# Temperature-Sensitive Poly(*N-tert*-butylacrylamide-*co*-acrylamide) Hydrogels Bonded on Cotton Fabrics by Coating Technique

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**ABSTRACT:** Different from the conventional method of developing stimuli-sensitive textiles by graft copolymerization of environmental responsive polymers onto the fabric, the coating technique was applied to bond temperature-sensitive hydrogels with cotton fabric through chemical covalent in our work. A temperature-sensitive linear copolymer of *N-tert*-butylacrylamide (NTBA) and acrylamide (AAm) was prepared in methanol. Then, the cotton fabrics were coated using an aqueous solution of this copolymer containing 1,2,3,4-butanetetracarboxylic acid as a crosslinker and sodium hypophosphite (SHP) as a catalyst, followed by drying and curing. The surface of the cotton fabrics was bonded on more or less coatings of poly(NTBA-*co*-AAm) hydrogels, as verified by Fourier transform infrared spectroscopy and scanning electron microscopy images. The poly(NTBA-*co*-AAm) hydrogels-coated fabrics exhibited temperature sensitive, and the tempera-ture interval of the deswelling transition was higher than lower critical solution temperature of linear copolymer solution. The coated fabrics presented good water-impermeable ability because of the swelling of hydrogels bonded, especially when the add-on was as high as 14.14%. Environmental scanning electron microscopy images revealed that coating hydrogels swelled and covered on the surface as a barrier to prevent water from penetrating once the coated fabric came into contact with water. The findings demonstrate that the temperature-sensitive hydrogels can be covalently bonded on the cotton fabrics by coating technique and the coated fabrics have potential on immersion fabrics. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2656–2662, 2009

**Key words:** stimuli-sensitive polymers; hydrogels; coatings; swelling; composites

## INTRODUCTION

Immersion suit protects a wearer against environments characterized by the wet and extremely cold temperature, which is absolutely needed by aviation and navigation personnel and others working in situation requiring exposure to the sea water. It was reported that people in immersion suit have been rescued after as much as 18 h in the Atlantic Ocean; without them, survival can often be measured in minutes. To keep the skin of drowning people from direct contact with cold water, the outer layer of immersion suits must be water-proof. Neoprene-coated cloth, high-density cotton fabrics, microporous membrane-laminated or coated fabrics, and hydrophilic polyurethane-coated fabrics are several kinds of immersion fabrics. However, all of them cannot be responsive to the environment, namely not intelligent. To improve the function of immersion fabrics, a novel concept of developing intelligent composites based on stimuli-sensitive polymers as immersion fabric was presented.

Hydrogels are three-dimensional polymer networks, which can swell by absorbing water between 10 and 1000 g per gram of dry gels. Certain temperature-sensitive hydrogels can swell in water at low temperatures but shrink as the temperature rises above the phase transition temperature, which has recently attracted a great deal of research interest. In particular, poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogels have found many important applications in controlled drug delivery,[1–4] separation membranes,[5,6] immobilization of enzymes,[7,8] and artificial muscles.[9] However, these hydrogels have poor mechanical strength, especially after swelling, which limits their applications. Incorporation of such polymers on the surfaces of conventional textiles would give enough strength and greatly reduced response time because of the high surface areas associated with fibers. Surface grafting of the fabric is a popular method to develop the modified textiles with temperature sensitivity,[10–24] which can be induced by ultraviolet light,[10–14] electron beam preirradiation,[15,16] γ preirradiation,[17] chemical initiator,[14,18–22] ozone,[23] and microwave plasma.[24] But the grafted

samples are usually not big enough to serve as dressing or technical textiles, and production in enormous quantities is not easy by grafting.

Compared to grafting method, coating technique is more convenient and feasible to crosslink stimuli-sensitive polymers with fibers. Because of the characteristics of swelling and deswelling in response to the environment temperature, temperature-sensitive hydrogels are selected as the coatings of fabric in this work; the coated fabrics obtained are desired to have good water-impermeable ability once they contact with cold water, and actively regulate water permeability because of the hydrogels swelling or deswelling according to the water temperature. In view of these facts, in this study, a temperature-sensitive linear copolymer of *N-tert*-butylacrylamide (NTBA) and acrylamide (AAm) was prepared and applied to the cotton fabrics in the presence of a crosslinker to produce hydrogels-coated fabrics by coating technique. The temperature response, surface morphology, and water-impermeable ability of the coated fabrics were also investigated.

## EXPERIMENTAL

### Materials

*N-tert*-butylacrylamide (97%+) was purchased from Alfa Aesar China (Tianjin), China. 1,2,3,4-Butanetetracaboxylic acid (98%+) (BTCA) was supplied by Changzhou Chemical Research Institute, China. Acrylamide, *N,N'*-methylenebisacrylamide (MBA), ammonium persulfate (APS), methanol, acetone, and sodium hypophosphite were all analytical grade. All reagents were used without further purification.

The fabrics used in this study were desized, scoured, and bleached cotton poplin.

### Synthesis of copolymer hydrogels and linear copolymer

The synthesis of poly(NTBA-*co*-AAm) was carried out in methanol, at 50°C in the presence of 0.3 mol % APS (with respect to the total monomers). The monomer concentration was fixed at $1M$ and the monomer feed composition was 50 mol % NTBA. Dry nitrogen was bubbled through the solution for 15 min before polymerization. Both copolymer hydrogels and linear copolymer were prepared. For the hydrogels, MBA (1.3 mol %) was used along with monomers. After 24-h polymerization, the reaction was stopped by cooling the reaction mixture.

The crude hydrogels were freed from the glass tube and cut into samples of about 2–3 mm length. Then, the samples were purified and dried at 50°C under vacuum to constant weight. The viscous reaction mixtures without MBA were precipitated in ace-tone while stirring vigorously. The purified linear copolymer obtained was dried in a vacuum oven at 50°C to constant weight.

### Coating of fabrics

The purified and dried linear copolymer was dissolved in distilled water by stirring for 30 min to prepare an 8.0 wt % solution. The required amount of crosslinker BTCA (2.3 wt %) and the catalyst SHP (2.2 wt %) were added to this polymer solution. Then, the mixtures were left in the refrigerator for 24 h for deaeration and further dissolving to obtain a viscous, clear, and homogeneous solution. The cotton fabrics were coated with the aforementioned solution and dried at 120°C for 5 min and cured at 200°C for 2 min in the drying oven. Different samples were prepared with double, triple, and four coatings. The coated sample was dried following each coating and cured only after the final coating was dried.

The coated fabrics were rinsed with distilled water to remove the unreacted impurities. For further purification, the fabrics were immersed in water at room temperature for 3 days with water being replaced many times. The obtained fabrics were dried at 80°C and then put into the desiccators for the next testing.

The add-on (A) of the coated fabrics was calculated using the following equation:

$$A = \frac{w_1 - w_0}{w_0} \times 100\% \qquad (1)$$

where $w_0$ and $w_1$ are the weight of the original and the coated cotton fabrics sample, respectively.

### Determination of transition temperature for the linear copolymers and the coated fabrics

Solutions of the linear copolymers were made at the concentration of 8.0 wt %. The lower critical solution temperature (LCST) was determined by optical transmittance at 500 nm through a 1-cm sample cell referenced against distilled water, using a 723 VIS spectrophotometer. The sample cell and the referenced cell were heated at the regulated temperature in a water bath before testing. The LCST was defined as the temperature corresponding to a 10% reduction in the original transmittance of the solution.

For the coated fabrics, the gravimetric method was employed to study the temperature sensitivity. The fabric samples were left at each predetermined temperature in the thermostatic bath until the equilibrium was achieved. They were taken out from the water and gently blotted with wet filter paper to remove surface water, followed by immediate

weighing. The equilibrium swelling ratio (ESR) was determined as:

$$\mathrm{ESR} = \frac{W_e - W_d}{W_d} \qquad (2)$$

where $W_e$ denotes the weight of coated fabric at equilibrium, and $W_d$ is the dry weight of coated fabric.

## Fourier transform infrared spectroscopy

The Fourier Transform Infrared Spectroscopy (FTIR) spectra of copolymer hydrogels, linear copolymer, and coated fabric were recorded on a Bruker Vector 22 Spectrometer. The hydrogels and the fabric sample were in ATR mode. However, the linear copolymer sample used the KBr pellet technique.

## Water-impermeable ability

The water-impermeable ability of the coated fabrics was measured using the water flow rate (WFR). WFR measurement was carried out using the WFR measuring device as well as the method reported by He and Gu.[25] WFR can be calculated according to the following equation:

$$\mathrm{WFR} = V/(tS) \qquad (3)$$

where WFR is the water flow rate (mL m$^{-2}$ s$^{-1}$), $V$ is the volume of the collected water (mL), $t$ is the water collected time (s), and $S$ is the effective size of the sample (0.00237 m$^2$).

## Scanning electron microscopy and environmental scanning electron microscopy

The surface of the original fabric and coated samples was studied with the help of scanning electron microscopy (SEM) (FEI Quanta 200 model). Thin layer gold was sputtered on the sample surface before the SEM measurement, and the images were collected at an accelerating voltage of 20 kV.

The cross sections of the dry and wet coated samples were investigated with environmental scanning electron microscopy (ESEM) (FEI Quanta 200 model). The samples were put into the sample chamber without spraying gold on the surface. Then, the chamber was closed immediately and deaerated to a desired pressure. The ESEM images were collected at an accelerating voltage of 30 kV.

## RESULTS AND DISCUSSION

## Surface morphology

The cotton fabrics were coated with the solution of the temperature-sensitive linear copolymer of NTBA and AAm in the presence of SHP and BTCA. BTCA

is generally used as nonformaldehyde crosslinking agent of the durable press finished cotton fabrics, which has four carboxylic acid groups and can make cellulose esterified and crosslinked with the help of catalyst SHP.[26] The esterification reaction between carboxyl groups of BTCA and hydroxyl groups of cellulose molecules generally occurs at elevated temperatures. So, the coated cotton fabrics were dried at 120°C, then cured at 200°C in order that the esterification occurred.

It is observed that the cotton fabrics' stiffness and weight are increased after being coated. More coatings can give higher add-ons. Because the coated fabrics have been treated by rinsing and immersing with water adequately, the left coatings bonded on the cotton fabrics are insoluble in water.

To make it clear how the coatings exist, the surface morphology of the original and coated fabric samples was examined by SEM (Fig. 1).The SEM images reveal that the original fabric appear smooth, and the coated fabric samples with add-on of 0.98 and 3.17% are clearly seen that there are irregular fragments on the fiber surface or in the intervals of fibers. At such a low add-on level, the twisted ribbon form of cotton fibers is still observable. As the add-on reached 8.08%, the fibers are covered with thicker and evener coatings layer and become more cylindrical, which make fibers seem to merge together and this phenomenon becomes more obvious for the coated fabric with add-on of 14.14%. Some fibers are nearly invisible for being covered by coatings, and the intervals of cotton fabrics were reduced or blocked after being coated.

The cross section morphology of the coated fabric with add-on of 14.14% in dry and swelling are exhibited in Figure 2(a,b), respectively. ESEM images can directly and vividly demonstrate the surface morphology of the samples with water. Comparing the dry fabric composites in Figure 2(a) and the fully swelled composites in Figure 2(b), it can be observed that the layer thickness has been increased and the hydrogels with honeycomb structure are formed. The hydrogels can absorb water and swell until the equilibrium is achieved. For the composites, when the coatings of hydrogels swelled in equilibrium, the surface is covered with thick hydrogel coatings.

## FTIR characterization

NTBA is the most hydrophobic monomer among the N-substituted AAms,[27] which can be used to modify the LCST of temperature-sensitive polymer solution or gels. The hypothetical LCST value of homopolymer of PNTBA is determined as about $-5$°C.[27] While AAm is a highly hydrophilic monomer that PAAm does not show the LCST temperature until the boiling point of water. The AAm has an amide
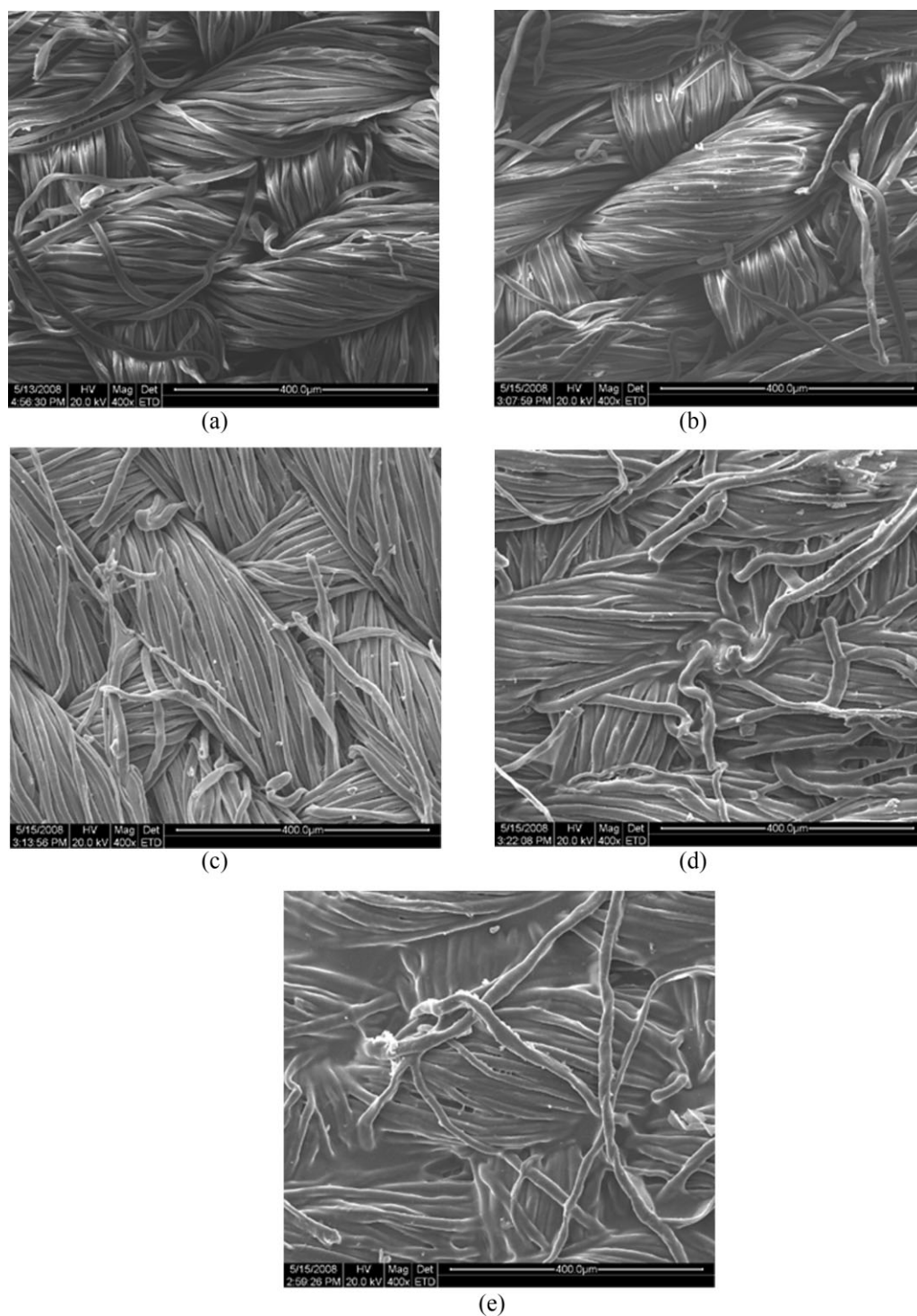
**Figure 1** SEM images of (a) original cotton fabric and coated fabrics with add-on of (b) 0.98%, (c) 3.17%, (d) 8.08%, (e) 14.14%, magnification ×400.

side group, which has certain reactivity and may be utilized for crosslinking reaction, which was verified by Save et al.[28] So, the linear copolymer of NTBA and AAm has the ability to react with some crosslinker and the possibility of linear copolymer translated into three-dimensional structure.

The FTIR spectra of the linear polymer, crosslinked hydrogels, and the coated cotton fabric with add-on of 14.14% were presented in Figure 3. As shown in Figure 3(a), the characteristic absorption peaks of NTBA units are shown at 1225 and 1365 cm$^{-1}$ because of the —C(CH$_3$)$_3$,[29] which indicates that the linear polymer is the copolymer of AAm and NTBA. Obviously, the characteristic absorbance bands in Figure 3(b,c) are identical to that in Figure 3(a). Because the unreacted linear copolymers are
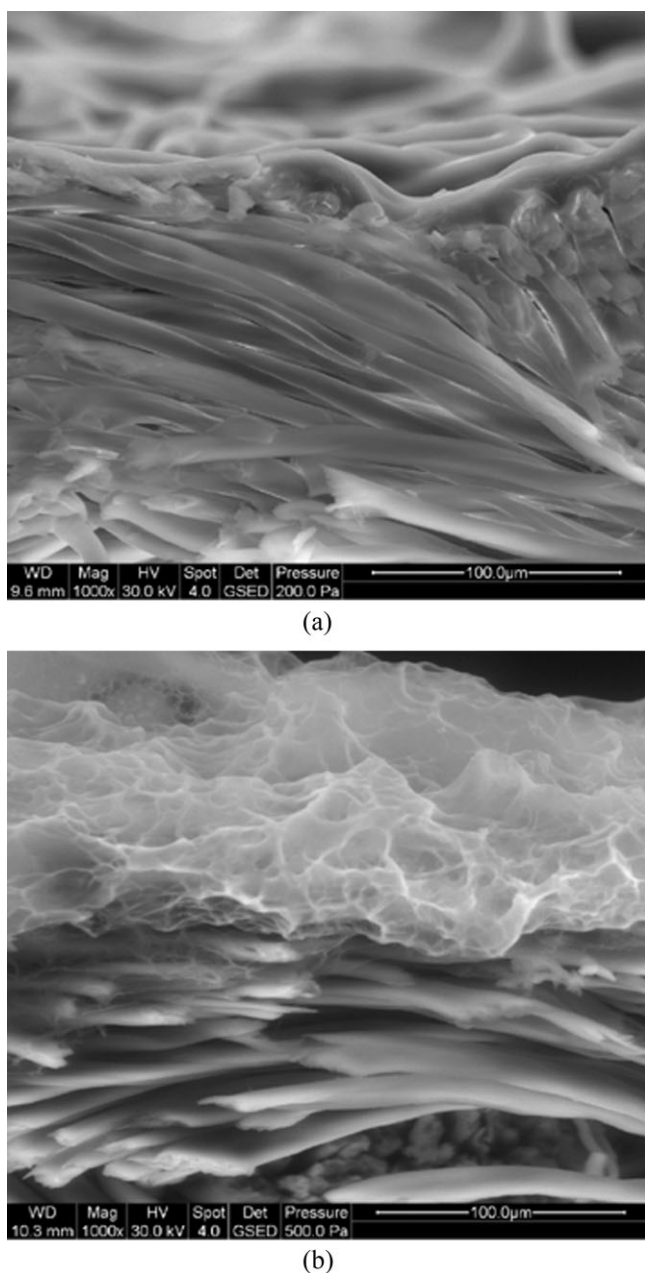
(a)



(b)

**Figure 2** ESEM images (cross section) of the composites with add-on of 14.14%, magnification ×1000 (a) dry composites, (b) fully swelled composites.

dissolved in water and have been removed from the coated fabrics by the purified treatment, the insoluble coatings were crosslinked poly(NTBA-*co*-AAm) hydrogels and covalently bonded on the cotton fabrics.

ESEM images of the coated fabric in Figure 2 give more information to confirm that three-dimensional hydrogels formed in the coating process. The mechanism is assumed that the ─COOH of BTCA reacts with the ─NH$_2$ of the linear poly(NTBA-*co*-AAm), thus the hydrogels without dissolving in water are formed after curing at high temperature. The FTIR

spectra of the coated fabric do not give the sufficient information in this study to prove the esterification between the ─COOH of BTCA and the ─OH of cellulose. However, the hydrogels can be bonded with the fabric after immersing and washing many times, which itself is an evidence for the reaction of BTCA and cellulose.

**Temperature response**

This study aimed to develop an intelligent fabric with temperature sensitivity. The response of the linear poly(NTBA-*co*-AAm) and the coated fabric with add-on of 14.14% with respect to temperature are shown in Figures 4 and 5, respectively. The LCST of aqueous solution of poly(NTBA-*co*-AAm) (8.0 wt %) is determined to be about 28.2°C. For the coated fabrics with add-on of 0.98, 3.17, and 8.08%, the obvious temperature sensitivity is not observed in this study because the coatings weight are much smaller than that of the fabrics, that the weight changes are not significant. However, as shown in Figure 5, with a high add-on of 14.14%, the fabric is
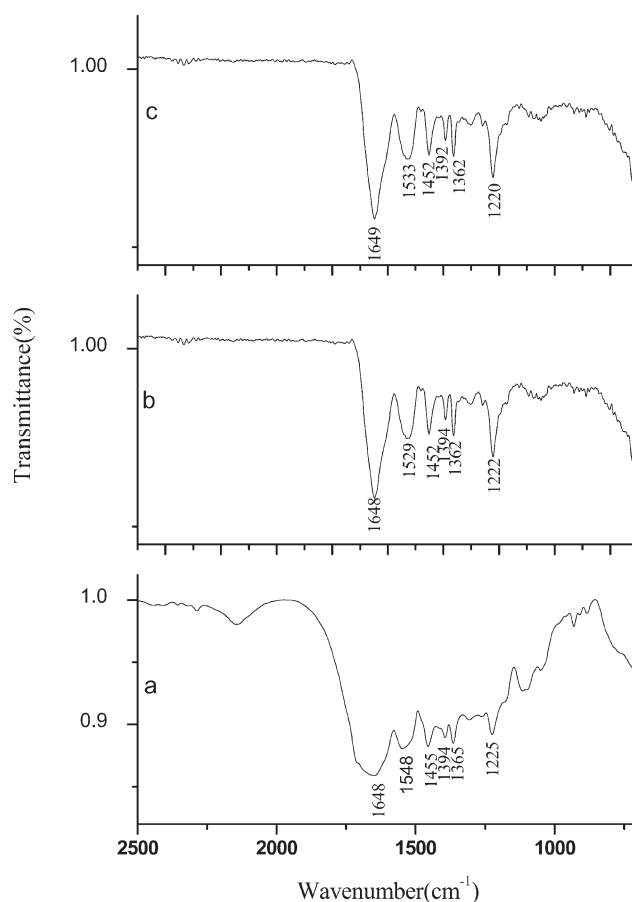


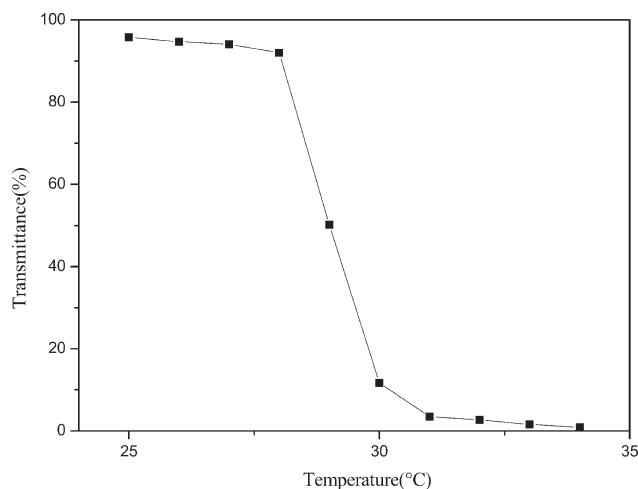**Figure 3** FTIR spectra of (a) linear polymer, (b) crosslinked hydrogels, (c) coated fabric with add-on of 14.14%.

**Figure 4** LCST determination of poly(NTBA-*co*-AAm) by optical method.



**Figure 6** Effect of add-on on the water-impermeable ability of the coated fabrics. Water temperature, $10°C \pm 1°C$ and measurement interval 15 s.

found to be temperature responsive. The onset temperatures of the phase transition begin near 32°C, with deswelling occurring between 32 and 60°C. The peak appeared at 28°C was possibly because of the operating error when blotting the samples' surface water with wet filter paper. The transition temperatures are higher and broader than that of the linear polymer solution. The reason may be ascribed to the more hydrophilic groups and the heterogeneous composition of the coating structure.

The occurrence of the broad transition temperature range is similar to that observed for grafted PNIPAAm on cellulose substates.[18] In grafted samples, the transition temperature was reported as the temperature range of 28–40°C, compared with the sharp transition observed in PNIPAAm hydrogels (at 32°C).
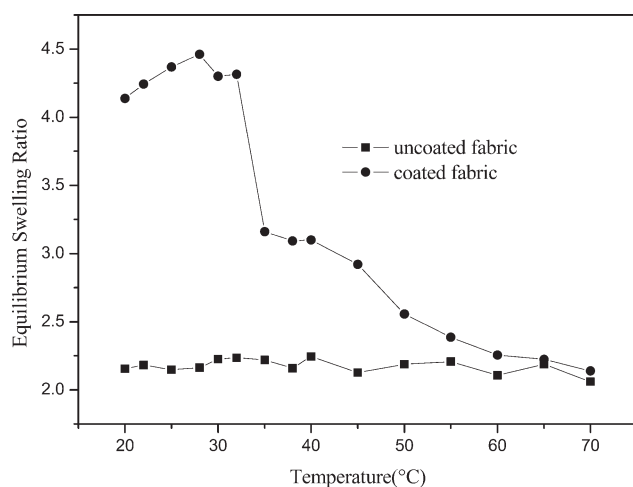


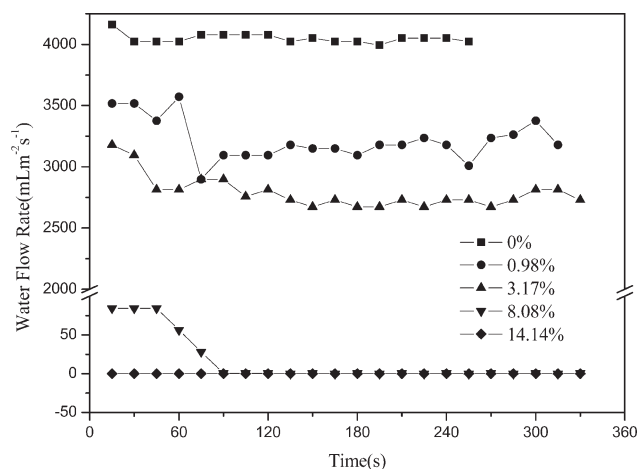**Figure 5** The ESR of fabric as a function of temperature.

## Water-impermeable ability

To evaluate the water-impermeable ability of coated cotton fabrics, the WFR of the samples was measured. Figure 6 exhibits the variation of WFR with time. WFR is defined as the volume of the water passing through fabrics with unit area in unit time. Obviously, lower WFR value presents better water-impermeable ability. The water temperature is 10°C $\pm$ 1°C, which is under the transition temperature of the composite samples and the hydrogels can swell at this temperature. As shown in the Figure 6, for the original fabric (0%), the WFR is nearly a constant after 15 s. But for the coated fabrics, the WFR decreases sharply with time at the beginning and tends to level off. Obviously, the WFR of the fabrics decreases with increasing add-on. Especially, when the add-on is 8.08%, there is a sharp reduction from 45 to 90 s, then the WFR kept 1.41 mL m$^{-2}$ s$^{-1}$, that is, about 0.5 mL flowed out in 15 s, finally even a drop in 30 s. For the add-on of 14.14%, there are only three to four drops penetrated and no water flowing out during the testing time even after a much longer time, for example 20 min. The WFR decreases drastically from 60 to 75 s for the coated sample with add-on of 0.98%, which was ascribed to the operating error in the experiment because the water flowed out was collected manually.

The changing of WFR with time implies that the coated fabrics could interact with water and then affect water penetrating. This interaction reaches a balance after a certain time and can be attributed to the incorporation of the hydrogel coatings onto the substrate, which absorb a large amount of water and swell so that the intervals between fibers and yarns are reduced. This is the reason that WFR of the coated fabric decreases with time. When the

hydrogels' swelling reaches equilibrium, the intervals keep constant so the WFR tends to level off. For the high add-on of 14.14%, large amounts of poly (NTBA-*co*-AAm) hydrogels are bonded on the fabric that most pores are blocked [Fig. 1(e)]. So, there is not water flowing out but several water drops penetrated from the initial measurement time. However, hydrogels absorb much water after being contact with water for a while. The swelled hydrogel coatings cover the fabrics surface [Fig. 2(b)] and become a thick barrier for water, which is benefit for maintaining the good water-impermeable ability. The coated fabric has the ability to prevent water from penetrating when the add-on is high as 14.14%. The water-impermeable ability is a prerequisite for the immersion suits, so the hydrogels-coated fabrics have the potential to be as the immersion suits.

However, the coated fabrics are desired as immersion fabrics where there is exposure to sea water. There are about 35 g salts per kg sea water and most salts are NaCl. In our previous work, the effect of salts on the swelling behavior of the poly(NTBA-*co*-AAm) hydrogels alone has been studied and the results showed that the swelling ratio decreased when NaCl concentration increased. Osmotic pressure π of a gel determines whether the gel tends to expand or shrink. More salts in water, the lower π; so, the sea water would inhibit the hydrogels swelling. The effect of sea water on the hydrogels bonded on the fabrics and the water-impermeable ability of the hydrogels composites will be investigated in next work.

## CONCLUSIONS

Temperature-sensitive linear poly(NTBA-*co*-AAm) could be translated into three-dimensional hydrogels and bonded on the cotton fabrics by coating technique. The add-on of the coated fabrics was dependent on the coating layers. At lower add-on, only a small amount of poly(NTBA-*co*-AAm) was bonded on the surface of the fabrics; at higher add-on, the fibers are covered with thicker and evener coatings layer. The coated fabric with higher add-on exhibits obvious temperature sensitivity, with a broad transition temperature range of 32–60°C, which is higher than the linear copolymer (28.2°C). It was found that the water-impermeable ability of the coated cotton fabrics was greatly improved. Especially, when the add-on was high as 14.14%, the fabrics composites can prevent water passing through. The hydrogels bonded could absorb water and swell immediately, so the intervals of coated cotton fabric were reduced

greatly or blocked. Furthermore, the swelled hydrogels layer seems to be a barrier for water, which is benefit for maintaining good water-impermeable ability. This kind of coated fabric has been called intelligent fabric not only because it is temperature sensitive but also it encounters water and provides a novel water-impermeable ability. The temperature-responsive poly(NTBA-*co*-AAm) hydrogels-coated fabrics hold a great potential as immersion suits and other temperature-sensitive fabrics with tunable water flow.

## References

1. Hsiue, G.-H.; Hsu, S.-H.; Yang, C.-C.; Lee, S.-H.; Yang, I.-K. Biomaterials 2002, 23, 457.
2. Zhang, X.-Z.; Wu, D.-Q.; Chu, C.-C. Biomaterials 2004, 25, 3793.
3. Zhang, X.-Z.; Lewis, P. J.; Chu, C.-C. Biomaterials 2005, 26, 3299.
4. Lim, Y. H.; Kim, D.; Lee, D. S. J Appl Polym Sci 1997, 64, 2647.
5. Guilherme, M. R.; Silva, R.; Rubira, A. F.; Geuskens, G.; Muniz, E. C. React Funct Polym 2004, 61, 233.
6. Wang, W. Y.; Chen, L. J Appl Polym Sci 2007, 104, 1482.
7. Sun, Y.-M.; Chen, J.-P.; Chu, D.-H. J Biomed Mater Res 1999, 45, 125.
8. Chen, J.-P.; Chu, D.-H.; Sun, Y.-M. J Chem Technol Biotechnol 1997, 69, 421.
9. Li, Y.; Hu, Z.; Chen, Y. J Appl Polym Sci 1997, 63, 1173.
10. Chen, K. S.; Tsai, J. C.; Chou, C. W.; Yang, M. R.; Yang, J. M. Mater Sci Eng C 2002, 20, 203.
11. Chen, K. S.; Ku, Y. A.; Lee, C. H.; Lin, H. R.; Lin, F. H.; Chen, T. M. Mater Sci Eng C 2005, 25, 472.
12. Chen, K. S.; Ku, Y. A.; Lin, H. R.; Yan, T. R.; Sheu, D. C.; Chen, T. M. J Appl Polym Sci 2006, 100, 803.
13. Kuwabara, S.; Kubota, H. J Appl Polym Sci 1996, 60, 1965.
14. Kubota, H.; Shiobara, N. React Funct Polym 1998, 37, 219.
15. Lopérgolo, L. C.; Catalani, L. H.; Aachado, L. D. B.; Rela, P. R.; Lugão, A. B. Radiat Phys Chem 2000, 57, 451.
16. He, C. C.; Gu, Z. Y. J Appl Polym Sci 2003, 89, 3931.
17. Liu, J. Q.; Zhai, M. L.; Ha, H. F. Radiat Phys Chem 1999, 55, 55.
18. Xie, J. B.; Hsieh, Y.-L. J Appl Polym Sci 2003, 89, 999.
19. Hu, J. L.; Liu, B. H.; Liu, W. G. Text Res J 2007, 76, 853.
20. Lee, M. H.; Yoon, K. J.; Ko, S.-W. J Appl Polym Sci 2000, 78, 1986.
21. Loría, M.; Carrillo, H.; Aguilar, M. J Appl Polym Sci 2002, 83, 368.
22. Liu, H. Q.; Hsieh, Y.-L. J Polym Sci Part B: Polym Phys 2003, 41, 953.
23. Karlsson, J. O.; Andersson, M.; Berntsson, P.; Chihani, T.; Gatenholm, P. Polymer 1998, 39, 3589.
24. Ma, X.-G.; Cui, G.-X.; Dong, S.-W. J Text Res 2006, 27, 13 (in Chinese).
25. He, C. C.; Gu, Z. Y. J Appl Polym Sci 2003, 89, 3939.
26. Wei, W. S.; Yang, C. Q. Text Res J 1999, 69, 145.
27. Liu, H. Y.; Zhu, X. X. Polymer 1999, 40, 6985.
28. Save, N. S.; Jassal, M.; Agrawal, A. K. J Ind Text 2002, 32, 119.
29. Ozturk, V.; Okay, O. Polymer 2002, 43, 5017.