

Article

Synthesis and Thermosensitive Behavior of Polyacrylamide Copolymers and Their Applications in Smart Textiles

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Abstract: We tuned the lower critical solution temperature (LCST) of amphiphilic poly(*N*-isopropylacrylamide) (PNIPAAm) via copolymerization with a hydrophilic comonomer of *N*-hydroxymethyl acrylamide (NHMAAm). A series of copolymers P(NIPAAm-*co*-NHMAAm) were synthesized by atom transfer radical polymerization (ATRP) using CuBr/(*N,N,N',N',N''*-Pentamethyldiethylenetriamine) (PMDETA) as a catalyst system and 2-bromo ethyl isobutyrate (EBiB) as an initiator. The copolymers were well characterized by Fourier transform infrared spectroscopy (FT-IR), ¹H Nuclear magnetic resonance (NMR), and Thermogravimetric analysis (TGA). The copolymers followed a simple rule in their thermosensitive behaviors and have a linear increase in the LCST as a function of NHMAAm mol%. The thermosensitive properties of the copolymer films were investigated and demonstrated hydrophilic-hydrophobic transitions. Finally, the copolymer was grafted onto cotton fabrics using citric acid (CA) as a crosslinking agent and sodium hypophosphite (SHP) as a catalyst following a two dipping, two padding process. The large number of hydroxyl groups in the copolymer makes grafting convenient and firm.

The grafted cotton fabrics show obvious thermosensitive behaviors. The results demonstrate that the cotton fabrics become more hydrophobic when the temperature is higher than the LCST. This study presents a valuable route towards temperature-responsive smart textiles and their potential applications.

Keywords: synthesis; thermosensitive behavior; copolymer; tunable LCST; smart textile

1. Introduction

Intelligent polymers are those that respond with large property changes to small physical or chemical stimuli such as temperature, pH, current, ionic strength, or chemical species [1,2]. In the past several decades, an increasing number of temperature-responsive polymers have been reported in the literature for various applications including drug delivery [2–5], tissue engineering [6–8], membrane transfer [9,10], smart clothing fabrication [11], Shape memory polymers [12], *etc.* Of these temperature-responsive polymers, poly (*N*-isopropylacrylamide) (PNIPAAm) has the lowest critical solution temperature (LCST) at 33 °C in aqueous solutions. This is near human body temperature and, at this temperature, it forms a single phase with water. It swells at low temperatures and collapses to form a separate phase above the LCST [13–15]. In addition, PNIPAAm has the sharpest phase transition of all thermosensitive *N*-alkylacrylamide polymers [16]. These features suggest that it may have applications in many areas like smart textiles.

Applications of temperature-responsive polymers in smart textiles imply that the transition temperature be tailored to the specific application. Examples include the thermo-regulating fabric used in hot weather. Here, the LCST should be higher than that of the textiles used for cold weather. Therefore, synthesis of temperature-responsive polymer with tunable LCST based on PNIPAAm is an important goal [17–19].

Immobilization of PNIPAAm onto textiles is another important goal. Many techniques have been used to immobilize polymers onto textiles. These techniques include methods varying from physical adsorption to covalent attachment [20]. Physical methods such as dip-coating and spraying coating techniques require relatively simple equipment and handling, and can be easily implemented in industrial processing. However, the interaction between polymer and textile is still weak and reversible [11]. These disadvantages can be overcome by covalent immobilization strategies. Two of the most common types of covalent immobilization methods of thermo-responsive polymers onto textile are the “grafting from” and “grafting onto” methods [21]. The later approach is relatively easy and facile because the functionalized textiles can be obtained by a simple reaction of the thermo-responsive polymer with the textile. The molecular weight and the chain length of the grafted polymer can be well-characterized, and the properties of the thermo-responsive polymer in different states (solution, film and textile surface) can be consequently studied [22,23]. Copolymerization of a monomer which not only adjusts the LCST of PNIPAAm but also introduces reactive functional groups to facilitate “grafting onto” is highly desired.

In this study, hydrophilic *N*-hydroxymethyl acrylamide (NHMAAm) was used as a comonomer to synthesize the temperature-sensitive polymers P(NIPAAm-*co*-NHMAAm) with the desired LCST by

controlling the amount of NHMAAm. The thermosensitive behavior of P(NIPAAm-*co*-NHMAAm) in aqueous solutions were investigated, and the results show a linear increase in LCST with increasing mol% of NHMAAm [24]. This is a convenient method to tune the LCST of PNIPAAm. The hydroxyl groups on the NHMAAm segment offer the possibility for crosslinking with cotton. Grafting of the copolymer onto cotton fabrics was achieved and produces remarkable changes to the surface properties of cotton fabrics. Such functional textiles may be applied in many fields such as smart cleaning clothes and smart breathable clothes.

2. Experimental Section

2.1. Materials

N-isopropylacrylamide (NIPAAm) (Aladdin, Shanghai, China, 98%) was recrystallized from hexane before use. *N*-hydroxymethyl acrylamide (NHMAAm) (Tianjin Chemical Reagent Research Institute, Tianjin, China, 95%) was purified by recrystallization from CH₂Cl₂. Copper (I) bromide (CuBr) (Shanghai Chemical Reagent Co. Ltd., Shanghai, China, 98.5%) was stirred overnight in acetic acid, filtered, successively washed with ethanol and diethyl ether, and dried in vacuum. Column chromatography purifications were performed by flash chromatography using neutral alumina (200–300). All other reagents and solvents were purchased from Aladdin and used as received unless otherwise stated. Deionized water was used throughout.

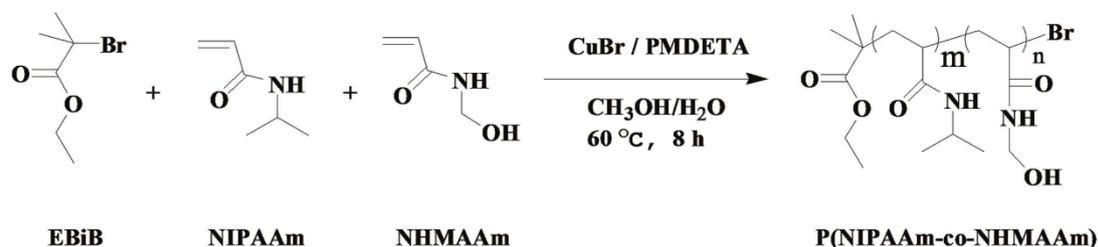
2.2. Analytical and Physical Methods

The ¹H Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance AV 400 MHz spectrometer (Fällanden, Switzerland). Chemical shifts in ¹H NMR were reported in parts per million (ppm) downfield from tetramethylsilane. The infrared (IR) spectra were measured with a Bruker Vertex 70 FT-IR spectrometer (Ettlingen, Germany). The lower critical solution temperature (LCST) was measured on a Perkin-Elmer Lambda 35 Ultraviolet-visible spectrophotometer (Waltham, MA, USA). Thermogravimetric analysis (TGA) was performed with a Pyris 1 TGA thermogravimetric analyzer (Shelton, CT, USA). Polymer films were prepared from solutions by spin-casting with a KW-4A coater (Institute of Microelectronics of Chinese Academy of Sciences, Shanghai, China) onto glass slides. The contact angle was measured by Krüss Easy Drop DSA-20 (Hamburg, Germany).

2.3. Synthesis of P(NIPAAm-*co*-NHMAAm)

The P(NIPAAm-*co*-NHMAAm) was synthesized via atom transfer radical polymerization (ATRP) copolymerization of NIPAAm and NHMAAm with 2-bromo ethyl isobutyrate (EBiB) as the initiator (Scheme 1). A typical example is given below. A solution of NIPAAm (1.9 g, 16.8 mmol), NHMAAm (0.06 g, 0.6 mmol), PMDETA (73 µL, 0.348 mmol), and CuBr (25 mg, 0.174 mmol) in methanol/water (3:2, total volume of solution is 5 mL) was degassed with three freeze-pump-thaw cycles. The initiator EBiB (26 µL, 0.174 mmol) was then added with a syringe. The reactor was sealed under N₂, and heated at 60 °C. After 8 h, the reaction mixture was exposed to air for 2 h to quench the polymerization reaction. The polymerization solution was then diluted with tetrahydrofuran (THF), filtered over alumina to remove the catalyst, and the solvent removed by vacuum evaporation. The reaction mixture

was then precipitated in hexane, redissolved in THF, and precipitated in hexane again. This cycle was repeated three times to obtain a pure product. We used feed ratios of NIPAAm and NHMAAm of 1:0, 29:1, 19:1, 9:1, and 3:1 to synthesize the copolymers.



Scheme 1. Synthesis of P(NIPAAm-co-NHMAAm) by atom transfer radical polymerization (ATRP).

2.4. Determination of Copolymers' LCST in Aqueous Solutions

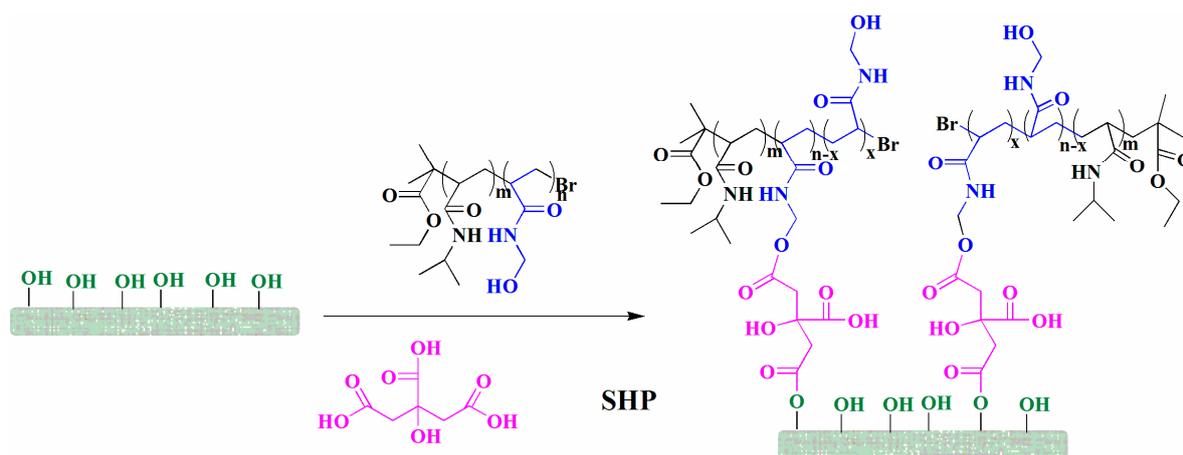
For each polymer, three solutions with different concentrations (1, 4, and 8 mg/mL) were prepared. The temperature was raised from 25 to 92 °C, and every test point was stabilized for 5 min before analysis. The transmittance at 500 nm was measured using a Perkin-Elmer Lambda 35 UV-Vis spectrometer equipped with a circulating water bath. The LCST was defined as the temperature at the highest point of the derivation curve of transmittance vs. temperature.

2.5. Determination of Thermosensitive Properties of Copolymer Films

To ensure prepare thick enough polymer films which can ignore the effect of substrates, solutions of copolymers with high concentration (100 mg/mL) were prepared in 1,4-dioxane at room temperature [25,26]. Copolymer films were created from solutions by spin-casting onto glass slides to form uniform, 50 nm thin films. The glass slides were rinsed with anhydrous ethanol and deionized water and then dried under nitrogen before use. Contact angle measurements were carried out on the thin films at different temperatures to determine the thermosensitive properties of the copolymer films.

2.6. Grafting of Copolymers onto Cotton Fabrics

Before use, the cotton fabrics were washed with acetone, alcohol, and deionized water twice. They were then immersed in boiling 10% sodium carbonate aqueous solution for 3 h, rinsed with deionized water, and dried. Grafting of the copolymer onto cotton fabrics was performed using citric acid (CA) as the crosslinking agent. The general process of grafting of copolymers onto cotton fabrics was presented in Scheme 2. Sodium hypophosphite (SHP) was used as the catalyst following a two dipping, two rolling process. The carboxyl groups of CA and the hydroxyl groups of cellulose can be condensed by the catalyst SHP. The treatment conditions were as follows: Pre-drying at 60 °C for 3 min, drying at 170 °C for 2 min, washing with deionized water, and vacuum dried at 60 °C overnight. The padding formulation was shown in Table 1. The grafted cotton fabrics were characterized with SEM imaging and contact angle measurements.



Scheme 2. Grafting of copolymers onto cotton fabrics.

Table 1. Padding formulation.

Material	wt%
Polymer	15
CA	2
SHP	3
Water	80

3. Results and Discussion

3.1. Synthesis and Structural Characterization of Copolymers

P(NIPAAm-co-NHMAAm) was synthesized via ATRP of NIPAAm and NHMAAm with EBiB as the initiator. Typical ^1H NMR spectra of P(NIPAAm-co-NHMAAm) was recorded in deuterated chloroform (Figure S1). The appearance of a singlet peak at 2.5 ppm (H, $-\text{OH}$) indicated the incorporation of NHMAAm monomer into the PNIPAAm. The molecular weights and the ratio of the two monomers segment were calculated by ^1H NMR by integration of specific groups of each monomer. The molecular weights of polymers were between 10,000 and 14,000 (e.g., P(NIPAAm-co-NHMAAm) 19:1 was 10,200). The ratio of the two monomers segment were calculated by the integration of $\text{CH}_3-\text{CH}-\text{CH}_3$ (4.0 ppm) for NIPAAm and $\text{NH}-\text{CH}_2-\text{OH}$ (5.3 ppm) for NHMAAm. The results show that the two monomers in the copolymer is close to the feed ratio. Table 2 showed the detail information of polymers.

Table 2. Information of polymers.

Entry	Sample Name	NHMAAm Ratio (%) ^a	Mn ^b	LCST (°C) ^c
1	PNIPAAm	0	10,913	33
2	29:1	3.1	13,852	36
3	19:1	3.8	10,200	37
4	9:1	10.4	10,738	52
5	3:1	23.5	12,561	87

^a The NHMAAm ratios of polymers were calculated by ^1H NMR; ^b the molecular weights of polymers were analyzed by ^1H NMR; ^c the LCSTs were measured by UV-Vis measurement.

FT-IR spectroscopy is an easy and convenient way to characterize the copolymers. Figure 1 presents typical FT-IR spectra of P(NIPAAm-*co*-NHMAAm) at feed ratios of 1:0, 19:1, and 3:1. The existence of strong absorption peaks at 1670 cm^{-1} (amide I), 1570 cm^{-1} (amide II) and the disappearance of 1655 cm^{-1} (C=C) indicated that the monomers were successfully polymerized into products. With increases in the feed amount of NHMAAm, the IR absorption strength of the copolymer at 3393 cm^{-1} (O–H) and 1050 cm^{-1} (C–O, –C–O–H) consequently increased. This demonstrates the increase in the NHMAAm segment length in the polymer chain. More FT-IR spectra are showed in Figure S2.

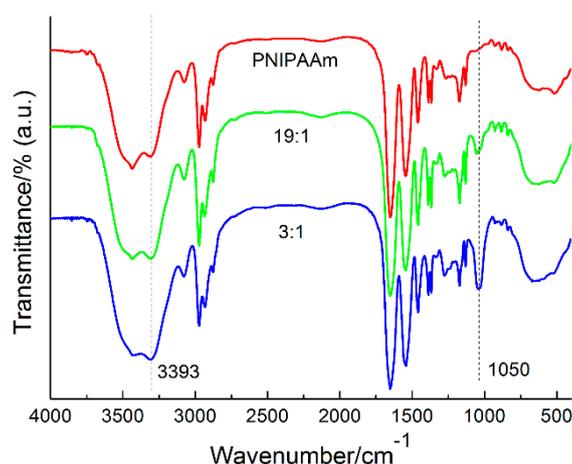


Figure 1. FT-IR spectra of typical P(NIPAAm-*co*-NHMAAm).

3.2. TGA Analysis

Thermo-gravimetric analysis (TGA) was performed at a heating rate of $10\text{ °C}\cdot\text{min}^{-1}$ under nitrogen. TGA curves indicated good thermal stability of the polymers (Figure S3). The initial weight loss could be attributed to loss of residual solvent or water absorbed from environment. The introduction of the hydrophilic monomer NHMAAm has little effect on the thermal stability of the copolymer. P(NIPAAm-*co*-NHMAAm) (19:1 and 3:1) exhibit good thermal stability like PNIPAAm and begins to thermally decompose at 325 °C ; it reaches half decomposition at 390 °C . Other samples showed similar TGA curves at the same experimental conditions.

3.3. Thermosensitive Behavior of Copolymers

3.3.1. Aqueous Solutions

The dependence of the polymer's optical transmittance on temperature was measured. To obtain an accurate LCST value, the differential of the transmittance with respect to temperature was performed. The temperature corresponding to the highest point of the derivation curve of transmittance vs. temperature was defined as the LCST value of the polymer (Figure 2a). As shown in Figure 2, the LCST values of the copolymers varied with the NHMAAm content. Much pioneering work has agreed that the LCST of PNIPAAm can be raised or lowered via introduction of hydrophilic or hydrophobic comonomers [27,28]. With increasing mol% of NHMAAm, the LCST increased gradually. In this case, due to the increases in the hydrophilic content of the copolymer, switching from hydrophilic interactions to hydrophobic interactions is hindered. This shifts the LCST to higher

temperatures. The PNIPAAm chains were hydrated in water below the LCST which makes it dissolved in water. If some hydrophobic chains substitute the PNIPAAm chains, the phase transition was easier to happen, because it contributes to micellization of the copolymer in water. While, the NHMAAm chains were always hydrophilic, it might weaken the phase transition of the copolymer solutions, which explained the decrease of transmittance was slighter when the mol% of NHMAAm increase [26,29].

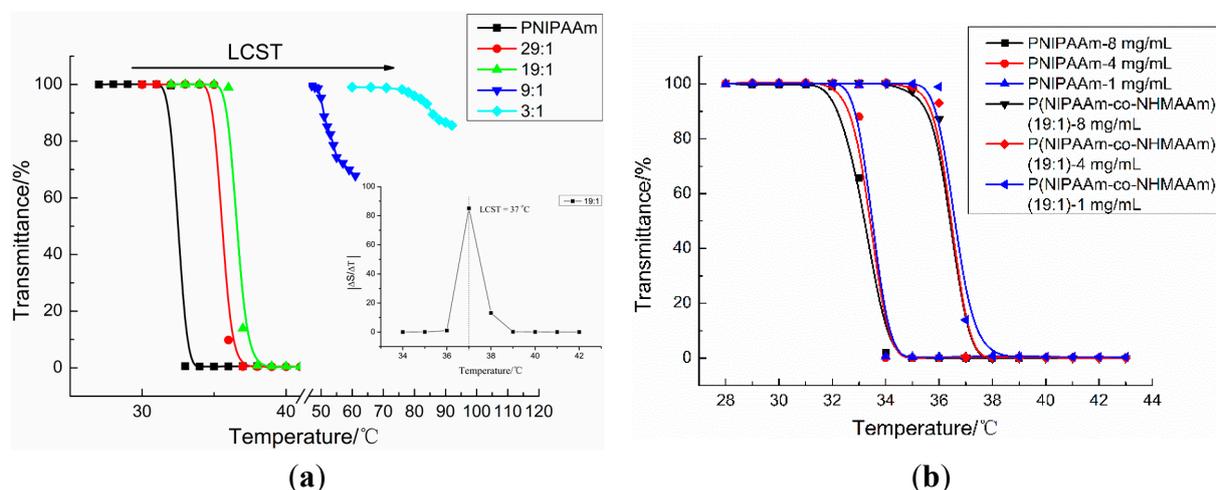


Figure 2. Temperature dependence for optical transmittance (500 nm) of copolymer solutions: (a) concentration: 1 mg/mL; (b) concentration: 1, 4, 8 mg/mL.

Interestingly, the LCST and ratio of NHMAAm displays a nearly linear relationship (Figure 3). It is worth noting that the LCST shifted to 37 °C (the human body temperature) when the feed ratio of NIPAAm and NHMAAm is 19:1. The effect of copolymer concentration on LCST was also investigated. The LCSTs of three different concentrations (1, 4, and 8 mg/mL) of polymer solutions were evaluated. The results show that the LCST remains unchanged. This indicates no concentration dependence in the range of 1–8 mg/mL for the copolymer solutions (Figure 2b), which is beneficial to the application of the polymer. The property of corresponding thermoresponsive materials will not change drastically with the alteration of concentration or molecular weight.

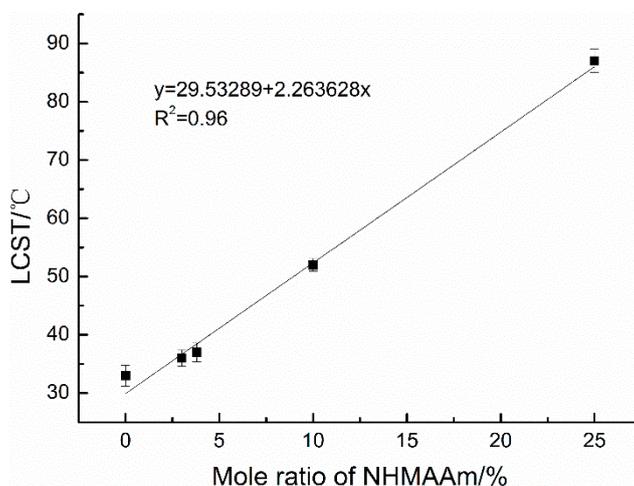


Figure 3. The lower critical solution temperature (LCST) of copolymer vs. the NHMAAm content.

3.3.2. Copolymer Films

The surface of a glass slide was coated with a ~50 nm thin layer of polymer and subjected to contact angle determination at 5 °C intervals (Figure 4). To ensure get thick enough polymer films, high concentration polymer solutions were prepared [26,27]. When the temperature is lower than the polymer's LCST (33 °C for PNIPAAm and 37 °C for P(NIPAAm-*co*-NHMAAm) (19:1)), the contact angle with the water drop is small—this represents a relatively hydrophilic surface. The contact angle obviously increases when the temperature becomes higher than the LCST. It displays a sudden change in surface properties along with a temperature increase. The P(NIPAAm-*co*-NHMAAm) (19:1) is more hydrophilic and reflects a smaller contact angle at the same temperature *versus* PNIPAAm. This is due to the introduction of the hydrophilic hydroxyl group. However, compares to polymer solution, wider range of transformation temperature was observed.

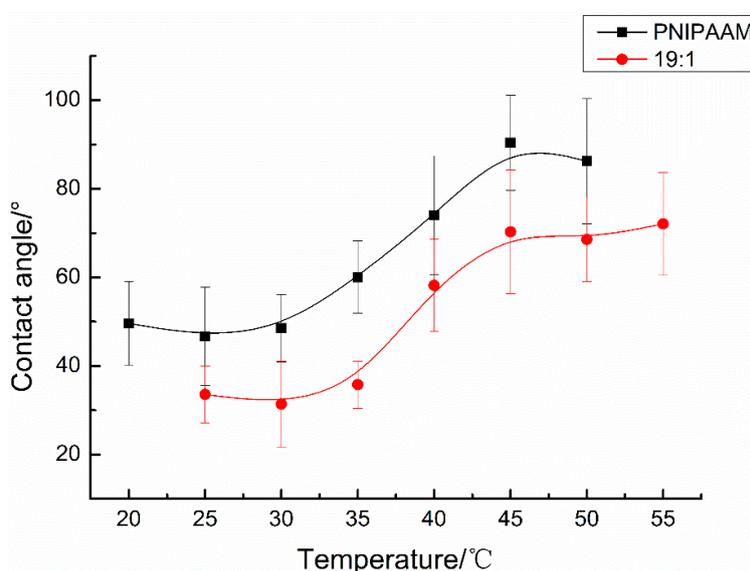


Figure 4. Contact angle measurements of the polymer films.

3.4. Grafting Copolymers onto Cotton Fabric

Currently, thermo-responsive textiles are widely studied. They play an increasingly important role in daily life as well as industrial, military, and medical applications. We next grafted polymers with reactive functional group onto cotton fabrics in the presence of a crosslinking reagent. Weight gain rates of the cotton fabrics are given in Table 3. Of these, there is no weight gain for PNIPAAm. This is because of the lack of reactive groups for crosslinking to the polymer.

Table 3. Weight gain rates of cotton fabrics.

Polymer	Liquid Retention (%)	Weight Gain (%)
PNIPAAm	170	−1.8
P(NIPAAm- <i>co</i> -NHMAAm) (29:1)	144	2.6
P(NIPAAm- <i>co</i> -NHMAAm) (19:1)	120	12.5

We also noted that by increasing the number of hydroxyl groups in the copolymer, the cotton weight gain rate increased significantly. A 12.5% weight increase was achieved when P(NIPAAm-*co*-NHMAAm) (19:1) was grafted onto cotton fabrics *versus* 2.6% for P(NIPAAm-*co*-NHMAAm) (29:1). There is no obvious weight loss after three washes of the grafted cotton fabrics, which means the polymers were cross-linked on surface of fabrics firmly.

The grafting of the P(NIPAAm-*co*-NHMAAm) layer attached to the cotton fabrics was confirmed by scanning electron microscopy (SEM, Figure 5). The surface of the untreated cotton fabrics (Figure 5a,b) appears smoother *versus* the treated one (Figure 5c,d). This shows that there is a thin polymeric film coating on the surface of the treated cotton fabrics. The coating appeared fairly uniform throughout the fabrics.

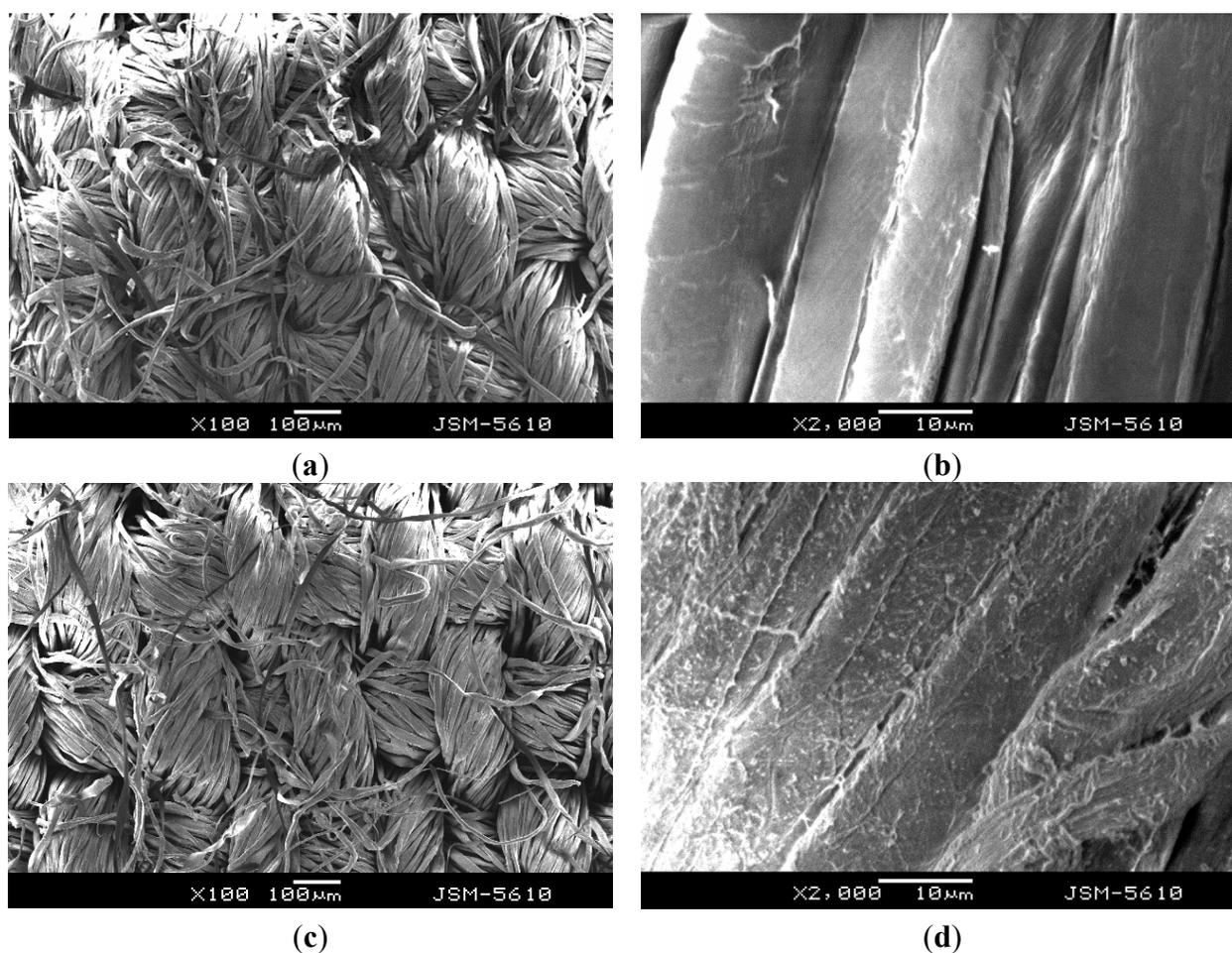


Figure 5. SEM micrographs of cotton fabrics (a,b) without treatment; and (c,d) after crosslinking with P(NIPAAm-*co*-NHMAAm) (19:1).

To investigate the thermosensitive behavior of grafted cotton fabrics, the contact angle measurements of water on cotton fabrics grafted with P(NIPAAm-*co*-NHMAAm) (19:1) were collected at 5 °C intervals from 25 to 45 °C (Figure 6). We found that the contact angle increased significantly when the temperature is higher than the copolymer's LCST (37 °C). This indicates a sudden increase in hydrophobicity of the cotton fabrics. This sudden change in hydrophilicity/hydrophobicity of the cotton fabrics with temperature change may make it applicable to many applications in smart textiles such as smart cleaning and intelligent protection.

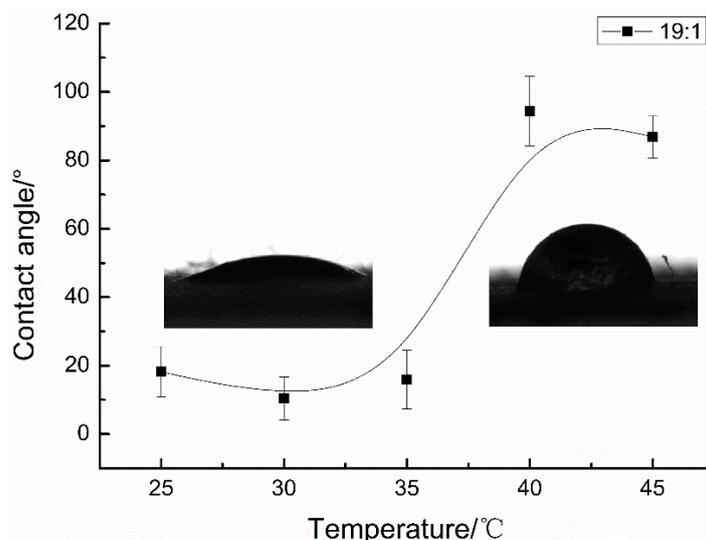


Figure 6. Contact angle measurements of the P(NIPAAm-*co*-NHMAAm) (19:1) grafted cotton fabrics at different temperatures.

4. Conclusions

In summary, well defined copolymers P(NIPAAm-*co*-NHMAAm) with tunable LCST consisting of reactive functional group were successfully synthesized by the ATRP technique. As the content of the hydrophilic monomer NHMAAm increased in the polymer, the LCST of the copolymer increased gradually. When the feed ratio of NIPAAm and NHMAAm is 19:1, the LCST is about 37 °C, which is similar to body temperature. The convenient control of LCST by varying the ratio of the two monomers offers a new approaching to engineering thermosensitive polymeric materials. The P(NIPAAm-*co*-NHMAAm) were successfully grafted onto cotton fabrics by crosslinking the hydroxyl groups in the copolymer with cotton fabrics. The modified cotton fabrics displayed obvious temperature sensitive behaviors, which produce remarkable changes in surface properties. Thus, this technology is applicable to the design of intelligent clothing as well as smart cleaning fabrics and other applications.

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Supplementary Information

Supplementary Information can be accessed at <http://www.mdpi.com/2073-4360/7/5/0909/s1>.

Author Contributions

Jiping Wang, Tao Chen and Qi Zhong designed the experiments; Qisheng Fang, Yangyi Chen performed the experiments; Tao Chen, Qisheng Fang and Qi Zhong analyzed the data; Tao Chen, Qisheng Fang wrote the paper.

Conflicts of Interest

The authors declare no conflict of interest.

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