microgels

Thermal response of PNIPAM microgels was investigated using UV-3010 spectrophometer (Hitachi, Japan) with temperature control equipment. The transmittance of the microgels aqueous solution was directly measured on the spectrophometer in the wavelength range 190–900 nm and the transmittance of the two kinds of PNIPAM microgels at 552 nm was compared from 20°C to 50°C (2°C interval). At each testing temperature, the microgels sample was stabilized for 10 min before being measured.

The thermal response of PNIPAM microgels was characterized by liquid differential scanning calorimetry (DSC) also. The purified PNIPAM microgels were diluted to 2 mg/mL and then characterized by DSC-204 (German, Netzsch). The temperature range from 10°C to 80°C, the rate of temperature increasing is 5°C/min, nitrogen-cooling atmosphere (50 mL/min).

The thermal response of PNIPAM microgels was further tested by detecting the hydrodynamic diameter of the microgels in latex at different temperatures with DLS technique. The mean diameter of microgels at various temperatures (20–50°C, 2°C interval) was measured using the instrument of Brookhaven Instruments (BI-200SM goniometer, BI-9000AT digital correlator) equipped with an argon laser at a wavelength of 532 nm. Scattering was measured at 90° angle. All testing microgels samples were filtered through 0.45 μm disposable filters (Whatman ANOTOP) before used. The concentration of the microgel solutions is 0.05 g/L

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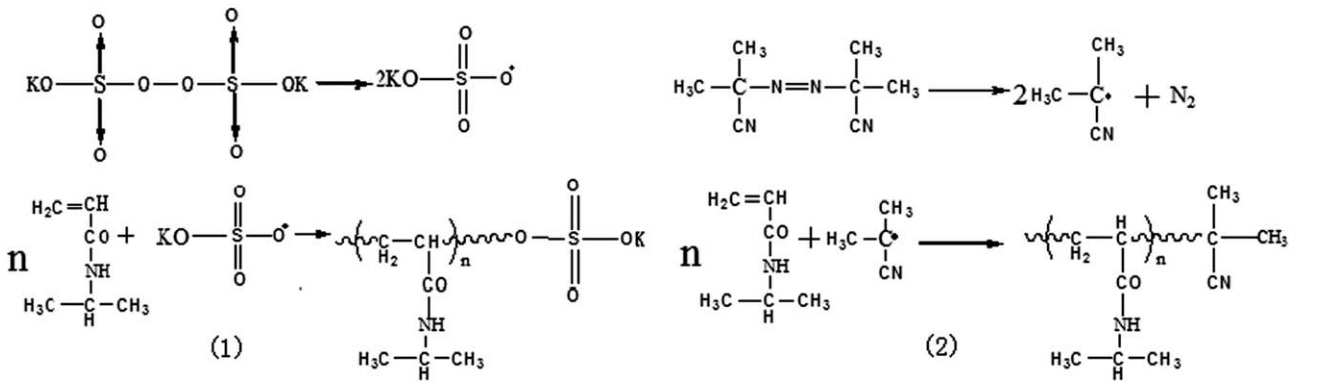


Scheme 1. Synthesis of PNIPAM containing different end groups by soap-free emulsion polymerization using (1) KPS and (2) AIBN as initiators, respectively.

Morphology of PNIPAM Microgels

The morphology of microgels was investigated using a scanning electron microscope (SEM: JEOL JSM-5900LV, Japan) operating at 20 kV. The original latex containing microgels were first heated to 75°C, then quenched in liquid nitrogen for one day. After that, the quenched samples were freeze-dried for three days and the samples for SEM were finally prepared. The dried samples were coated with gold in vacuum before being viewed under SEM.

Molecular Weight and Molecular Weight Distribution of PNIPAM

The gel permeation chromatographic (GPC) analysis of the polymer samples was done on an Agilent 1100 Series high performance liquid chromatograph, equipped with an Agilent PLgel column using THF (Fisher, HPLC grade) as eluent at a flow rate of 1 mL/min. The number (M_n) and weight (M_w) average molecular weights of the PNIPAM were determined with Polyethylene Glycol standards purchased from Agilent.

Elementary Analysis of Surface of PNIPAM Microgels

Surface compositions of the PNIPAM microgels were examined by X-ray photoelectron spectrometer (XPS) of KRATOS Instrument with Mg Kα source (1253.6 eV) at 10 kV and 7 mA. High resolutions scans with a good signal ratio were obtained in C1s, N1s, O1s, and S^2p. All the binding energies were references to the C1s peak at 284.8 eV of the surface adventitious carbon.

Thermal Analysis of PNIPAM Microgels

The glass transition temperature (T_g) of purified PNIPAM microgels was characterized by DSC-204 (German-Netzsch). The temperature range from 10°C to 200°C, the rate of temperature increasing is 10°C/min, nitrogen-cooling atmosphere (50 mL/min).

RESULTS AND DISCUSSION

Chemical Structure of PNIPAM Microgels

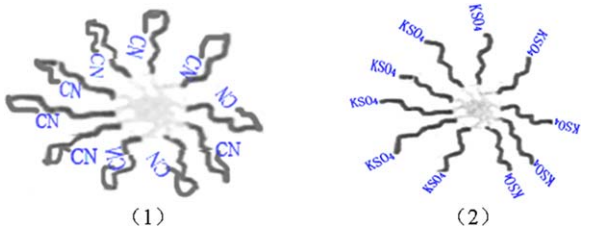
The chemical structure of PNIPAM microgels based on different initiators has been characterized by FT-IR [Figure 1(1)] and ^{1}-HNMR [Figure 1(2)]. Figure 1(1) shows the infrared spectra of the PNIPAM microgels based on different initiators. The infrared spectrum of PNIPAM shows that the carbonyl (–C=O) stretching vibration appears as strong absorption band at 1764.2 cm^{-1}. Amide I (–NH I) and Amide II (–NH II) peaks appear at 1649 and 1546.8 cm^{-1}, respectively. The bands appearing at 2973–2975 cm^{-1} can be attributed to stretching and bending vibrations of $–CH_2$ and –CH groups, respectively.

Figure 1(2) indicates the structure information of PNIPAM: δ 3.938 ppm (b, –CH lone pair proton of isopropyl group), δ 2.052–2.763 ppm (c, –CH backbone of polymer chain which links to carbonyl), δ 1.187–1.956 ppm (a, d, $–CH_2$, $–CH_3$ of isopropyl group), δ 7.5–7.9 ppm (e, –NH group of NIPAM and MBA). The mole ratio of signal integral area of the two kinds of –CH (δ: c 2.052–2.763 ppm and δ: b 3.938 ppm) is 1:1.

From Figure 1 we can observe that the composition of two kinds of PNIPAM microgels is similar. The only difference of the two types of microgels is the end groups of polymers coming from initiator residues, and the result will be presented in the latter part.

Thermal Response of PNIPAM Microgels

We used the cloud-point method to characterize the thermal response of PNIPAM microgels to investigate the effects of the initiator type on the thermal response of PNIPAM microgels. Figure 2(1) shows the transmittance vs temperature curves at 552 nm of PNIPAM microgels aqueous solution (2 g/L) based on AIBN and KPS, respectively. The solid curves are the transmittance curves of PNIPAM microgels in the heating process and the dotted lines present the transmittance curves of PNIPAM microgels in the cooling process. The more coincident of the solid and dotted lines means the better time effectiveness of



Scheme 2. Schematic illustrations for surface groups of PNIPAM microgels based on AIBN and KPS, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

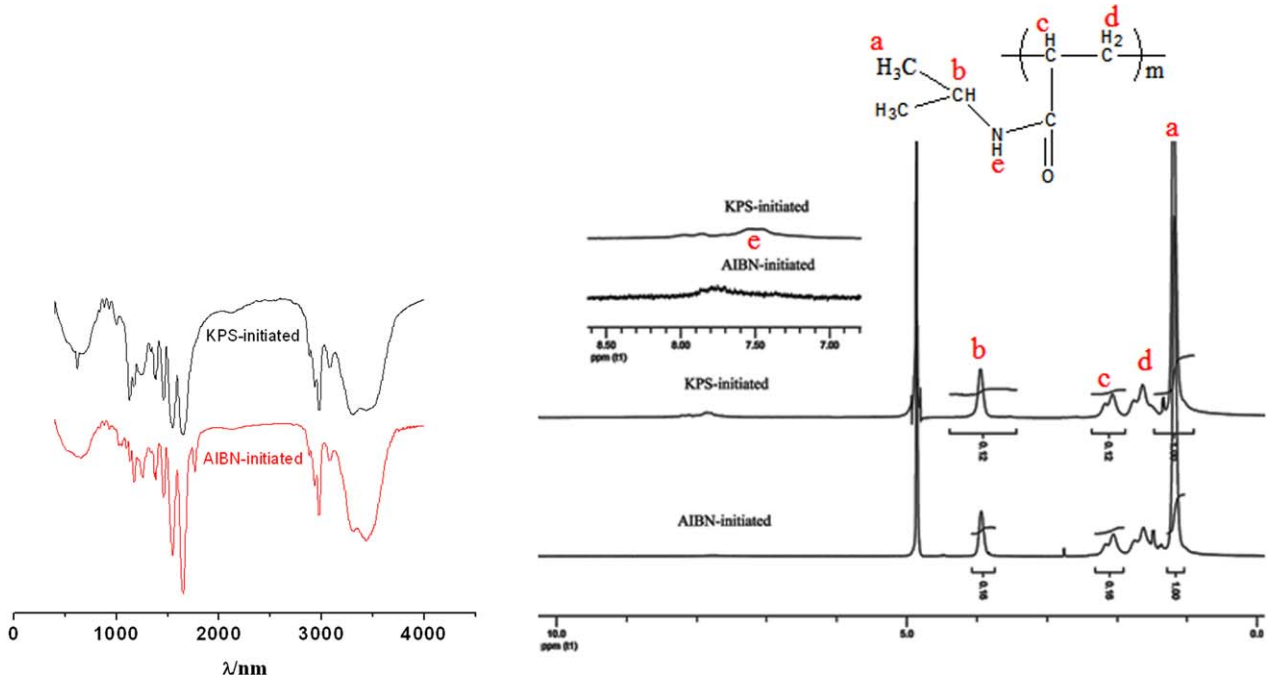


Figure 1. (1) FTIR spectra of PNIPAM microgels initiated by KPS and AIBN, respectively, and (2) ^{1}H-NMR spectra of KPS-initiated PNIPAM microgels and AIBN-initiated PNIPAM microgels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the thermal response PNIPAM microgels. It can be observed from Figure 2(1) that the time effectiveness of AIBN-initiated PNIPAM microgels is better than that of KPS-initiated one. The reason will be interpreted in the latter text. From Figure 2 we can see that the phase transition of the AIBN-initiated PNIPAM microgels takes place from 29°C and the transmittance decreases sharply with increasing temperature until 33°C. Oppositely, the phase transition of KPS-initiated PNIPAM microgels starts at higher temperature until 34°C, and the transmittance change degree with increasing temperature is less than that of AIBN-initiated PNIPAM microgels. The transmittance changes degree with temperature can indicate the thermal response sensitivity of PNIPAM microgels. So we compared the transmittance change degree ($\triangle T$) of PNIPAM microgels latex at the main phase transition temperature range at 552 nm (to AIBN-initiated PNIPAM microgels the main phase transition range is 29°C–33°C, whereas that of KPS-initiated PNIPAM microgels is 35–39°C). The result shows that the $\triangle T$ of AIBN-initiated PNIPAM microgels is 59.4% larger than that of KPS-initiated PNIPAM microgels 43.5%; it indicates that the AIBN-initiated PNIPAM microgels have better thermal response sensitivity than KPS-initiated one.

Figure 2(2) shows the differential curves of the transmittance vs temperature curves in Figure 2(1), the inflection point temperature of differential curves is the LCST of PNIPAM microgels aqueous solution and the change of transmittance. From Figure 2(2) we can get the LCST of PNIPAM microgels as 31°C (based on AIBN initiator) and 36°C (based on KPS initiator), respectively, the former is 5°C lower than the latter. The full width half maximum of the differential curves can indicate the thermal response sensitivity of PNIPAM microgels also; the narrower the full width half maximum means the better the thermal response sensitivity. Through the result, we can know that the full width half maximum of PNIPAM microgels based on AIBN and KPS are 5.83 and 8.54, respectively, which means the AIBN-initiated PNIPAM microgels are presenting the better thermal response sensitivity.

We using the liquid DSC method to characterize the thermal response of PNIPAM microgels also, the result is shown in Figure 3. The result of liquid DSC indicates the same problem that the AIBN-initiated PNIPAM microgels present higher LCST and better thermal response than KPS-initiated PNIPAM microgels.

All the results indicate that the oil-initiator may decrease the LCST of PNIPAM microgels and improve the thermal response sensitivity; if it is true, which means that we found a simple method to adjust the LCST of PNIPAM microgels. But it needs more experiment data to support our guess, so we further do a series of experiments.

Because the concentration of PNIPAM microgels aqueous solution based on AIBN and KPS is the same, so the concentration of the testing sample can be excluded from the effect factor on the LCST and thermal response of PNIPAM microgels. There are only three factors remaining that can affect the LCST and thermal response of PNIPAM microgels. They are the molecular weight, the crosslinkage, and the end groups of polymer chains, respectively. We will check the factors, respectively.

First, we prepared PNIPAM polymers according to Table I just without cross-linking additives MBA. The effect of molecular weight on the PNIPAM polymers is the same as that on the PNIPAM microgels in theory. The molecular weight information of PNIPAM polymers is shown in Table II. Figure 4 shows the transmittance vs temperature curves at 552 nm of AIBN-

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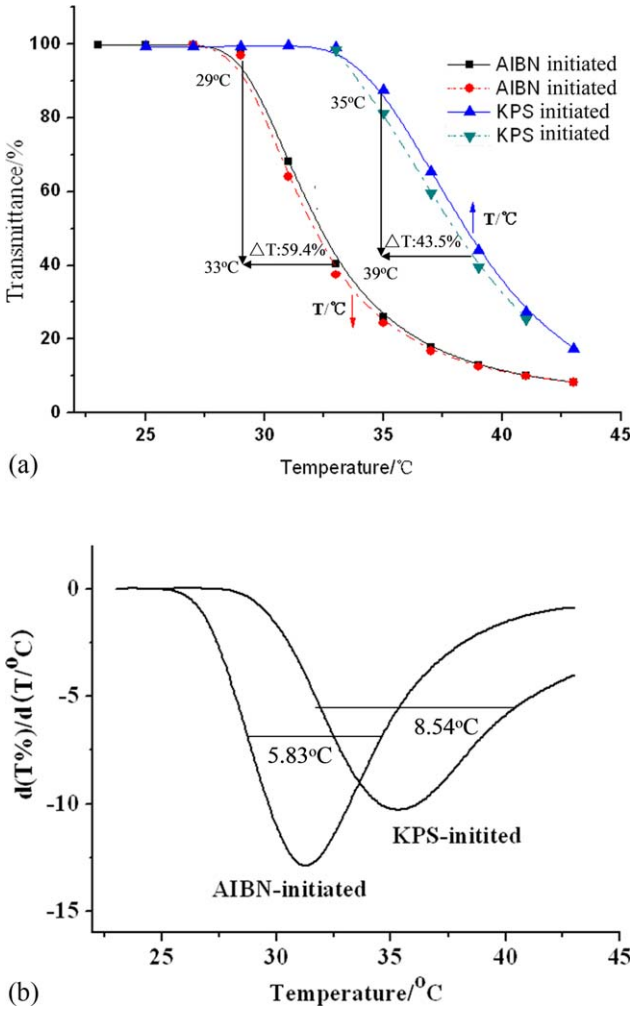


Figure 2. (1) The changes of transmittance of PNIPAM latex based on different initiators with increasing temperature at 552 nm and (2) the differential curves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

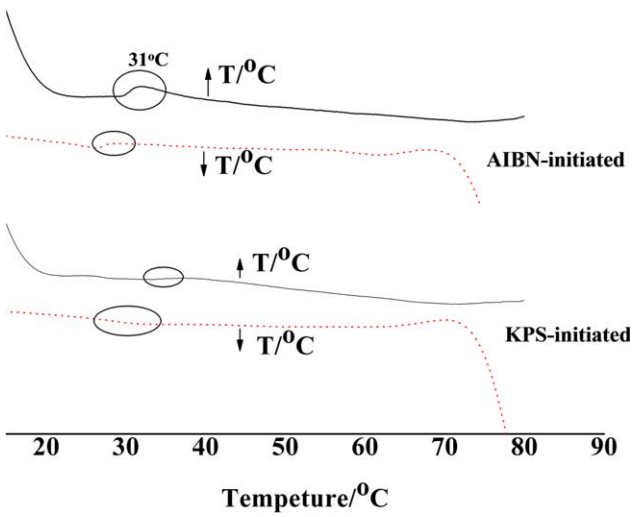


Figure 3. The liquid DSC of PNIPAM microgels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. GPC Result of PNIPAM Obtained by Soap-Free Emulsion Polymerization

Sample	M_w (g/mol)	M_n (g/mol)	M_w/M_n
L_p-1	0.917×10^4	0.254×10^4	3.61
L_p-2	1.23×10^4	0.266×10^4	4.12
L_p-3	1.28×10^4	0.315×10^4	4.07
L_p-5	0.845×10^4	0.256×10^4	3.30

initiated or KPS-initiated PNIPAM polymers with different molecular weights and distributions. From the result, we can see that the molecular weight and distribution have little influence on the LCST and thermal response sensitivity of AIBN-initiated PNIPAM polymers. This result is similar to the previous reported work.[37] Further, the AIBN-initiated PNIPAM polymers presenting lower LCST (about 31°C) and better thermal response sensitivity compare to KPS-initiated PNIPAM one (LCST 36°C) even these two kinds of polymers have the same molecular weight and distribution (according to L-1, L-5).

Second, we check the crosslinking effect on the thermal response of PNIPAM microgels, the result is shown in Figure 5. Figure 5 indicates the transmittance vs temperature curves of crosslinked PNIPAM microgels and uncrosslinked PNIPAM, it can be seen that the crosslinked and uncrosslinked PNIPAM polymers based on same initiator have the similar thermal response. From the result, we can know that the crosslinkage influences little on thermal response of PNIPAM microgels.

Therefore, the three reasons that can affect the thermal response (LCST) of PNIPAM microgels have been removed; secondly, we can get the conclusion that the reason for the different thermal response of PNIPAM microgels based on different types of initiators is the different end groups of PNIPAM polymers coming

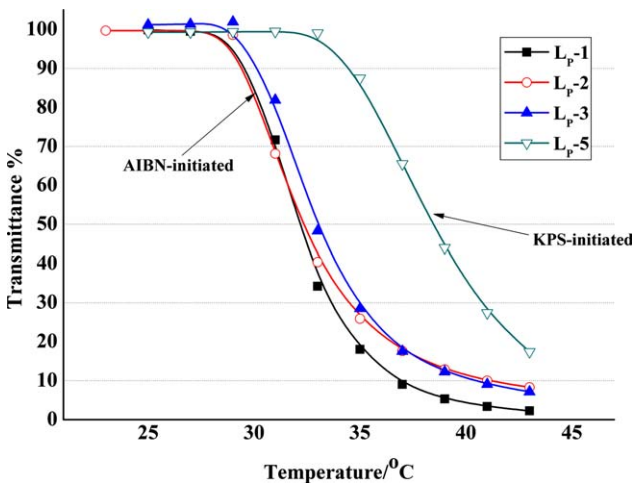


Figure 4. The transmittance vs temperature curves at 552 nm of PNIPAM polymers with different molecular weights. AIBN-initiated : (L_P-1: M_w: 0.917×10^4 g/mol, M_w/M_n: 3.61; L_P-2: M_w: 1.23×10^4 g/mol, M_w/M_n: 4.12; L_P-3: M_w: 1.28×10^4 g/mol, M_w/M_n:4.07). KPS-Initiated: (L_P-5: M_w: 0.845×10^4 g/mol, M_w/M_n: 3.30). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

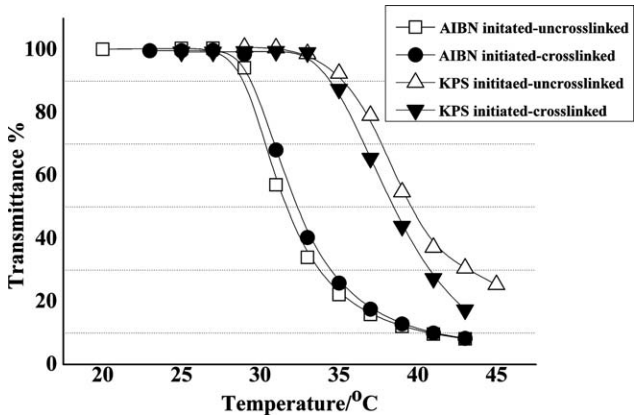


Figure 5. The transmittance vs temperature curves at 552 nm of crosslinking-PNIPAM microgels and noncrosslinking PNIPAM polymers.

from different initiators. The result provides a possible way that through changing the initiator type to modulate the LCST and thermal response sensitivity of PNIPAM microgels. The method is very simple but effective. Further, we can get the reason that why the AIBN-initiated PNIPAM microgels have better thermal response time effectiveness. The most possible reason is that the hydrophobic end groups of AIBN-initiated PNIPAM microgels increase the thermal response sensitivity of PNIPAM microgels, in this case, the AIBN-initiated PNIPAM microgels can change more enough than the KPS-initiated microgels during the limited time, so the AIBN-initiated PNIPAM microgels present better time effectiveness than the KPS-initiated one.

The mean diameter changes of PNIPAM microgels with increasing temperature were determined also through dynamic light scattering techniques and the result is shown in Figure 6. The samples were prepared by diluting purified and frozen-drying microgels to 0.05 g/L. From Figure 6 we can observe that the mean diameter of PNIPAM microgels based on AIBN first decreases, and then when the temperature is above 29°C, the mean diameter increases sharply. The reason is that with

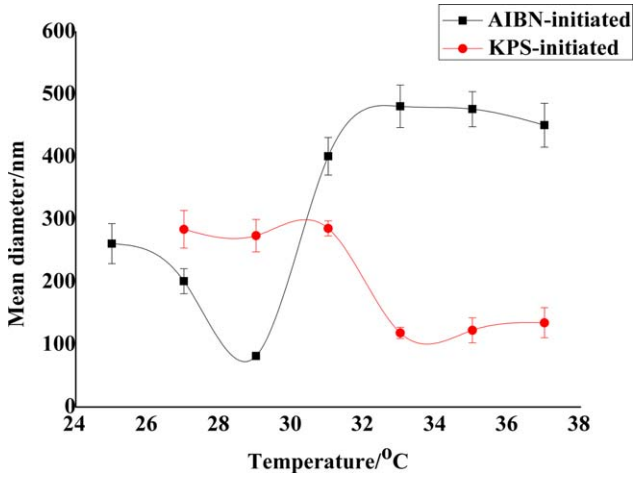
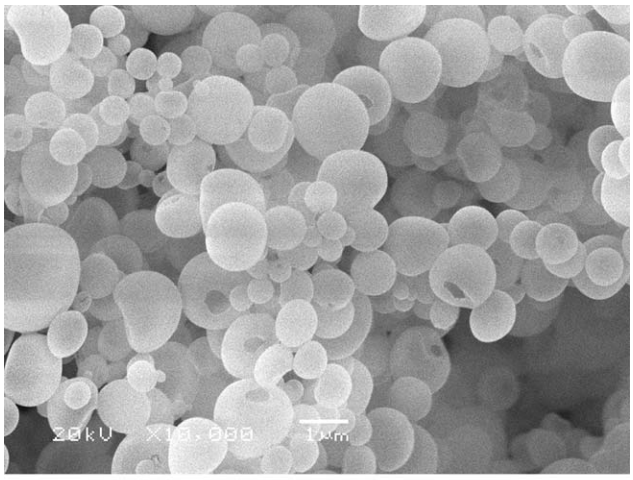


Figure 6. The changes of mean diameter of PNIPAM microgels based on different initiators with increasing temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



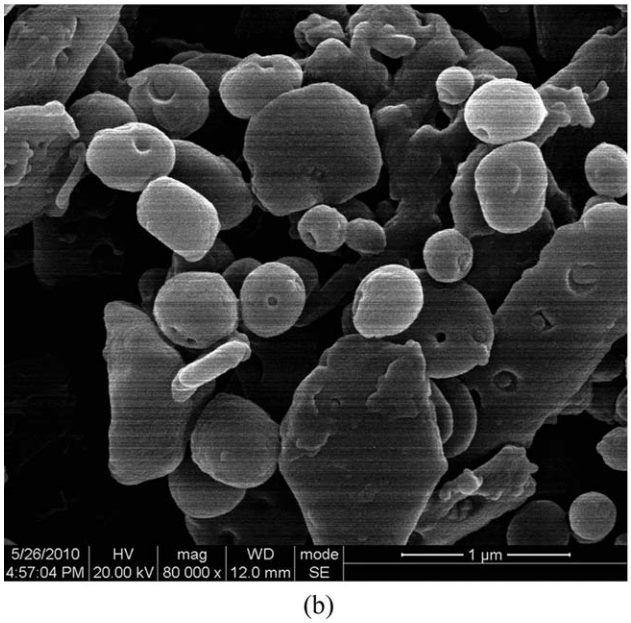


Figure 7. SEM images of PNIPAM microgels based on (1) AIBN and (2) KPS.

increasing temperature, the polymer chains first become curling and shrinking, and the mean diameter of microgels decreases, but the repellency between initiator AIBN fragment and –NH 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. Oppositely, it was reported[9,10,20–22] that when KPS was used as initiator, the mean diameter of PNIPAM microgels decreased sharply in a narrow temperature range of 31–33°C, and then reached constant. The schematic illustrations for surface groups of PNIPAM microgels based on different initiators are shown in Scheme 2.

Morphology of PNIPAM Microgels

Figure 7 shows SEM images of PNIPAM microgels based on different initiators. When using AIBN as initiator, the obtained PNIPAM microgels are regular and smooth, no agglomeration, and the dispersed microgels are stable,[4] although the

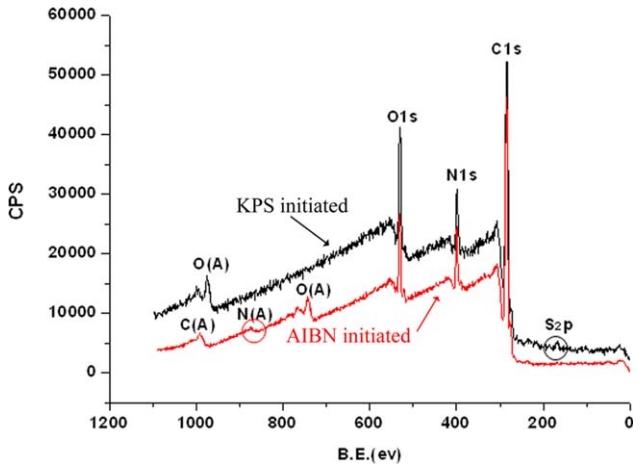


Figure 8. XPS spectra of PNIPAM microgels based on AIBN and KPS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

distribution of the microgels is not homogeneous and some big microgels present an obvious hollow structure. The agglomeration between microgels is stronger when using KPS as initiator, and they are easier to distort after absorbing water molecules. The reason is the water-soluble residues of KPS (persulfate anion) distributed at the surface of microgels and intend to absorb water. Oppositely, residues of oil-soluble AIBN can effectively prevent the absorption procedure and better stabilize the microgels.

XPS Analysis of PNIPAM Microgels

For further identifying the surface compositions of PNIPAM microgels, the microgels were examined by X-ray photoelectron spectroscopy (XPS) and the results are shown in Figure 8. The N1s (399.5 ev), O1s (531.0 ev), C1s (284.8 ev) XPS signals are the elemental marker for the PNIPAM component. The S^2p (169.9 eV) and O (A) (974.4 ev) signals are the elemental marker for the KPS initiator residue. The N (A) (872.5 ev), C (A) (989.1 ev), and O (A) (742.8 ev) signals come from AIBN initiator residue. From the result of XPS spectra, we can conclude that some initiator residues distribute on the surface of PNIPAM microgels and just because these different initiator residues result in the differences of thermal response of PNIPAM microgels based on different initiators.

Thermal Analysis of PNIPAM Polymers

The polymer microgels were freeze-dried and then characterized by DSC method, the result is shown in Figure 9. It indicates that the glass transition temperature (T_g) of AIBN-initiated PNIPAM microgels is higher than the KPS-initiated one. There is mainly two possible reasons result in the difference: first, the mobility of the end groups of polymer chain. Because the molecular weight of the two PNIPAM polymer chains is low (AIBN: L-2 M_w :12,300 g/mol; KPS: L-5 M_w : 8450 g/mol), so the mobility of end groups influence severely on the flexibility of polymer chains. Because the end groups have better mobility than other groups in polymer chain, the higher molecular weight means the fewer content of end groups in the polymer chain, so the flexibility of polymer chains decreases and the T_g increases. The AIBN-initiated PNIPAM polymers have higher molecular weight, so the T_g of AIBN-initiated one is higher than KPS-initiated PNIPAM polymers. On the other hand, the space volume of $-C(CH_3)_2CN$groups coming from AIBN is larger than $-SO_4^-$ groups coming from KPS, so the space obstruction of former is larger than the latter, result in the AIBN-initiated PNIPAM microgels have higher T_g.

CONCLUSION

The different structure of polymer extremity groups that come from residues of initiator results in the different thermal response of PNIPAM microgels. The LCST of AIBN-initiator microgels is 31°C, whereas that of KPS-initiated microgels is 36°C, the former is lower 5°C than the latter, and the change of transmittance of AIBN-initiated microgels is larger than that of KPS-initiated microgels at the temperature range of phase transition, which means the AIBN-initiated PNIPAM microgels have better thermal response sensitivity. The result indicates that the hydrophobic end group can decrease the LCST of PNIPAM microgels and increase the thermal response sensitivity, which providing a newly simple and effective method to regulate the thermal response of PNIPAM microgels.

PNIPAM microgels were synthesized through soap-free emulsion polymerization of NIPAM initiated by AIBN and KPS, respectively. PNIPAM microgels based on AIBN are more regular and smooth and not easier to distort by absorbing water than PNIPAM microgels based on KPS. The thermal response of PNIPAM microgels is also different when using different initiators. Phase transition of AIBN-initiated PNIPAM microgels starts from 29°C, whereas KPS-initiated one starts from higher temperature reaching 34°C. With increasing temperature, the mean diameter of PNIPAM microgels based on AIBN first decreases until 29°C, and then increases, whereas that of KPS-initiated PNIPAM microgels decreased sharply in a narrow temperature range of 31–33°C, and then reached a stable value. The reason for the differences of PNIPAM microgels can be attributed to different surface groups of microgels that come from residues of initiator.

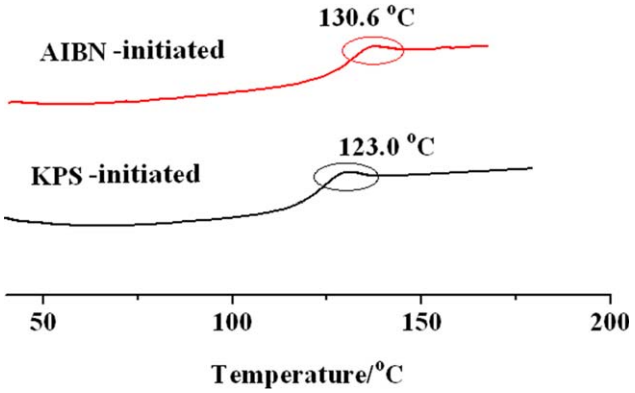


Figure 9. DSC curves of freeze-dried polymer microgels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

REFERENCES

1. Heskins, M.; Guillet, J. E. J. *Macromol. Sci. Chem. A2.* **1968**, *2*, 1441.
2. Schild, H. G. *Prog. Polym. Sci.* **1992**, *12*, 163.
3. Saeed, A.; Georget, D. M. R.; Mayes A. G. *React. Funct. Polym.* **2010**, *70*, 230.
4. Cheng, C. J.; Chu, L.Y.; Zhang, J.; Wang, H. D.; Wei, G. *Colloid Polym. Sci.* **2008**, *286*, 571.
5. Chen, S. F.; Jiang, L.; Dan, Y. *J. Appl. Polym. Sci.* **2011**, *121*, 3322.
6. Qiu, Y.; Park, K. *Adv. Drug Deliv. Rev.* **2001**, *53*, 321.
7. Kikuchi, A.; Okano, T. *Adv. Drug Deliv. Rev.* **2002**, *54*, 53.
8. Hoffman, A. S. *J. Control. Release* **1987**, *6*, 297.
9. Stile, R. A.; Burghardt, W. R.; Healy, K. E. *Macromolecules* **1999**, *32*, 7370.
10. Peppas, N. A.; Bures, P.; Leobandung, W.; Ichikaw, H. *Eur. J. Pharm. Biopharm.* **2000**, *50*, 27.
11. Holtz J. H.; Munro C. H.; Asher S.A. *Anal. Chem.* **1998**, *70*, 780.
12. Bergbreiter, D. E.; Case, B. L.; Liu, Y. S.; Caraway, J. W. *Macromolecules* **1998**, *31*, 6053.
13. Debord, J. D.; Eustis, S.; Debord, S. B.; Lofye, M. T.; Lyon, L. A. *Adv. Mater.* **2002**, *14*, 658.
14. Osada, Y.; Okuzaki, H.; Hori, H.; *Nature* **1992**, *355*, 242.
15. Ramkissoon-Ganorkar, C.; Liu, F.; Baudys, M.; Kim, S. W. *J. Control. Release* **1999**, *59*, 287.
16. Pelton R.; Chibchate P. *Colloid Surf.* **1986**, *20*, 247.
17. Garcia-Salinas M. J.; Romero-Ccano M. S.; Nieves F. J. D. *J. Colloid Interface Sci.* **2002**, *248*, 54.
18. Dong L. C.; Yan, Q.; Hoffman A. S. *J. Control. Release* **1992**, *19*, 171.
19. Yoo M. K.; Lee, Y. M.; Cho. C. S. *Polymer* **1998**, *39*, 3703.
20. Ma, J. H.; Fan, B.; Xu, J. *J. Colloid Interface Sci.* **2010**, *341*, 88.
21. Debord J. D.;Lyon L. A. *J. Phys. Chem. B* **2000**, *104*, 6327.
22. Khan, A. *J. Colloid Interface Sci.* **2007**, *313*, 697.
23. Wu, C.; Zhou, S. Q. *Macromolecules* **1997**, *30*, 574.
24. Zhou, S.; Chu, B. *J. Phys. Chem. B* **1998**, *102*, 1364.
25. Takei, Y. G.; Aoki, T.; Sanui, K.; Ogata, N.; Sakurai, Y.; Okano, T. *Macromolecules* **1994**, *27*, 6163.
26. Chung J. E.; Yokoyama M.; Aoyagi T.; Sakurai Y.; Okano T. Effect of molecular architecture of hydrophobically modified poly (*N*-isopropylacrylamide) on the formation of thermoresponsive core-shell micellar drug carriers. In 8th International Symposium on Recent Advances in Drug Delivery Systems, Salt Lake City, Utah; Elsevier Science Bv: Salt Lake City, Utah, **1997**, p 119.
27. Yoshioka, H.; Mikami, M.; Mori, Y. In a synthetic hydrogel with thermoreversible gelation. 2. effect of added salts, microsymposium on organization and performance of polyelectrolyte assemblies, at the protein/polyelectrolyte complexes seminar, Tokyo, Japan, Dec, 1992; Tokyo, Japan, **1992**, p 121.
28. Park, T. G.; Hoffman, A. S. *Macromolecules* **1993**, *26*, 5045.
29. Zhang, Y. J.; Furyk, S.; Bergbreiter, D. E.; Cremer, P. S. *J. Am. Chem. Soc.* **2005**, *127*, 14505.
30. Eliassaf, J. *J. Appl. Polym. Sci.* **1978**, *22*, 873.
31. Zhang, J. T.; Liu, X. L.; Jandt, K. D. *Colloid Polym. Sci.*; **2008**, *286*, 1209.
32. Ma, J. H.; Fan, B.; Xu, J. *J. Colloid Interface Sci.* **2010**, *341*, 88.
33. Mai-ngam, K.; Boonkitpattarakul, K.; Mai-ngam, B. *Euro. Polym. J.* **2009**, *45*, 1260.
34. Matsumura, Y.; Iwai, K. *J. Colloid Interface Sci.* **2006**, *296*, 102.
35. Fitch, R. M. *Brit. Polym. J.* **1973**, *5*, 467.
36. Hearn, J.; Wilkinson, M. C.; Goodall, A. R.; Chainey, M. *J. Polym. Sci. Polym. Chem. Ed.* **1985**, 23, *1869.*
37. Zhen, T.; Fang, Z.; Xu, Z.*Macromolecules* **1999**, *32*, 4488.