

Fast Responsive and Strong Swelling Hydrogels Based on *N*-Isopropylacrylamide with Sodium Acrylate

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ABSTRACT: Poly(*N*-isopropylacrylamide-*co*-sodium acrylate) gels with *N,N*-methylene bisacrylamide (BIS) as crosslinker were prepared by free radical polymerization method at the temperature of 35°C, which was just around the lower critical solution temperature (LCST) of the hydrogels. The gels synthesized at 35°C demonstrated strong swellability and fast responseability when compared with the gels synthesized at the temperature of 0 and 18°C (below the LCST) and 50 and 80°C (above the LCST). The response rate and swelling behavior of poly(*N*-isopropylacrylamide-*co*-sodium acrylate) gels was investi-

gated and characterized by the temperature-dependent swelling ratio and swelling and deswelling kinetics. The swelling behavior of the gels indicated that the synthesis temperature was the main factor when the swellability concerned and also had effect on the responseability of the resulting hydrogels. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 123–128, 2009

Key words: poly(*N*-isopropylacrylamide-*co*-sodium acrylate); hydrogels; swelling behavior; fast responsive; strong swellability

INTRODUCTION

Poly(*N*-isopropylacrylamide) (PNiPAAm) hydrogel attracts lots of researchers as a best-known thermosensitive polymeric network, which exhibits a reversible volume transition at a transition temperature or lower critical solution temperature (LCST) of ~33°C.^{1,2} This property is due to the reversible formation and cleavage of the hydrogen bonds between the amide group and surrounding water molecules with changing temperature.³ The thermal sensitivity of *N*-isopropylacrylamide (NiPAAm) gels has resulted in numerous applications such as in biotechnology and pharmaceuticals.^{4–6} Recently, the study of NiPAAm gels is focused on improving their thermosensitive properties and fast response rate,^{7–13} including phase separation techniques which were reported to prepare heterogeneous structure of hydrogels.¹⁴ The potential of phase separation technique for making fast response gels is due to the chemically crosslinking phase-separated microstructures. Polymerization of a monomer with crosslinker

below the low critical solution temperature of the polymer is initiated and then the solution is heated above the LCST to the spinodal region causing microscale phase separation and microporous structure.¹⁵

In this article, we describe a method to create fast responsive and strong swelling thermosensitive poly(*N*-isopropylacrylamide-*co*-sodium acrylate) gels. The hydrophilic comonomer sodium acrylate (SA) was added into NiPAAm system to enhance the swellability. Polymerization was conducted at the temperature around the LCST of hydrogels to result in phase separation to adjust the response rate. The temperature-dependent swelling ratio, response kinetics upon heating and cooling, and oscillatory swelling–deswelling kinetics over temperature cycles of the PNiPAAm-*co*-SA hydrogels were examined to manifest the fast responseability and strong swellability of obtained hydrogels.

EXPERIMENTAL

Materials

NiPAAm monomer (WUJING Chemical, Shanghai, China) was used after recrystallization from *n*-hexane. Sodium acrylate (SA) was synthesized from

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acrylic acid and sodium hydroxide. *N,N'*-Methylenebisacrylamide (BIS), tetramethylethylenediamine (TEMED), and ammonium persulfate (APS) were purchased from Sinopharm Chemical Reagent (Shanghai, China) and used as received. The water used for experiment was deionized water.

Synthesis of poly(*N*-isopropylacrylamide-*co*-SA) hydrogels

PNiPAAm-*co*-SA hydrogels with NiPAAm/SA mole ratio 98 : 2 were synthesized using BIS as a cross-linking agent. APS and TEMED were used as initiator and accelerator by free radical polymerization. The hydrogels were prepared as follows: a total of 1.02 g of NiPAAm and 0.028 g of BIS [5% (mol/mol) to NiPAAm] were dissolved in 20 mL deionized water, which was nitrogen-bubbled for 10 min, and then 0.04 mL SA solution was added (3.95 mol/L) and bubbled with nitrogen for another 5 min. 1.7 mL APS [2% (mol/mol) to NiPAAm] and 0.9 mL TEMED [5% (mol/mol) to NiPAAm] were subsequently mixed into the aqueous solutions and bubbled with nitrogen for 5 min. After the first 20 min of polymerization at 18°C, the reaction was conducted in water bath at required temperature of 0, 16, 35, 50, and 80°C, respectively, for 1 h with nitrogen protection, and then stayed at the conditioning room with constant temperature of 18°C for 1 day. The resulting hydrogels were then separated from the vessel and purified by immersing in deionized water for 1 week to remove unreacted chemicals and fully swell. The water was replaced 3–4 times every day. The swollen hydrogels were cut into disk-like pieces of 1-cm diameter and 2-mm thickness, and then dried under vacuum for 2 days at 40°C to constant weight. The resulted PNiPAAm-*co*-SA hydrogels were designated as G_x , where G represented the gels and x indicated the synthesis temperature. It should be noted that the hydrogels produced at 50°C cannot be cut into pieces because of their poor shape retention, so a definite weight of G_{50} gel as one disk-like piece was used as G_{50} test sample.

FTIR

The completely dried hydrogel samples were analyzed by FTIR (Thermo Nicolet 5700, USA) spectrophotometer in the region of 4000–700 cm^{-1} .

Measurement of swelling ratio under different temperature

For the temperature-dependent swelling study, the hydrogel disc-shape pieces were swollen in deionized water at room temperature for 24 h to equilibrium. It was confirmed that a period of 24 h was more than adequate to ensure the attainment of

swelling equilibrium. Each swollen sample was then put in small beakers moved into shaking water bath at a predetermined temperature for 24 h. The gravimetric method was employed to study the hydrogel's swelling ratio. The gel samples were dried with wet filter papers carefully to remove excess surface water without pressure and weighed directly using an electrobalance. Swelling ratio (r) was calculated from the following formula:

$$\text{Swelling ratio} = (W_t - W_d)/W_d \quad (1)$$

where W_t = gel weight at temperature t (°C); W_d = gel dry weight.

Measurement of deswelling kinetics

The deswelling kinetics of the PNiPAAm-*co*-SA hydrogels was measured gravimetrically at 50°C, which was far above the LCST so that drastic shrinkage in volume could be attained within a short time. The swollen equilibrated hydrogel samples at room temperature were quickly immersed into 50°C water bath. At predetermined time interval, 1 h, the samples were removed from the hot water bath and weighed after quickly wiping off the excess water on the surface. Water retention in gels as a function of temperature was calculated as

$$\text{Water retention (\%)} = (W_{50} - W_d)/W_0 \times 100 \quad (2)$$

where W_{50} = the weight of the wet hydrogel at time t at temperature 50°C; W_d = the dry weight of the hydrogel; W_0 = the weight of the hydrogel at equilibrated swelling at 18°C.

Measurement of swelling kinetics

For swelling kinetics study, the swollen gel samples were first immersed into hot water bath (50°C) for about 24 h, and then immersed in deionized water at room temperature and removed from water at predetermined interval 1 h. After wiping off the surface water of gels, the hydrogels were weighed and the water uptake was defined as follows:

$$\text{Water uptake (\%)} = (W_{18} - W_d)/W_0 \times 100 \quad (3)$$

where W_{18} = the weight of the wet hydrogel at time t at temperature 18°C; W_d = the dry weight of hydrogel; W_0 = the weight of the hydrogel at equilibrated swelling at 18°C.

Measurement of deswelling–swelling kinetics over temperature cycles

The deswelling–swelling kinetics of the hydrogels over the 10-min temperature cycles between 18°C (below LCST) and 50°C (above LCST) in deionized

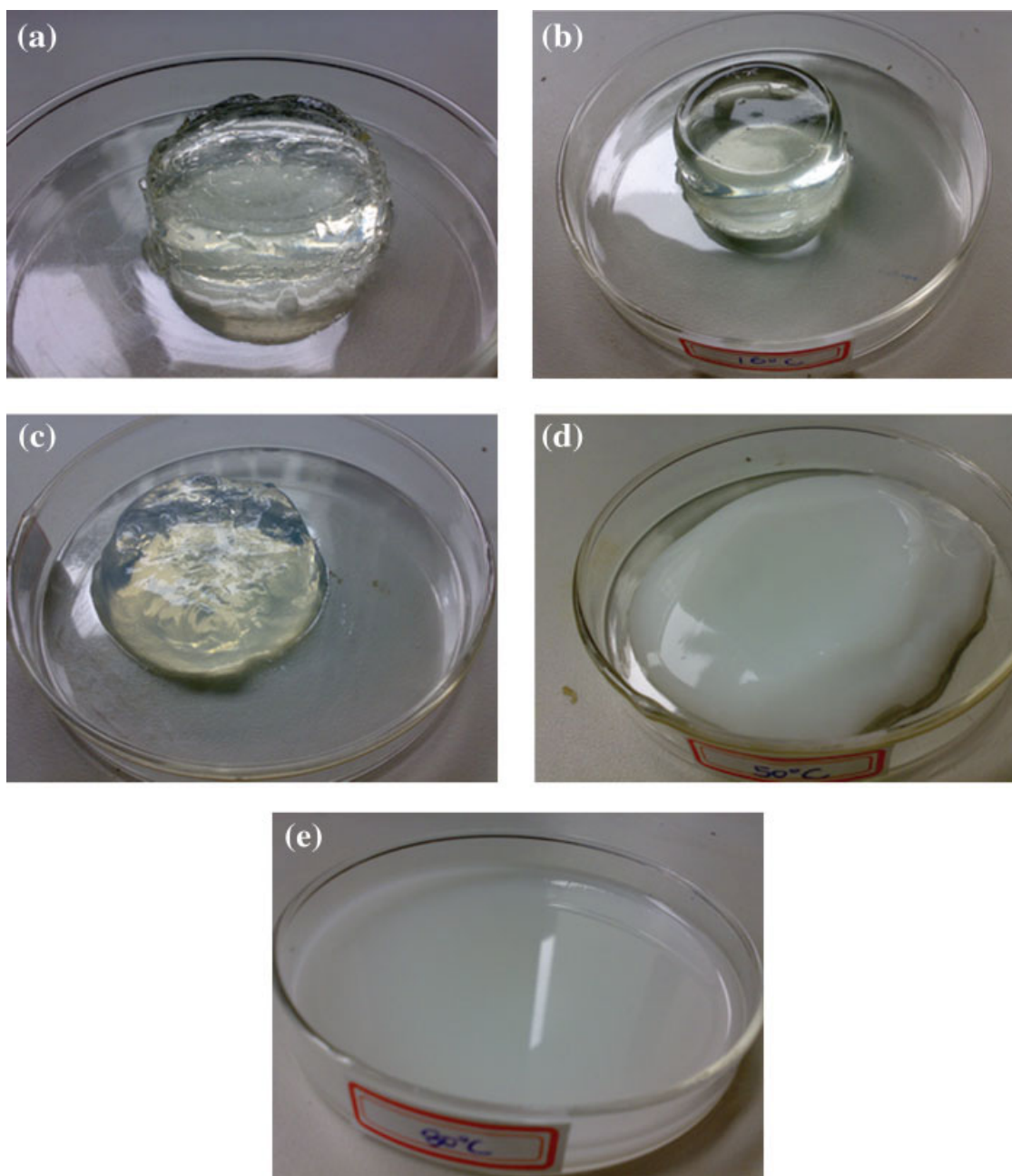


Figure 1 Photographs taken for the PNiPAAm-*co*-SA hydrogels after polymerization of (a) G_0 (b) G_{16} (c) G_{35} (d) G_{50} (e) G_{80} (from left to right) at room temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

water were further investigated for determining the response rate of the hydrogels upon temperature cycling. The well-swollen hydrogel samples were first immersed in deionized water at 50°C and showed shrinking behavior. After 5 min, the samples were taken out and the excess surface water was removed and weighed quickly. Then the samples were transferred back to 18°C for another 5-min swelling and weighed. The 10-min cycle was continued for several cycles to determine the oscillatory deswelling–swelling kinetics of the hydrogels.

RESULTS AND DISCUSSION

Observation of hydrogels

The PNiPAAm-*co*-SA hydrogels were fabricated under the same synthesis conditions except at different synthesis temperature. The gels G_0 and G_{16} were appeared to be transparent and had compact shapes. G_0 was the tightest in structure with poor flexibility and harder to break. Compared to G_0 in appearance, G_{16} retained a smooth surface even after cutting, and had better flexibility. The gel G_{35} was a bit cloudy in

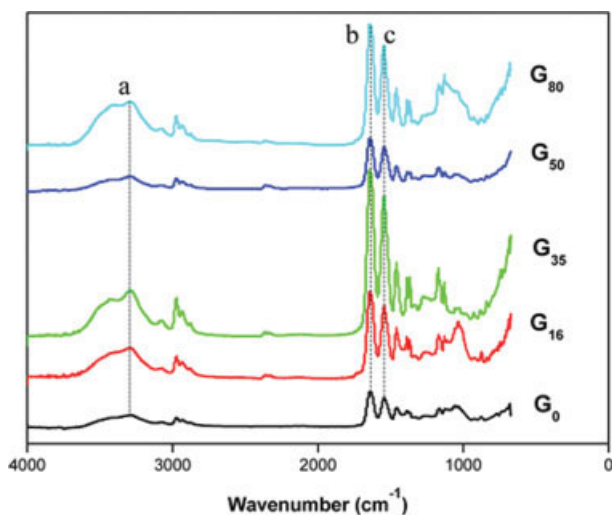


Figure 2 FTIR spectra of the PNiPAAm-*co*-SA hydrogels G_0 , G_{16} , G_{35} , G_{50} , and G_{80} . (a) 3100–3700 cm^{-1} , (b) ~ 1650 cm^{-1} and (c) 1550 cm^{-1} . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

transparence and the shape of gel cannot be retained as well as G_0 and G_{16} because of its loose structure. The gel G_{50} was opaque in appearance, and could not keep the shape. At 80°C, the transparent pregel solution became opaque after polymerization, and no gel-like substance was obtained, as a result, G_{80} was excluded in the following test. It could be explained that when the polymerization temperature was much higher than the LCST of gels, the gel forming stage was destroyed. G_0 and G_{16} were transparent, whereas G_{35} and G_{50} became translucent and opaque, indicating that their network structure may be heterogeneous.¹⁶ Figure 1 presented the optical photos of G_0 , G_{16} , G_{35} , G_{50} , and G_{80} , respectively.

FTIR

The FTIR spectra of PNiPAAm-*co*-SA hydrogels were displayed in Figure 2. The spectra of different hydrogels were similar. Each spectrum showed a broad band in the range of 3100–3700 cm^{-1} , which belonged to N–H stretching vibration. The typical amide I and II bands in the NiPAAm were evident at ~ 1650 and 1550 cm^{-1} . The similar spectra of different hydrogels proved that the synthesis temperature had less effect on the chemical structure of PNiPAAm-*co*-SA hydrogels.

Swelling ratio under different temperatures

Figure 3 showed the temperature-dependent swelling ratio of the PNiPAAm-*co*-SA hydrogels G_0 , G_{16} , G_{35} , G_{50} , and the pure PNiPAAm gels. G_{35} exhibited strong swellability with the swelling ratio r up to

260 and 2–6 times greater than other gels. From the phenomena of the hydrogel dramatically deswelling and color changing from transparent to opaque around the LCST, the LCST of G_0 , G_{16} , and G_{35} were defined at the range of 34–36°C. Consequently, the synthesis temperature at 35°C was just around the LCST in the polymerization. It should also be noticed that the polymerization of NiPAAm was an exothermic reaction and increase of temperature of 3–5°C can be observed,¹⁶ which made the actual synthesis temperature a litter higher than LCST. The strong swellability of G_{35} was believed to attribute to the microscale phase-separated structure when heating the solution above the LCST during polymerization. Consequently, the heterogeneity of the gels was enhanced due to the incipient thermal phase separation and the gels became cloudy.¹⁴ The microporous structures arising from the phase separation techniques resulted in the strong swellability of the obtained hydrogels. The LCST of PNiPAAm-*co*-SA hydrogels was affected by the introduction of SA comonomer, which enhanced the hydrophilicity of gels and made the LCST higher than pure PNiPAAm gels.

From Figure 3, we can see that the swelling ratio of the PNiPAAm-*co*-SA hydrogels increased with the increasing synthesis temperature. G_{16} showed better swellability than G_0 . G_{50} had the worst swellability during the test. As a result, when the synthesis temperature was much above the LCST, the swellability of hydrogels was affected strongly. It was believed that the reaction between NiPAAm and SA was affected strongly when the synthesis temperature at 50°C, and accordingly affected the swellability of the hydrogels. The swelling ratio of G_{50} was close to pure PNiPAAm gels with the swelling ratio only

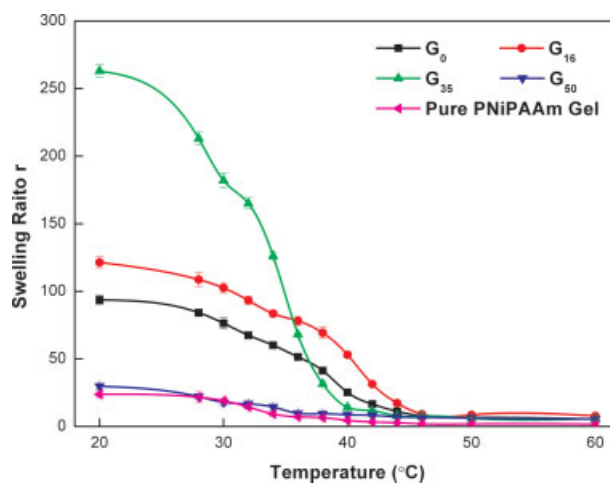


Figure 3 Temperature dependence of swelling ratio of the PNiPAAm-*co*-SA hydrogels over the temperature from 20 to 60°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

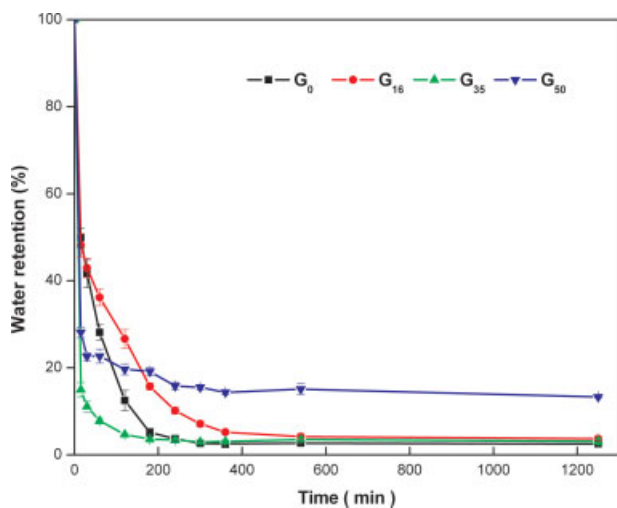


Figure 4 Deswelling kinetics of the PNiPAAm-*co*-SA hydrogels at 50°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

about 20–30. The introduction of small quality of hydrophilic comonomer SA enhanced the swellability of NiPAAm gels dramatically.^{17,18}

Deswelling kinetics

Figure 4 presented the deswelling kinetics of the PNiPAAm-*co*-SA hydrogels G_0 , G_{16} , G_{35} , and G_{50} after transferring the equilibrated swollen hydrogels at room temperature (18°C) to hot water at 50°C. G_{35} gels responded to the temperature increment much faster than other gels. For example, after 15 min at 50°C, G_{35} shrank and lost 85% water. In contrast, G_0 , G_{16} , and G_{50} lost about 50, 52, and 72% water at the same condition. The fast response rate of G_{35} was contributed by the microporous structure of gels,

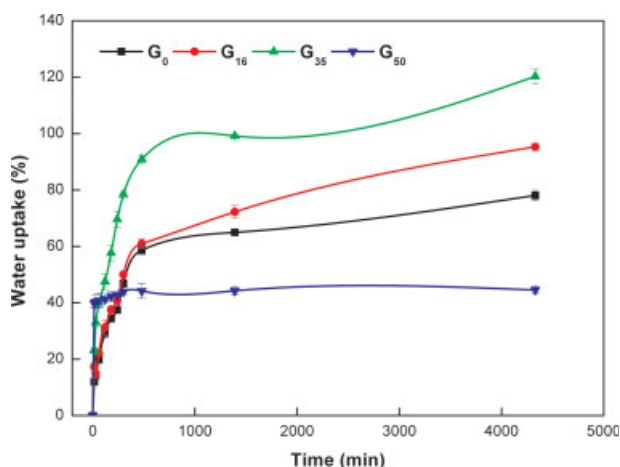


Figure 5 Swelling kinetics of the PNiPAAm-*co*-SA hydrogels at 18°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and consequently, the interior water in gel was easy to lose. The same reason can be applied to G_{50} , although it had poor swellability. G_0 responded to the temperature a little faster than G_{16} . Observation during the deswelling process showed that the skin layer of G_0 was easier to be broken than G_{16} .

Swelling kinetics

Figure 5 showed the swelling kinetics of the PNiPAAm-*co*-SA hydrogels G_0 , G_{16} , G_{35} , and G_{50} after transferring the equilibrated swollen hydrogels at 50°C–18°C. G_0 and G_{16} exhibited similar water uptake capacity during the first 500 min, and G_{35} was the largest one in magnitude, and they all exhibited ascending water uptake ability gently. G_{16} had a slightly better water uptake capacity than G_0 , which would account for the higher swelling ratio of G_{16} than G_0 caused by the higher synthesis temperature. G_{50} nearly showed no change of the water uptake during the tests. In this test, we observed that, for dehydrated G_{35} at 50°C, it had relatively poor water uptake capacity when compared with its swellability from the original state, which could be the tight, comparatively dry structure caused by deswelling, which made the skin layer was hard to break and could not revert to the quite loose structure that contained a large amount of water at the original equilibrated state. The results indicated that the fast responseability of G_{35} was not totally thermoreversible, and the microporous structure of the gels was easy to lose water and comparatively hard to absorb water after dry, but G_{35} still had the fast responseability when compared with other gels in this experiment.

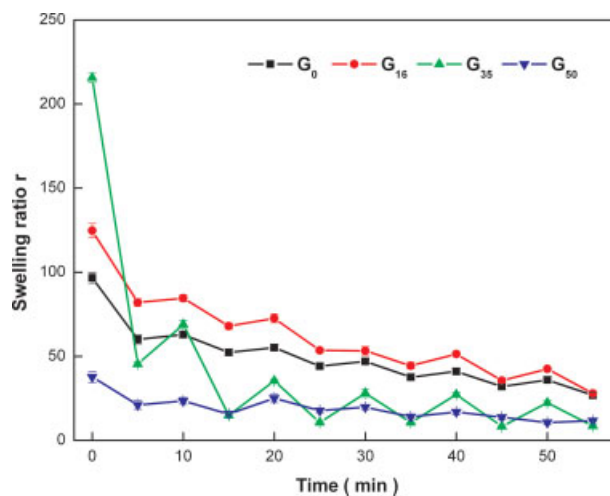


Figure 6 Deswelling–swelling kinetics of the PNiPAAm-*co*-SA hydrogels over 10-min temperature cycles in deionized water between 18 and 50°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Deswelling–swelling kinetics

The deswelling–swelling kinetics of the PNiPAAm-*co*-SA hydrogels G_0 , G_{16} , G_{35} , and G_{50} was investigated over the 10-min temperature cycle between 18°C (<LCST) and 50°C (>LCST) in deionized water for five cycles, and the data are shown in Figure 6. The hydrogel samples were swollen to equilibrium before test. The cycle started the first 5 min at the temperature of 50°C and finished the second 5 min at the temperature of 18°C. The data showed that G_0 , G_{16} , and G_{35} exhibited a successive reduction in the swelling ratio because of their relatively slow reswelling rate when compared with their deswelling rate. When compared with G_0 and G_{16} , G_{35} showed much rapid, sharper, and larger deswelling–swelling changes, and there was not much difference between G_0 and G_{16} . G_{50} did not exhibit much change in the deswelling–swelling kinetics, which confirmed that the effect of the synthesis temperature on the properties of the PNiPAAm-*co*-SA hydrogels was strong.

CONCLUSIONS

To improve the swellability of the NiPAAm hydrogels, small amount of anionic sodium acrylate was added without changing the thermosensitivity of NiPAAm hydrogels. The gels displayed strong swelling capacity with the LCST at 34–36°C and the swell-

ing ratio r was dramatically increased when compared with pure NiPAAm gels. On the basis of the NiPAAm-SA gel system, the phase separation techniques were employed to obtain fast responsive hydrogels. The results proved that the resulting hydrogels exhibited fast response rate and strong swellability when compared with other gels.

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