

Preparations and Properties of Thermosensitive Terpolymers of *N*-Isopropylacrylamide, Sodium 2-Acrylamido-2-methyl-propanesulfonate, and *N*-*tert*-Butylacrylamide

Dan Shao, Caihua Ni

School of Chemical and Material Engineering, Southern Yangtze University, Wuxi 214036, People's Republic of China

Received 31 August 2006; accepted 17 January 2007

DOI 10.1002/app.26275

Published online 26 April 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Terpolymers based on *N*-isopropylacrylamide, sodium 2-acrylamido-2-methyl-propanesulfonate, and *N*-*tert*-butylacrylamide were synthesized by free-radical copolymerization with 2,2'-azobisisobutyronitrile as an initiator. The lower critical solution temperatures (LCSTs) of the linear polymer aqueous solutions were determined by the measurement of the transmittance on UV at different temperatures. The influence of the polymer concentration, polymer composition, and ionic strength on the LCSTs of the linear polymers was investigated. The LCST decreased with increases in the hydrophobic monomer *N*-*tert*-butylacrylamide, polymer concentration, and ionic strength. The

phase transition became sharp when the polymer concentration and ionic strength increased. Meanwhile, the cross-linked hydrogels were prepared with the same recipe used for the linear terpolymers, but a crosslinker was added to the reaction system. The swelling ratios of the hydrogels at various temperatures and salt solutions were determined. The hydrogels possessed both high swelling ratios and thermosensitivity. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2299–2305, 2007

Key words: hydrogels; phase separation; radical polymerization; swelling; thermal properties

INTRODUCTION

A thermosensitive hydrogel is a kind of stimuli-sensitive hydrogel that exhibits a volume phase transition in response to slight environmental changes. This kind of hydrogel has received extensive attention because of its significance both in theories and in applications such as drug delivery, the immobilization of enzymes, the dewatering of protein solutions, solute separation, baby diapers, water-blocking tapes, and absorbent pads.^{1–9} The volume-phase-transition temperature is essential for a thermosensitive hydrogel to be used. It is known that poly(*N*-isopropylacrylamide) (PNIPA) undergoes a rapid and reversible phase transition in response to a small temperature change around its lower critical solution temperature (LCST; 31–33°C) in an aqueous solution. Copolymers of *N*-isopropylacrylamide (NIPA) with hydrophilic (or hydrophobic) monomers have a higher (or lower) LCST than the homopolymer PNIPA.^{10,11} This property is often used for adjusting LCST (or the phase-

transition temperature) of copolymers. We previously reported the copolymerization of NIPA, sodium acrylate, and *N*-tetrabutylacrylamide and studied the thermosensitivity of the copolymer.¹¹ Some other reports regarding the copolymerization of monomers containing hydrophilic and hydrophobic segments can be found in the literature.^{12–14}

Sodium 2-acrylamido-2-methyl-propanesulfonate (AMPS) contains strongly ionizable sulfonic groups and can dissociate completely in the overall pH range. The copolymers derived from AMPS exhibit pH-independent phase-transition behavior. Therefore, AMPS is often incorporated into thermosensitive gels as a hydrophilic component. Szczubialka et al.¹⁵ prepared a copolymer of NIPA and AMPS and studied the influence of the content of AMPS on the LCST of the copolymers in aqueous solutions. They also studied the properties of micelles made from a terpolymer of NIPA, AMPS, and cinnamoyloxy ethyl methacrylate.¹⁶ Durmaz and Okay¹⁷ synthesized a hydrogel based on acrylamide and AMPS and studied the characteristics. More studies on copolymers containing AMPS have been reported.^{18–21}

In this study, we are interested in the preparation of hydrogels with both a high swelling ratio and excellent thermosensitivity. For the aforementioned reason, we have selected NIPA as a thermosensitive mono-

Correspondence to: C. Ni (nicaihua2000@163.com).

Contract grant sponsor: Southern Yangtze University of China.

mer, AMPS as a hydrophilic monomer to obtain a high swelling ratio, and *N*-*tert*-butylacrylamide (NTBA) as a hydrophobic monomer to control the volume-phase-transition temperature of the hydrogels. We have synthesized linear terpolymers and cross-linked hydrogels by employing these monomers. The LCSTs of the linear polymers and swelling behaviors of the hydrogels have been extensively investigated in this study.

EXPERIMENTAL

Materials

NIPA, AMPS, NTBA, 2,2'-azobisisobutyronitrile (AIBN), dimethylformamide (DMF), and NaCl were purchased from Aldrich Chemical Co. (Milwaukee, WI). NIPA and AIBN were recrystallized from *n*-hexane and ethanol, respectively. AMPS and NTBA were used as received. DMF was dried through stirring overnight with calcium hydride and was then redistilled after the removal of calcium hydride by filtration. NaCl was dried in an oven at 105°C overnight before use.

Linear polymer synthesis

Monomers of NIPA, AMPS, and NTBA with various molar ratios (100/5/0, 100/5/5, 100/5/10, and 100/5/20) were dissolved in DMF to form a 14.5 wt % solution in a flask (100 mL). AIBN (0.1 mol % with respect to the total monomers) was added to the solution. The reactant solution was degassed with nitrogen for 30 min. Then, the reactor was sealed and immersed in a thermostated oil bath at 60°C with magnetic stirring for 24 h. The polymers were poured into abundant ether with stirring for precipitation. The precipitates were redissolved in deionized water. The polymer solution was dialyzed with dialysis tubes with a cutoff molecular weight of 14,000 for at least 5 days in deionized water, which was replaced daily. The solid polymers were obtained after freeze drying. The polymers were made into aqueous solutions for the measurements of the LCST. The four samples with different molar ratios of NIPA, AMPS, and NTBA (100/5/0, 100/5/5, 100/5/10, and 100/5/20) were named NAN-0, NAN-5, NAN-10, and NAN-20, respectively. The compositions were determined by elemental analysis (Rario EL III, Analysen Systeme, Hanau, Germany).

Preparation of the crosslinked hydrogels

In a glass tube (1.5 × 15 cm), monomers NIPA, AMPS, and NTBA in various molar ratios were dissolved in DMF to form a 14.5 wt % solution; 0.5 mol % *N,N'*-methylene (bis)acrylamide with respect to the total moles of the monomers was added. The reactant solution was degassed with nitrogen for 30 min. Then, the

initiator AIBN (0.5 mol % with respect to the total moles of the monomer) was added. The glass tube was sealed and immersed in a thermostated oil bath at 60°C for 24 h, and this ensured that the polymerization was adequately completed. After the polymerization, the glass tube was broken by a force. The hydrogel was taken out, cut into small pieces, and swollen in excess deionized water thoroughly. The swollen gel was washed several times with deionized water to remove unreacted monomers and linear polymers. Finally, the hydrogels were freeze-dried to a constant weight for further experiments. The compositions of the hydrogels were determined by analysis and calculation.

LCST measurements

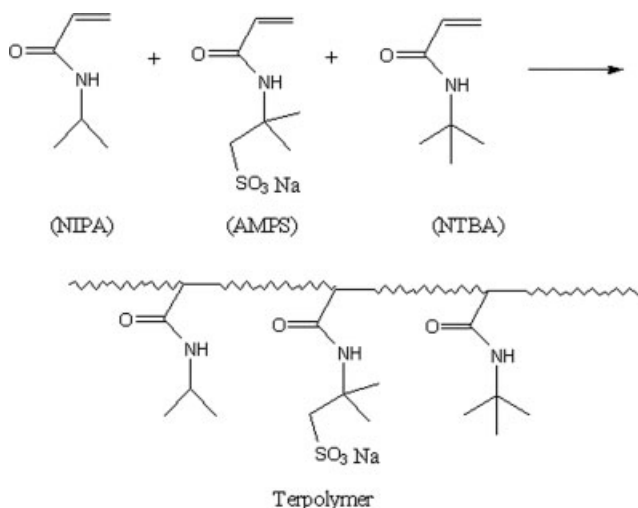
The LCSTs of the terpolymers were determined by the measurement of the optical transmittance on an ultraviolet-visible spectrometer (TU-1901, Beijing Purkinje General Instrument, Co., Ltd., Beijing, China) equipped with a temperature controller. The temperature was raised from 20 to 70°C during the measurements (the temperature rising interval was set at 1°C, whereas near LCST, it was at 0.4°C.). The sample cell was equilibrated at a given temperature for 10 min, and the end-point value of the transmittance was recorded. The LCST value of a polymer aqueous solution was defined as the temperature at which the transmittance was 50%. The transmittances of the polymer solutions with different polymer concentrations and ionic strengths were measured and were monitored at 400 nm.

Determination of the swelling ratio

A xerogel sample (the crosslinked terpolymer before the absorption of water) was placed in a nonwoven fabric bag and immersed in deionized water controlled to an optional temperature (20, 22, 25, 30, 35, 38, 40, 42, 45, 50, 55, 60, 65, 70, 75, or 80°C) for 1 day. The bag was removed from the water and sufficiently drained. The water on the surface of the bag was rapidly blotted with tissue, and the bag was weighed. The nonwoven fabric bag not containing the sample was treated in the same manner and used as a blank before the measurement of the sample. The blank was subtracted from the measured value with the sample. The swelling ratio was calculated via eq. (1):

$$S_r = (W_w - W_d)/W_d \quad (1)$$

where S_r stands for the equilibrium swelling ratio and W_w and W_d are the sample weights in the wet and dry states, respectively. The sample in water was then brought to an increased temperature for 8 h to attain equilibrium. The swelling ratio at the new tempera-



Scheme 1 Terpolymerization of NIPA, AMPS, and NTBA.

ture was measured with the method mentioned previously. The measurements were carried out at the temperatures from the lowest to the highest.

RESULTS AND DISCUSSION

Copolymer syntheses

The syntheses of the terpolymers are shown in Scheme 1. The three monomers—NIPA, AMPS, and NTBA—were selected for our study for the following reasons: NIPA is the most often used monomer in the preparation of temperature-sensitive polymers, and its homopolymer has an LCST between 25 and 37°C (human body temperature); AMPS has excellent solubility, electric capability, and stability; and NTBA is used to modify the hydrophobicity of the terpolymers and consequently to adjust the LCSTs of the copolymers. The linear terpolymer compositions have been calculated from elemental analysis. The molar ratios for terpolymers NAN-0, NAN-5, NAN-10, and NAN-20 are 100 : 4.3 : 0, 100 : 4.1 : 3.1, 100 : 4.0 : 9.5, and 100 : 3.5 : 18.4, respectively.

Effect of the polymer composition on the LCST

The homopolymer solution of NIPA possesses an LCST of 32.5°C.^{6,11} As the hydrophilic monomer AMPS is incorporated into the copolymer, the LCST shifts toward a high temperature. This occurs because the sulfonic groups in AMPS enhance the hydrophilicity of the copolymer, and this results in the copolymer becoming more soluble in water. However, as the hydrophobic component NTBA is incorporated into the terpolymer, the LCST decreases. For example, in Table I, at the polymer concentration of 0.2 wt %, when the molar ratio of NIPA to AMPS is fixed at 100/5, but the molar percentage of NTBA gradually

increases to 5, 10, and 20% with respect to NIPA, the LCST decreases from 50.3°C for NAN-0 to 48.2, 45.3, and 41.3°C, respectively. At the polymer concentration of 1.0 wt %, the LCST of the terpolymer with the NIPA/AMPS/NTBA molar ratio of 100/5/20 drops to 33.4°C, close to the LCST of PNIPA. It is easily understood that the introduction of the hydrophobic groups into NTBA causes the decrease in LCST. This result suggests that a copolymer with a desirable LCST can be obtained by the adjustment of the composition of the hydrophilic and hydrophobic monomers incorporated into the copolymer.

Effect of the polymer concentration on the LCST

Figure 1 shows the effect of the polymer concentration on the LCST for an NIPA/AMPS copolymer and three NIPA/AMPS/NTBA terpolymers with different molar ratios. For the NIPA/AMPS copolymer (molar ratio = 100/5), the LCST is 50.3°C at a polymer concentration of 0.2 wt %, and the LCST decreases to 46.9, 45.0, 43.1, and 42.5°C as the polymer concentration gradually increases to 0.4, 0.6, 0.8, and 1.0 wt %, respectively. For the three terpolymers with NIPA/AMPS/NTBA molar ratios of 100/5/5, 100/5/10, and 100/5/20, the same trend is observed. The higher the polymer concentration is, the lower the LCST is. The influence of the polymer concentration on the LCST can be explained. The turbidity reflects the number of polymer chains aggregated around the phase-transition temperature. If the polymer concentration is high, more polymer chains are present in the solution than in solutions with lower polymer concentrations. As the temperature is close to the LCST, more polymer chains will aggregate, and this will increase the turbidity of the solution and consequently decrease the LCST. It is concluded that the turbidity of a solution with a high polymer concentration is bigger than that of a solution with a lower polymer concentration at the same temperature. Consequently, the LCST appears at a lower temperature region. We have also noted that the rate of the LCST decrease is varied in different polymer concentration regions. In other words, the obvious decrease in the LCST occurs only in a dilute polymer concentration range. When the polymer concentration changes from 0.2 to 0.4 wt %,

TABLE I
LCSTs (°C) of the Copolymers at Different
Polymer Concentrations

Sample	Polymer concentration (wt %)				
	0.2	0.4	0.6	0.8	1.0
NAN-0	50.3	46.9	45.0	43.1	42.5
NAN-5	48.2	44.2	42.1	40.3	39.7
NAN-10	45.2	41.2	38.9	37.4	36.8
NAN-20	41.3	37.5	35.0	34.8	33.4

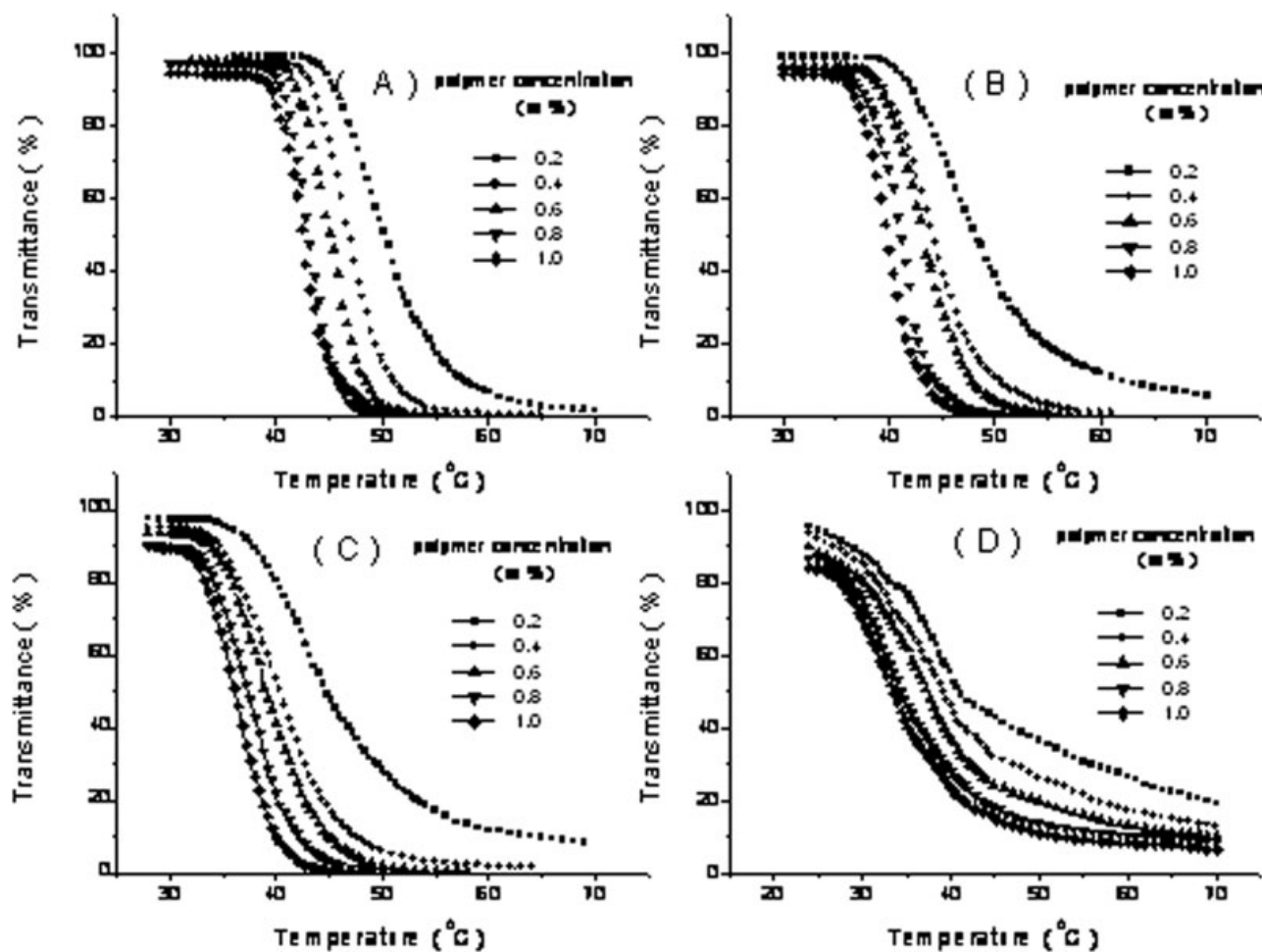


Figure 1 Transmittance dependence on the temperature at different polymer concentrations for the terpolymers with NIPA/AMPS/NTBA molar ratios of (A) 100/5/0, (B) 100/5/5, (C) 100/5/10, and (D) 100/5/20.

the LCST decreases by 3.4, 4.0, 4.1, and 3.8°C for polymers NAN-0, NAN-5, NAN-10, and NAN-20, respectively. However, when the polymer concentration changes from 0.8 to 1.0 wt %, the LCST decreases by 0.6, 0.6, 0.6, and 0.7°C for the same polymer group. With a further increase in the polymer concentration, the LCST almost remains constant.

Sensitivity of the phase-transition temperature

In this study, the LCST is defined as the temperature point at which the transmittance is 50%. Actually, the phase transition crosses a temperature range. For the homopolymer NIPA, the LCST range is very narrow, and this means that the turbidity of the polymer solution undergoes an abrupt change at a definite temperature. The sensitivity of PNIPA to the temperature is excellent. However, for a thermosensitive copolymer, the LCST range is broadened, and this means that the phase transition is less sensitive. The temperature sensitivity is an important property and is affected by some factors, such as the polymer composition, poly-

mer concentration, and ionic strength. It is observed from Figure 1 that the polymer concentration affects the sensitivity obviously. To quantitatively investigate the sensitivity, we defined the average transmittance change rate (R_t) as follows:

$$R_t = \Delta T(\%) / \Delta \text{LCST} \quad (2)$$

where ΔT (%) is the transmittance change and ΔLCST is the phase-transition temperature range. The physical meaning of R_t is the average transmittance change caused per degree of temperature change. It can be calculated from Figure 1. The result is shown in Table II. R_t increases with the increase in the polymer concentration. For sample NAN-0, R_t is 4.18% at a polymer concentration of 0.2 wt %, but it increases to 10.86% as the polymer concentration rises to 1.0 wt %. This reflects that the turbidity increases more for the condensed polymer solution than for the dilute polymer solution within the same temperature change. The same results can be observed for the three terpolymers NAN-5, NAN-10, and NAN-20. The higher the polymer concentration is, the larger R_t is. Figure 1

TABLE II
 R_t Values at the Phase Transition ($^{\circ}\text{C}$)

Sample	Polymer concentration (wt %)				
	0.2	0.4	0.6	0.8	1.0
NAN-0	4.18	6.57	8.55	10.32	10.86
NAN-5	3.18	5.10	7.11	8.42	9.95
NAN-10	2.90	4.85	6.23	6.91	8.94
NAN-20	1.75	2.51	4.23	5.36	6.54

shows that the curves gradually become steep with the increase in the polymer concentration. Moreover, R_t decreases with the increase in NTBA. Because NTBA is a nonthermosensitive monomer, the thermosensitivity is weakened with the increase in the nonthermosensitive components. This fact agrees with our observations in the previous work.¹¹ It is concluded that the sensitivity can be enhanced by increases in the polymer concentration and thermosensitive components.

Effect of salt on LCST

The ionic strength has a significant influence on the LCST of the copolymers. The plots of the transmittance versus the temperature at various NaCl concen-

trations are shown in Figure 2. For samples NAN-0, NAN-5, and NAN-10, the transmittances at the polymer concentration of 0.1 wt % are greater than 50%, indicating no LCST occurrence. However, the addition of NaCl dramatically decreases transmittances, that is, decreases the LCST. The more NaCl is added, the more the LCST decreases. We also note that the LCSTs of the different copolymers are affected by salt to various degrees. Figure 3 plots the LCST dependence on the NaCl concentration. The LCST of the copolymer without NTBA (NAN-0) is not very strongly affected by NaCl, and this means that the LCST decreases slowly as the NaCl concentration increases. The LCST changes from 45.8 to 30.9 $^{\circ}\text{C}$ when the NaCl concentration increases from 0.2 to 1.0 wt %. As more NTBA is incorporated into the terpolymers, the LCST is more significantly affected by NaCl. For the NIPA/AMPS/NTBA terpolymer (molar ratio = 100/5/20), the LCST drops from 41.0 to 30.2 $^{\circ}\text{C}$ when the NaCl concentration changes from 0.2 to 0.5 wt %. The curve slope is much larger than those of the other polymers.

Some explanations have been proposed for the effect of the ionic strength on the LCST of thermosensitive polymers.^{12,15} In this study, we illustrate the salt effect with the chemical potential of water molecules (μ_w°) in the solution. The chemical potential of water

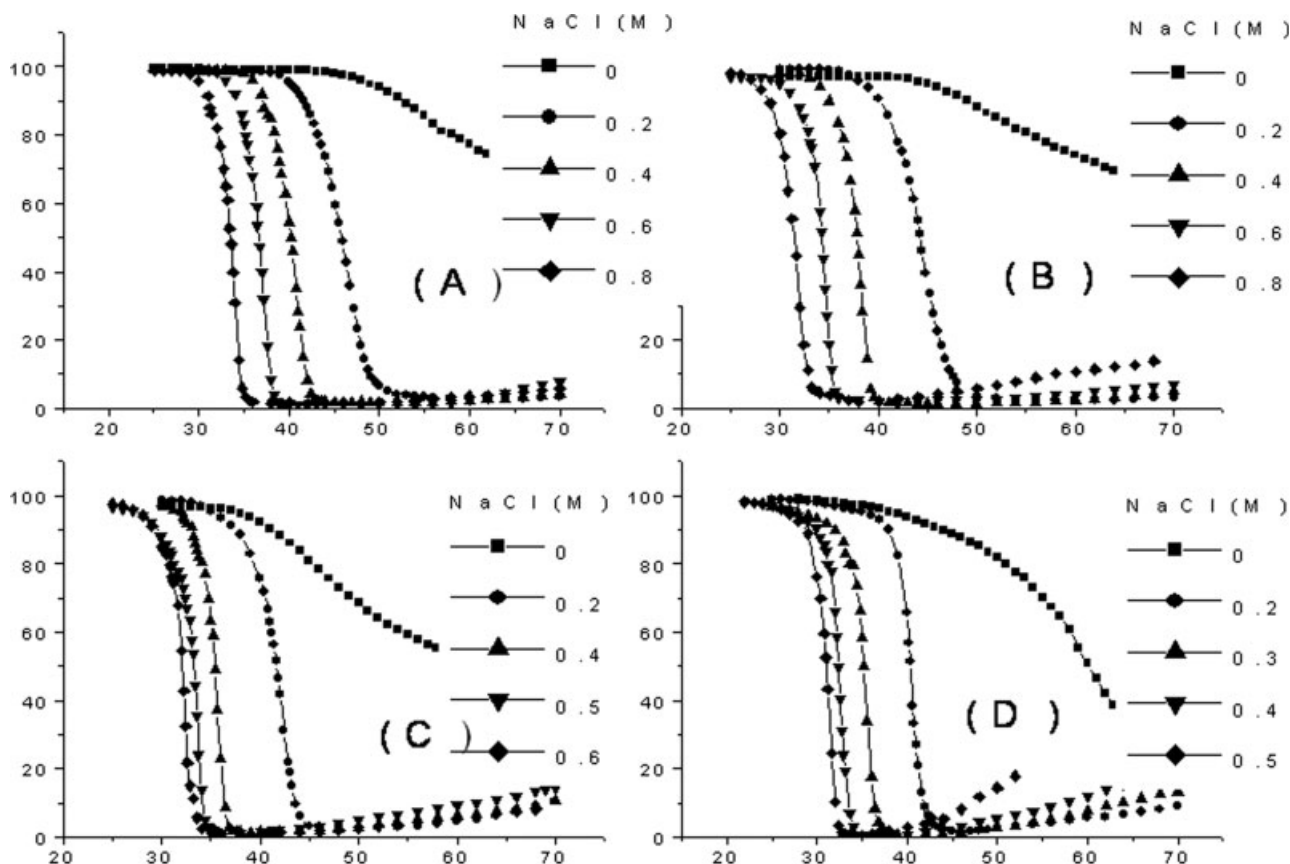


Figure 2 Transmittance dependence on the temperature at different ionic strengths for the terpolymers with NIPA/AMPS/NTBA molar ratios of (A) 100/5/0, (B) 100/5/5, (C) 100/5/10, and (D) 100/5/20 at the polymer concentration of 0.1 wt %.

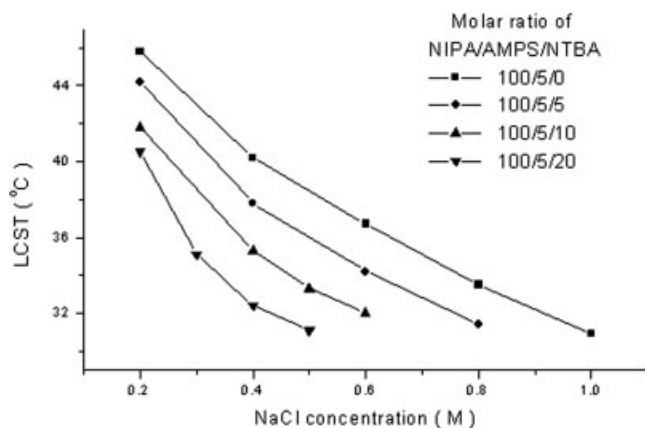


Figure 3 Decrease in the LCST with an increase in the NaCl concentration for different terpolymers at the polymer concentration of 0.1 wt %.

molecules in the salt solution [$\mu_w^o(C_s, T)$, where C_s is the concentration of the salt and T is the temperature] is expressed by the following equation:²²

$$\mu_w^o(C_s, T) = \mu_w^o(0, T) + RT \ln a_w(C_s) \quad (3)$$

where $\mu_w^o(0, T)$ stands for the chemical potential of water in a salt-free solution, R is the molar gas constant, and $a_w(C_s)$ is the activity of water molecules in the presence of salt. The activity is usually a monotonically decreasing function with the increase in the salt concentration. In a salt-free solution, $a_w(C_s) = 1$, and $\mu_w^o(C_s, T) = \mu_w^o(0, T)$. However, with the addition of salts, $a_w(C_s) < 1$, so $\mu_w^o(C_s, T) < \mu_w^o(0, T)$. To compensate for the decrease in the chemical potential, water molecules bound to the polymer chain dissociate from it and return to the solution, causing $\mu_w^o(C_s, T)$ to increase until a new equilibrium is established. When water molecules leave the polymer chain, the hydrophobicity of the polymer increases, and this results in an LCST decrease.

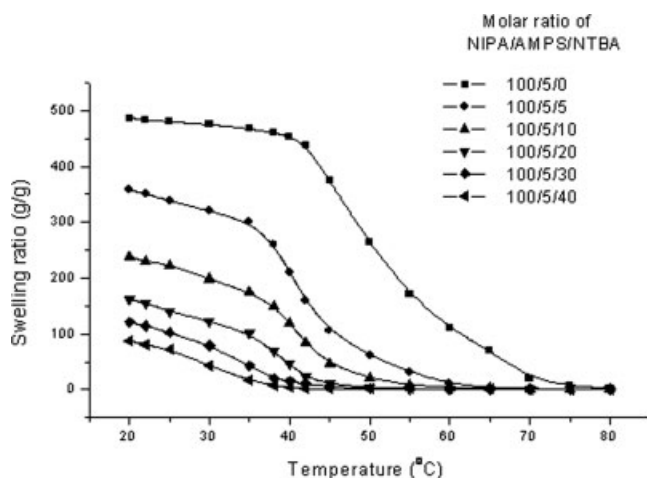


Figure 4 Swelling ratio dependence on the temperature for the thermosensitive hydrogels in deionized water.

Swelling ratio of the hydrogels

A three-dimensional network hydrogel is formed if a crosslinking agent is added to the monomers during the polymerization. For a PNIPA hydrogel, the water uptake is limited. In a common case, its swelling ratio is not more than 30 g/g, which restricts its applications as a superabsorbent. To improve the water uptake, many researchers have tried to introduce a hydrophilic monomer into PNIPA by copolymerization. The swelling ratio of the copolymer of NIPA to the hydrophilic monomer can be greatly enhanced; unfortunately, the volume phase transition will shift to a high temperature region. In this study, we have employed three monomers to synthesize hydrogels to compromise the contradiction between the swelling ratio and phase-transition temperature. The swelling ratios of the hydrogels are displayed in Figure 4.

The swelling ratio of the NIPA/AMPS copolymer (molar ratio = 100/5) is close to 500 g/g, but its volume-transition temperature shifts to a much higher region. It starts to deswell at 44°C until it completely deswells at 70°C. The swelling ratios of the terpolymers decrease with the increase in hydrophobic component NTBA. The swelling ratios at 20°C are 490, 360, 237, 163, 122, and 92 g/g, respectively, when the NTBA contents are 0, 5, 10, 20, 30, and 40 mol % with respect to NIPA. As the temperature drops to 35°C, the swelling ratios decrease to 468, 299, 175, 98, 44, and 10 g/g for the terpolymers, respectively. Apparently, the swelling decrease results from the function of the hydrophobic component NTBA. A comparison of the swelling ratios at 20 and 35°C is shown in Table III. The difference in the swelling ratios at 20 and 35°C increases as NTBA is increased, the change ranging from 4.5% in the terpolymer without NTBA to 80.4% in the terpolymer with 40 mol % NTBA. Some of the terpolymer hydrogels have both significant swelling ratios and thermosensitivity. This suggests that the

TABLE III
Preparation and Swelling for Terpolymer Hydrogels

Sample	NIPA/AMPS/NTBA molar ratio		Yield (%)	Swelling ratio (g/g)	
	Feed ^a	Found ^b		20°C	35°C
1	100/5/0	100/4.86/0	95.7	490	468
2	100/5/5	100/4.93/4.71	97.6	360	299
3	100/5/10	100/4.87/9.60	98.3	237	175
4	100/5/20	100/4.29/19.3	96.8	163	98
5	100/5/30	100/4.37/28.7	95.3	122	44
6	100/5/40	100/4.25/37.3	97.1	92	18

^a The amount of NIPA was 2.26 g, and the amount of AMPS was 0.23 g; they were kept constant for each sample, but the amounts of NTBA were 0, 0.127, 0.254, 0.508, 0.762, and 1.016 g for samples 1, 2, 3, 4, 5, and 6, respectively. The crosslinker and initiator concentrations were 0.5 mol % with respect to the total monomers.

^b Determined by elemental analysis and calculations.

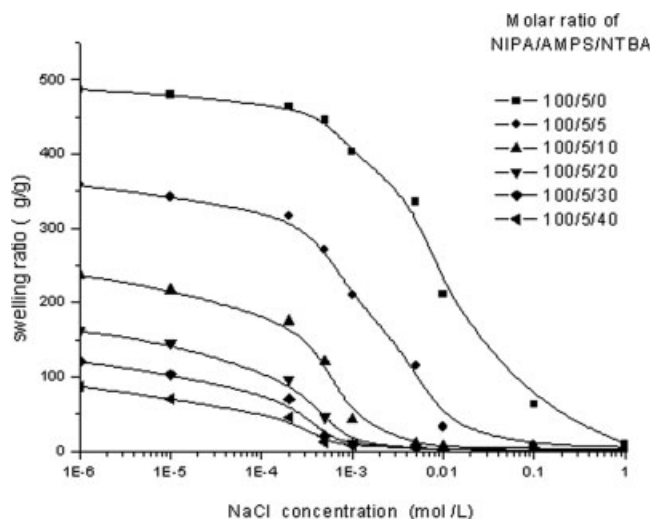


Figure 5 Swelling ratio dependence on the concentration of an external NaCl solution at 20°C for the thermosensitive hydrogels.

hydrogels have potential applications as thermosensitive materials.

Effect of salt on the swelling ratio of the hydrogels

The swelling ratios of the hydrogels at different NaCl concentrations at 20°C are shown in Figure 5. The swelling ratios remain very slightly changed in the range of dilute NaCl concentrations. The volume phase transition induced by the salt takes place at different NaCl concentrations for different polymers. The greater the hydrophobic content is in the terpolymers, the more dilute the NaCl concentration is that is needed for inducing the phase transition. In other words, the hydrogels with greater hydrophobic content are more significantly affected by an external salt solution. This fact agrees with the observation of the salt effect on the LCST of the linear terpolymers. This is explained as we have discussed previously. As a salt is added to the hydrogel solution, the chemical potential of water will decrease. Some of the water molecules are forced to dissociate from the hydrogel and return to the solution, increasing the chemical potential of water and resulting in the deswelling of the hydrogels. A hydrogel with greater hydrophobic content absorbs less water and hence is affected by salt more significantly. However, a hydrogel with more hydrophilic content absorbs more water; there-

fore, a more condensed salt solution is needed to deswell the hydrogel.

CONCLUSIONS

Terpolymers based on NIPA, AMPS, and NTBA can be synthesized by free-radical polymerization with AIBN as an initiator. Both linear and crosslinked polymers can be obtained. The LCST of the linear polymer aqueous solution is affected by the polymer composition, polymer concentration, and ionic strength. The thermosensitivity is enhanced by an increase in the polymer concentration and ionic strength. The crosslinked hydrogels show obviously higher swelling ratios than the PNIPA gel, and at the same time, the hydrogels display good thermosensitivity. The hydrogels are potentially used as superabsorbent materials for solute separation and drug controlled delivery.

References

- Schild, H. G. *Prog Polym Sci* 1992, 17, 163.
- Pelton, R. *Adv Colloid Interface Sci* 2000, 85, 1.
- Champ, S.; Xue, W.; Huglin, M. B. *Macromol Chem Phys* 2000, 201, 931.
- Xue, W.; Champ, S.; Huglin, M. B. *Polymer* 2001, 42, 2247.
- Kim, J. H.; Lee, S. B.; Kim, S. J.; Lee, Y. M. *Polymer* 2002, 43, 7549.
- Liu, H. Y.; Zhu, X. X. *Polymer* 1999, 40, 6985.
- Chen, G.; Hoffman, A. S. *Nature* 1995, 373, 49.
- Yamamoto, K.; Serizawa, T.; Muraoka, Y.; Akashi, M. *Macromolecules* 2001, 34, 8014.
- Serizawa, T.; Chen, M. Q.; Akashi, M. *J Polym Sci Part A: Polym Chem* 1998, 36, 2581.
- Taylor, L. D.; Cerankowski, L. D. *J Polym Sci Polym Chem Ed* 1975, 13, 2551.
- Ni, C. H.; Zhu, X. X. *Eur Polym J* 2004, 40, 1075.
- Liu, X. M.; Wang, L. S.; Wang, L.; Huang, J.; He, C. B. *Biomaterials* 2004, 25, 5659.
- Lee, W. F.; Yeh, Y. C. *Eur Polym J* 2005, 41, 2488.
- Liu, X. M.; Pramoda, K. P.; Yang, Y. Y.; Chow, S. Y.; He, C. B. *Biomaterials* 2004, 25, 2619.
- Szczubialka, K.; Loska, R.; Nowakowska, M. *J Polym Sci Part A: Polym Chem* 2001, 39, 2784.
- Szczubialka, K.; Nowakowska, M. *Polymer* 2003, 44, 5269.
- Durmaz, S.; Okay, O. *Polymer* 2000, 41, 3693.
- Kobayashi, A.; Matsuzaki, F.; Yanaki, T.; Morishima, Y. *J Appl Polym Sci* 1999, 73, 2447.
- Xue, W.; Champ, S.; Huglin, M. B. *Polymer* 2000, 41, 7575.
- Lehto, J.; Vaarmaa, K.; Vesterinen, E.; Tenhu, H. *J Appl Polym Sci* 1998, 68, 355.
- Bune, Y. V.; Barabanova, A. I.; Bogachev, Y. S.; Gromov, V. F. *Eur Polym J* 1997, 33, 1313.
- Sasaki, S.; Kawasaki, H.; Maeda, H. *Langmuir* 1999, 15, 4266.