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Cotton-Fabric-Grafted Poly(*N*-isopropyl acrylamide) Initiated by Ammonium Peroxydisulfate

Nenmei Jian, Tao Xu
College of Material and Metallurgy, Guizhou University, Guiyang, Guizhou 550025, People's Republic of China
Correspondence to: T. Xu (E-mail: xxlhtt@sina.com)

ABSTRACT: In this article, we report that thermoresponsive poly(*N*-isopropyl acrylamide) (PNIPAAm) was successfully grafted onto a cotton fabric (CF) surface by free-radical solution grafting polymerization; we obtained a thermoresponsive CF-grafted PNIPAAm. This reaction system only contained four constituents: the monomer, solvent, initiator, and CFs. Ammonium peroxydisulfate was chosen as the initiator, and water was chosen as the solvent. A series of initiator concentrations and grafting polymerization temperatures were used in the experiments, and their effects on the grafting ratio (*G*) were also studied. Also, the effects of the *G* of CF-*g*-PNIPAAm on their corresponding thermoresponses was studied further. The structure of CF-*g*-PNIPAAm was characterized by Fourier transform infrared spectroscopy–attenuated total reflectance analysis and scanning electron microscopy analysis. The *G* of CF-*g*-PNIPAAm was measured by a gravimetric method. The thermoresponse of CF-*g*-PNIPAAm was characterized by modulated differential scanning calorimetry, water contact angle measurements, and wetting time measurements. The experiments manifested the following results: (1) the initiator concentration and grafting polymerization temperature both influenced *G*, (2) the grafted PNIPAAm covered the CF surface, (3) the CF-*g*-PNIPAAm showed thermoresponsive hydrophilicity/hydrophobicity, and (4) a relationship existed between the thermoresponse of CF-*g*-PNIPAAm and the corresponding *G*. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41193.

KEYWORDS: functionalization of polymers; grafting; phase behavior; radical polymerization; surfaces and interfaces

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INTRODUCTION

Smart polymers have become a useful and important class of polymers,[1] attracting more and more interest among researchers all over the world. Actually, the characteristic feature of smart polymers, which makes them "smart" is their ability to reversibly respond to environmental triggers. These responses manifest some changes in one or more aspects, including shape, solubility, surface characteristics,[2] and transitions from solution to gel. These environmental triggers can be changes in the temperature,[3] pH,[4] ionic concentration, charge characteristics, light wave, solvent,[5] stress, and others. Poly(*N*-isopropyl acrylamide) (PNIPAAm) as a thermoresponsive polymer can reversibly transform its own molecular conformation near its lower critical solution temperature (LCST) of about 33°C in water. So, PNIPAAm can be dissolved in water below its LCST and precipitate from aqueous solution above its LCST.[6] In the recent several decades, various studies have been done to apply the thermoresponse of PNIPAAm to other materials, including membranes,[7,8] silica,[9] metallic materials,[10] polymer films[11] and particles,[12] and cellulose fibers.[13,14] A majority of these researchers chose a grafting-from approach to graft a PNIPAAm brush or gel onto the surface of their studied materials. The grafted PNIPAAm could endow them with a thermoresponse. Also, the thermoresponsive performance that the previous materials obtained behaved mainly through changes in their surficial hydrophilicity and hydrophobicity around the LCST.

Cotton fiber as a natural polymer material is easily obtainable, nontoxic, biodegradable, and environmentally friendly, and it is used for variety of purposes, especially for clothing. Up to this point, several researchers have paid attention to the idea that the grafting of PNIPAAm onto cotton fibers endows the cotton fibers with their thermoresponse. The main grafting polymerization method that these researchers have selected is atom transfer radical polymerization (ATRP). Also, cerium(IV), potassium peroxydisulfate (KPS), and H_2O_2[15,16] have been selected as initiators to directly initiate cotton fibers to graft onto PNIPAAm because of the plentiful hydroxyl groups along the cotton-fiber chain. In addition the previous several grafting polymerization methods, Zhai et al.[17] used the radiation of ^{60}Co γ rays to successfully initiate cotton fibers to graft onto PNIPAAm. However, ATRP possesses disadvantages. Not only is its process complex, but also the reaction conditions are demanding because, before and during the grafting polymerization, special handling procedures are required to remove oxygen from the reaction system

to avert the oxidation of the low-value catalyst. Previous research with KPS revealed that inorganic peroxide initiators produced free radicals that could initiate vinyl polymerization and grafting polymerization. In addition, the initiated grafting by inorganic peroxide initiators has advantages, such as few side reactions, the requirement of simple and inexpensive equipment, and the use of an ecofriendly solvent (water).

In this study, we selected another inorganic peroxide initiator [ammonium peroxydisulfate (APS)] to initiate cotton fabric (CF) to graft onto PNIPAAm in water. The obtained CF-*g*-PNIPAAm had a thermoresponse. Also, its grafting ratio (*G*) reached 42 wt %; this was higher than that of cerium(IV) (ca. 9 wt %) and KPS (ca. 20 wt %). Compared with the complexity of ATRP, the low *G* by cerium(IV) and KPS, and the instability of H_2O_2, this grafting polymerization method was simple, easily operated, and effective. Moreover, it will promote development in the industry of thermoresponsive function textiles.

EXPERIMENTAL

Materials

CFs woven directly by natural cotton fibers were purchased at a market. Before the grafting modification, the CFs were repeatedly reflux-extracted in ethanol for 5 h by a Soxhlet extractor, then boiled in a 1 wt % NaOH aqueous solution for 3 h, washed repeatedly by ultrapure water to neutrality, and finally dried *in vacuo* at 50°C. The *N*-isopropyl acrylamide (NIPAAm) monomer was purchased from Aladdin (with a 98% purity) without any further treatment. The APS initiator (Tianjin Kemiou Chemical Reagent Co.) was purified by recrystallization with ultrapure water at 40°C. Ethanol (Tianjin Kemiou Chemical Reagent Co.) was used directly without any further treatment.

Preparation of the CF-Grafted PNIPAAm

Five pieces of CFs (ca. 3 × 3 cm^2 each) were immersed in a flask containing H_2O (15 mL) and APS with certain concentrations (0.015, 0.03, 0.06, 0.09, 0.12, and 0.15 mol/L). The aqueous solutions were deoxygenized by bubbling with nitrogen and stirred by a magnetic stirrer for 1 h at room temperature. Then, NIPAAm (0.5092 g) was added to the previous aqueous solution. After NIPAAm was dissolved, the reaction system filled with nitrogen was heated to temperatures of 30, 40, 50, 60, 70, 80, and 90°C, respectively, to initiate grafting polymerization for 3 h. After the grafting modification, the CFs were taken out, washed with ultrapure water several times, immersed in 250 mL of ultrapure water, stirred for 12 h two times, finally dried *in vacuo* at 50°C, and weighed.

Characterization

A Fourier transform infrared (FTIR) spectrometer from Bruker (Germany) was used to study the surface chemistry structure of the CFs before and after the grafting modification by attenuated total reflectance (ATR)–FTIR spectroscopy analysis with a silicon crystal under Tensor 27 and 32 scans at a spectral resolution of 4 cm^{-1}. Field emission scanning electron microscopy (SEM; JSM-7500F, JEOL Co., Japan) was used to observe the surface morphology of the CFs before and after grafting modification. At the same time, SEM–energy-dispersive spectrometry (EDS) analysis was used in unison to detect the chemical elements of the observed samples. Modulated differential scanning calorimetry (MDSC; Q2000, TA Co.) was used to characterize the thermoresponse of the CF-*g*-PNIPAAm. The MDSC technique was applied to directly measure the reversing heat capacity at the heating rate of 1°C/min from 0 to 60°C with a temperature modulation amplitude of 1°C and a period of 60 s. The water contact angles (CAs) of the surface of CF-*g*-PNIPAAm was measured by a CA meter (JC2000C1, Shanghai) at 21 and 41°C. Before the CA measurements, the water drop remained for 10 s on the surface. The wetting times of CF-*g*-PNIPAAm at 21 and 41°C were measured according to a part of AATCC 79-2000 (absorbency test).[18] A drop of water was allowed to fall from a height of 1 cm onto the CF-*g*-PNIPAAm surface. The time required for the specular reflection of the water drop to disappear was measured and recorded as the wetting time. The hydrophilicity/hydrophobicity of CF-*g*-PNIPAAm was determined by the wetting time. A longer wetting time indicated a better hydrophobicity; on the contrary, a shorter wetting time indicated a better hydrophilicity. *G* was calculated from the weight increase of CF through grafting modification according to the following equation:

$$G=(W_2-W_1)/W_1 \times 100\%$$

where W_1 and W_2 are the weights of the pristine CF and the CF after grafting modification, respectively.

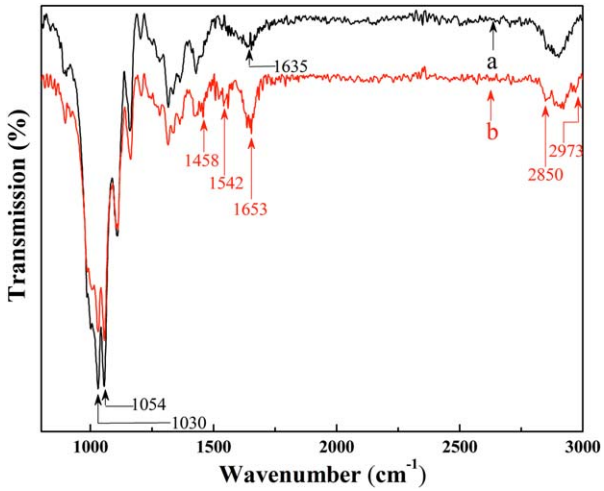

Figure 1. FTIR spectra of the (a) pristine CFs and (b) CFs after grafting modification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Structural Characterization

The pristine CF and the CF after grafting modification were characterized by ATR–FTIR spectroscopy, a surficial characterization technology. ATR–FTIR analysis showed that in addition to the typical bands from the pristine cotton, the CF after grafting modification also showed the typical bands of PNIPAAm, as shown in Figure 1. On the FTIR spectrum of the CF after grafting modification, the bands at 1653 and 1542 cm^{-1} corresponded to the typical amide I and II stretching vibrations of PNIPAAm chain, respectively, and the bands at 2850, 2973, and

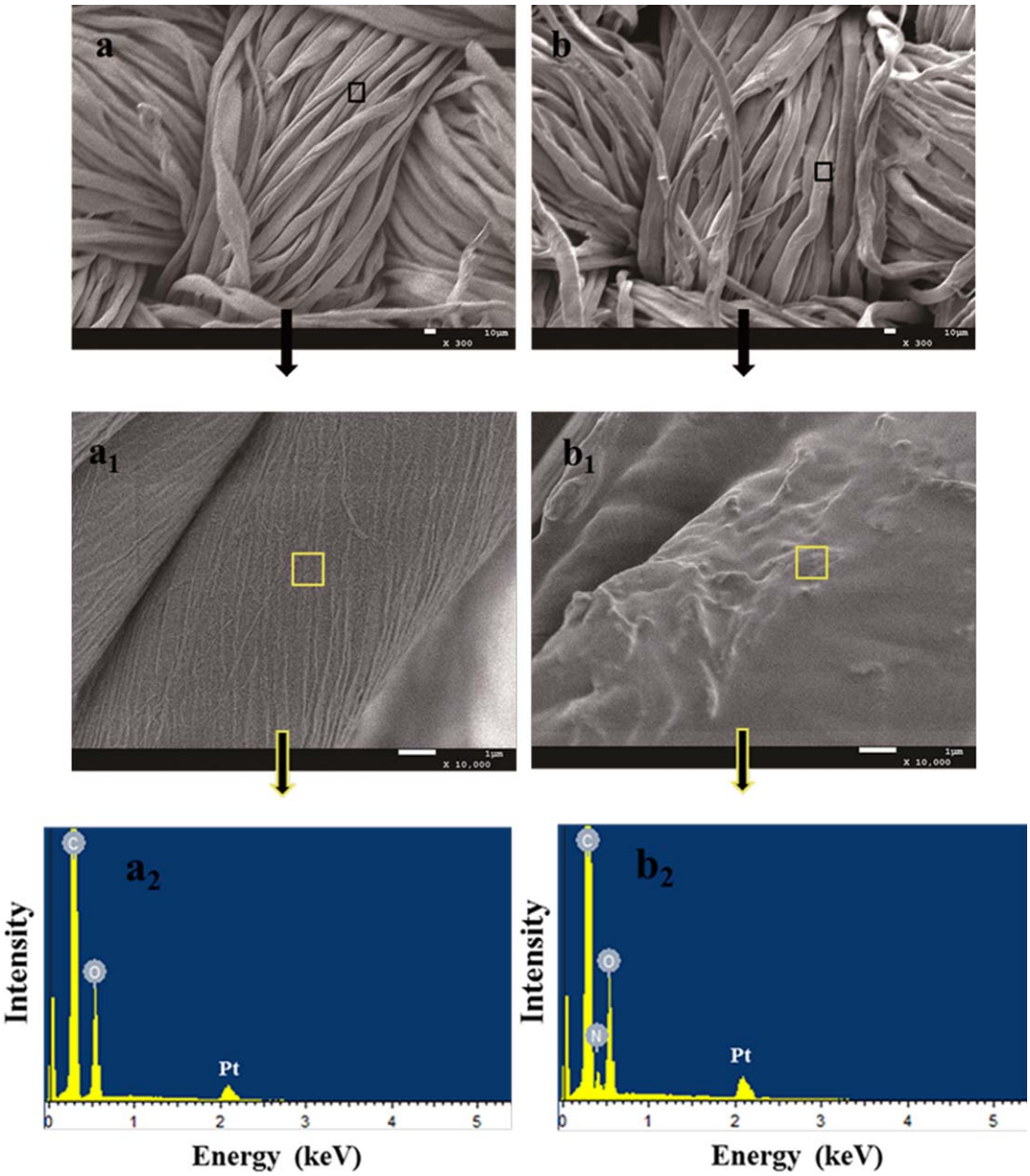

Figure 2. SEM images of the (a) pristine CFs at 300×, (b) CF-*g*-PNIPAAm (0.06 mol/L) at 300×, (a1) pristine CFs at 10,000×, and (b1) CF-*g*-PNIPAAm (0.06 mol/L) at 10,000×. SEM–EDS spectra of the (a2) pristine CFs and (b2) CF-*g*-PNIPAAm (0.06 mol/L). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1458 cm^{-1} corresponded to the stretching vibrations and deformation vibrations, respectively, of the C—H bond from methyl groups on the PNIPAAm chain.[15,19] On the FTIR spectrum of pristine cotton, the weak band at 1635 cm^{-1} was attributed to absorbed water.[20] This revealed that PNIPAAm was successfully grafted onto the CF with the APS initiator, and we obtained CF-*g*-PNIPAAm. In addition, as shown in Figure 1, it was obvious that the strength of the bands at 1030 and 1054 cm^{-1} on the FTIR spectrum of the CF after grafting modification, corresponding to the stretching vibrations of the hydroxyl groups on the cotton fiber chain, were both weaker than that on the FTIR spectrum of the pristine CF. This further manifested that the grafted PNIPAAm layer covered the CF surface, and this led to the reduction of its cotton content on the surface. So, theoretically, the microcosmic procedure of this grafting polymerization was as follows: first, the CF surface was initiated by APS to form free radicals because of the abundant hydroxyls along its chain. Then, the formed free radicals continuously initiated the NIPAAm monomer to polymerize onto the CF chain on the surface.

The surface morphologies of the pristine CF and CF-*g*-PNIPAAm were investigated by SEM analysis. As shown Figure 2(a), the fiber surface of the pristine CF was clean. However, Figure 2(b) shows an obvious and certain nonuniform coating covering on the CF surface; this was just formed by the grafted PNIPAAm

layer. As shown clearly in Figure 2(a1), the fiber surface of the pristine CF was rough and showed uniformly distributed nanogrooves on the surface. Obviously, as shown in Figure 2(b1), the CF-*g*-PNIPAAm surface showed an entirely different surface morphology: a thick grafted PNIPAAm layer covering previous nanogrooves. Meanwhile, in addition to the C and O peaks from the pristine CF, the SEM–EDS spectrum of the CF-*g*-PNIPAAm also showed an N peak at 0.4 keV, which manifested the existence of nitrogen from just the grafted PNIPAAm on the CF-*g*-PNIPAAm surface, as shown in Figure 2(a2,b2). The peak at 2.1 keV came from the platinum sprayed on the sample surface before it was detected. Therefore, the SEM analysis and SEM–EDS analysis not only further confirmed that PNIPAAm was successfully grafted on the CF surface but also showed their different surface morphologies.

G

In this study, we examined the effect of the initiator concentration and grafting polymerization temperature on *G*. In the first step, the grafting polymerization took place at 60°C with a series of initiator concentrations (0.015, 0.03, 0.06, 0.09, 0.12, and 0.15 mol/L). Because 60°C was higher than the PNIPAAm LCST, this free-radical solution grafting polymerization was a precipitating polymerization. In the second step, a series of grafting polymerization temperatures (30, 40, 50, 60, 70, 80, and 90°C) were examined.

As shown in Figure 3(a), with a 60°C grafting polymerization temperature, with increasing initiator concentrations from 0.015 to 0.15 mol/L, *G* rose from 10.53 wt % at 0.015 mol/L to 42.8 wt % at 0.06 mol/L and then fell to 11.11 wt % at 0.15 mol/L. That is, the initiator concentration possessed an optimal value, and at the optimal initiator concentration, CF-*g*-PNIPAAm obtained a high *G* for the grafting polymerization system. It was near 0.06 mol/L. The reasons why the grafting polymerization system displayed an optimal initiator concentration were as follows: (1) during the grafting polymerization, free radicals produced by APS in the solution but not on the cotton could initiate the homopolymerization of the NIPAAm monomers; (2) this polymerization belonged to precipitating polymerization, and its reaction ratio depended on the speed of monomer diffusion; and (3) mutual competition existed between the homopolymerization and the grafting polymerization; this mainly depended on the diffusion of the monomers. If the initiator concentration was too low, the amount of free radicals on the cotton was scarce, and this led to infrequent grafting polymerization and a low *G*. In contrast, when the initiator concentration was too high, free radicals in the solution were abundant to the benefit of homopolymerization because the diffusion of the monomers in the solution was superior to that across the CF. So, in the second step, an initiator concentration of 0.06 mol/L was selected.

As shown in Figure 3(b), with increasing grafting polymerization temperature, the *G*s at 30 and 40°C both stayed below 10 wt %, started to increase to the maximum at 60°C, dropped rapidly to 19.05 wt % at 70°C, and continually decreased to 14 wt %. The reason for this experimental phenomenon was that APS owned a high value of activation energy of decomposition

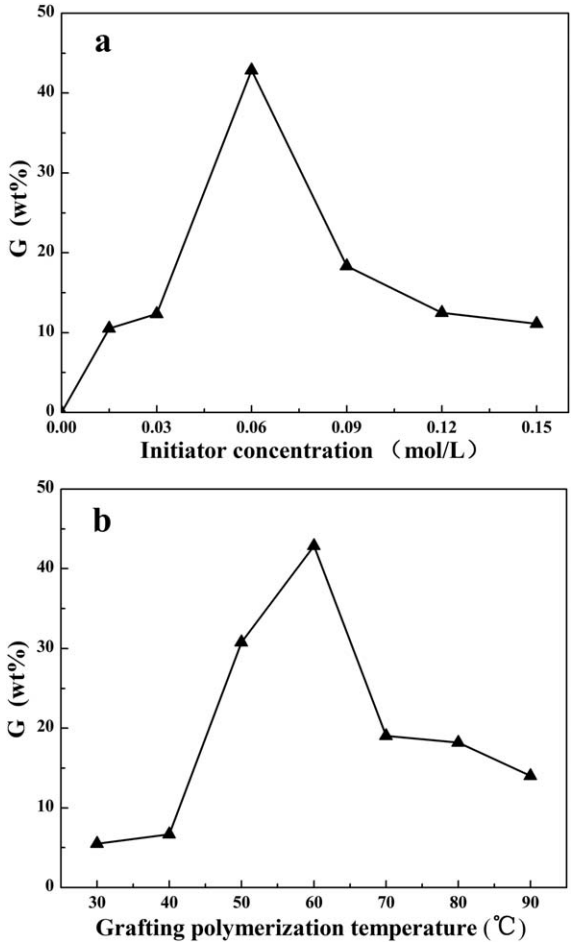

Figure 3. *G*s of CF-*g*-PNIPAAm at (a) various initiator concentrations and (b) various grafting polymerization temperatures.

(E_d = 140 kJ/mol). So, at a low temperature, the decomposition ratio of APS was too slow to produce enough free radicals for the subsequent grafting polymerization. However, at high temperatures (>60°C), it was too fast, and this was in favor of the homopolymerization because of the superiority of the monomer diffusion in the solution to that across the CFs and led to a lack of monomers for the grafting polymerization. Therefore, for the 3-h grafting polymerization, a medium temperature (60°C) was the most suitable.

So, *G* of CF-*g*-PNIPAAm at an initiator concentration of 0.06 mol/L and a grafting polymerization temperature of 60°C gave the highest concentration (42.8 wt %). In addition, the *G*s of all of the CF-*g*-PNIPAAm samples were mainly distributed near the following five values: 5, 12, 19, 30, and 42 wt %.

Thermoresponse

Pristine cotton without a thermoresponse function is hydrophilic. PNIPAAm shows a thermoresponsive hydrophilicity/hydrophobicity near its LCST. In essence, the phenomenon in which PNIPAAm exhibits a sharp phase transition in water when heated above its LCST is the result of the transformation of PNIPAAm chain conformations from the extended state below the LCST to the collapsed globular above its LCST. The phase transition of PNIPAAm near its LCST is a reversing phase

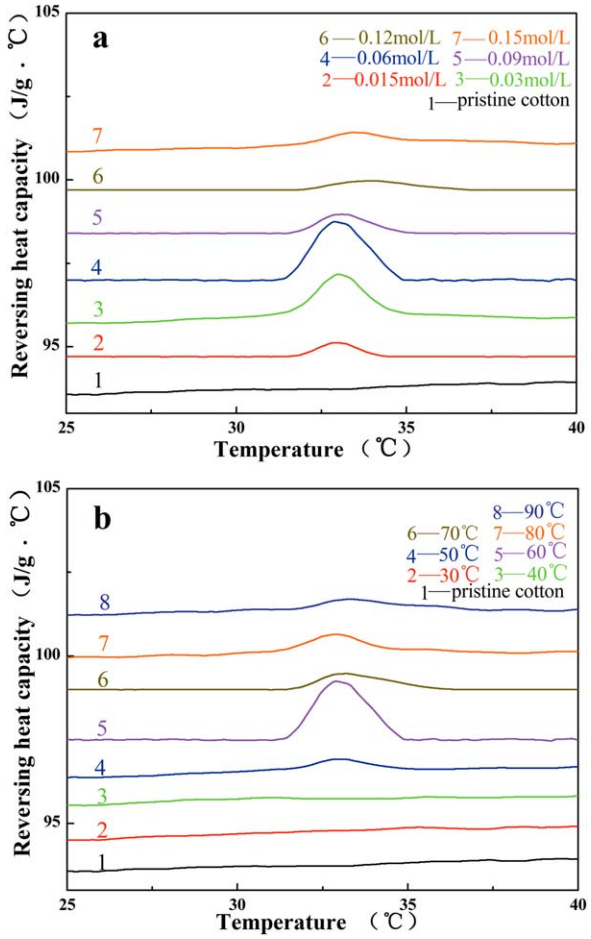

Figure 4. MDSC spectra of CF-*g*-PNIPAAm (a) with various initiator concentrations and (b) with various grafting polymerization temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

transition. So, the reversing phase transition can be characterized by the signal of the transformation of the reversing heat capacity, which is obtained directly by MDSC technology.

Figure 4(a) shows that those CF-*g*-PNIPAAm samples with various initiator concentrations (0.015, 0.03, 0.06, 0.09, 0.12, and 0.15 mol/L) at 60°C all showed a transformation peak near 33°C on their MDSC spectra; this corresponded to the reversing phase transition of PNIPAAm, but the pristine CF did not show this. Moreover, with increasing initiator concentration, it was obvious that their corresponding transform peak areas increased from 0.015 to 0.06 mol/L first and then sharply dropped from 0.06 to 0.15 mol/L. The area of the reversing phase transition peak was the reversing enthalpy change. So, at 0.06 mol/L, the reversing enthalpy change was at the maximum; this indicated that the CF-*g*-PNIPAAm at an initiator concentration of 0.06 mol/L showed the most obvious thermoresponse.

At an initiator concentration of 0.06 mol/L, CF-*g*-PNIPAAm samples were obtained at the following seven grafting polymerization temperatures: 30, 40, 50, 60, 70, 80, and 90°C. Figure 4(b) shows that just those CF-*g*-PNIPAAm samples at grafting polymerization temperatures of 50, 60, 70, 80, and 90°C, respectively, showed a transformation peak near 33°C on their reversing heat capacity–temperature spectra, but the other two and the pristine cotton did not. This revealed that just those CF-*g*-PNIPAAm samples at grafting polymerization temperatures of 50, 60, 70, 80, and 90°C showed thermoresponses, but those at 30 and 40°C did not. Also, with increasing grafting polymerization temperature, it was obvious that at 50°C, the reversing enthalpy change just began to increase. After being up to the maximum at 60°C, the reversing enthalpy change started to decrease from 60 to 90°C. This indicated that the CF-*g*-PNIPAAm obtained at an initiator concentration of 0.06 mol/L and at a grafting polymerization temperature of 60°C showed the most obvious thermoresponse.

In this experiment, for all of the obtained CF-*g*-PNIPAAm samples, the distribution of their *G*s was not even, and their *G*s were close to several values: 5, 12, 19, 30, and 42 wt %. Further analysis on the cause of the thermoresponses of those CF-*g*-PNIPAAm samples revealed that a relationship between their reversing enthalpy changes and their corresponding *G*s existed, as shown in Figure 5. When the *G* value of the CF-*g*-PNIPAAm was below 10 wt %, the reversing enthalpy change of the CF-*g*-PNIPAAm was zero. However, when the *G* value of the CF-*g*-PNIPAAm increased to greater than 10 wt %, the reversing enthalpy change of the CF-*g*-PNIPAAm rose sharply to 0.5676 J/g from 0. Subsequently, with increasing *G* to 42.8 wt %, their corresponding reversing enthalpy changes significantly improved to 3.525 J/g. This indicated that a CF-*g*-PNIPAAm with a *G* of less than 10 wt % did not show a thermoresponse, but when the *G* of the CF-*g*-PNIPAAm was greater than 10 wt %, their corresponding thermoresponse function arose and was continuously enhanced with the growth of their *G*. So, this further revealed that the thermoresponse function owned by the CF-*g*-PNIPAAm came from the grafted PNIPAAm layer on the surface and was enhanced along with the growth of the quantity of the grafted layer when the *G* of the CF-*g*-PNIPAAm was above 10 wt %.

PNIPAAm is thermoresponsive hydrophilic/hydrophobic near its LCST. In theory, the CF-*g*-PNIPAAm surface can obtain its thermoresponsive hydrophilicity/hydrophobicity. So, the water CA of the CF-*g*-PNIPAAm surface at two kinds of environmental temperatures (21 and 41°C) was measured to characterize their surficial hydrophilicity/hydrophobicity. As shown in Figure 6, the CAs of pristine CF at 21 and 41°C were both 0° because

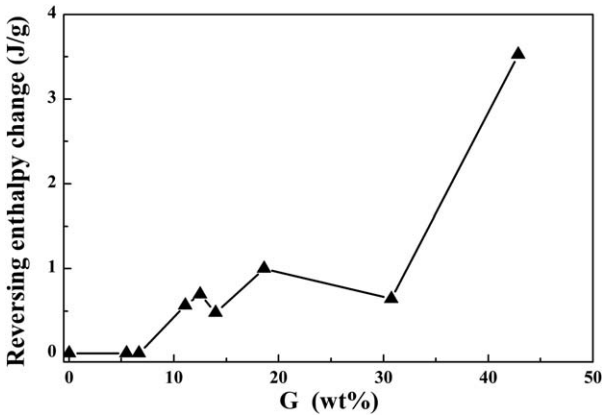

Figure 5. Reversing enthalpy change of CF–PNIPAAm with various *G*s.

pristine cotton is hydrophilic and not thermoresponsive. For the CF-*g*-PNIPAAm samples with *G* values of less than 10 wt %, their corresponding CAs at 21 and 41°C were all 0°. This indicated that when the *G* values of the CF-*g*-PNIPAAm samples were below 10 wt %, the CF-*g*-PNIPAAm surface was also hydrophilic and not thermoresponsive. However, for those CF-*g*-PNIPAAm samples with *G* values of greater than 10 wt %, at 21°C, their CAs were all 0°; this indicated that their surfaces were hydrophilic below their LCST, and at 41°C, with increasing *G*, their CAs showed an upward trend. What is more, when the *G* value of the CF-*g*-PNIPAAm was over 14 wt %, the CA of the CF-*g*-PNIPAAm surface, except the one with the *G* of 30.7 wt %, was greater than 100°; this indicated that the CF-*g*-PNIPAAm surface was hydrophobic above its LCST. Moreover, at the *G* of 42.8 wt %, the CA of the CF-*g*-PNIPAAm surface at 41°C was at a maximum (120.5°); this also showed that the thermoresponse of the CF-*g*-PNIPAAm with the *G* of 42.8 wt % was the most obvious. This conclusion was consistent with that achieved by the MDSC analysis.

The thermoresponsive hydrophilicity/hydrophobicity of CF-*g*-PNIPAAm could also be determined by the wetting times of CF-*g*-PNIPAAm at different temperatures. The wetting time of CF-*g*-PNIPAAm was measured by AATCC test method 79 (an absorbency test) at 21 and 41°C, respectively, as shown in Figure 7. When the *G* of the CF-*g*-PNIPAAm was less than 10 wt %, the wetting times of CF-*g*-PNIPAAm at 21 and 41°C were all 0 s. This indicated that the CF-*g*-PNIPAAm samples with a *G* of less than 10 wt % did not show a thermoresponse function. However, when the *G* of the CF-*g*-PNIPAAm was greater than 10 wt %, at 21°C with the growth of *G*, the wetting times of CF-*g*-PNIPAAm increased from zero and then stabilized near 17 s. At 41°C, with the growth of *G*, the wetting times of CF-*g*-PNIPAAm rose rapidly from 0 s and finally reached a maximum (180 s). In addition, it was obvious that the gap between the wetting time at 21°C and that at 41°C also increased greatly with increasing *G* starting from values greater than 10 wt %. At a *G* value of 42.8 wt %, the gap was at a maximum; this revealed the CF-*g*-PNIPAAm with the *G* of 42.8 wt % showed the most obvious thermoresponse.

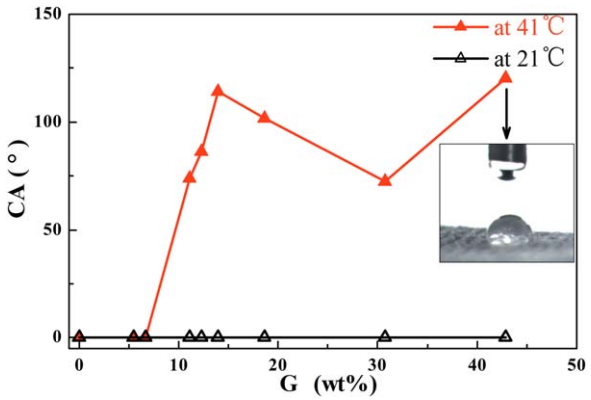

Figure 6. Water CAs of CF-*g*-PNIPAAm with various *G*s at 41 and 21°C and the photo of water drop on the CF-*g*-PNIPAAm surface at 41°C with a *G* of 42.8 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

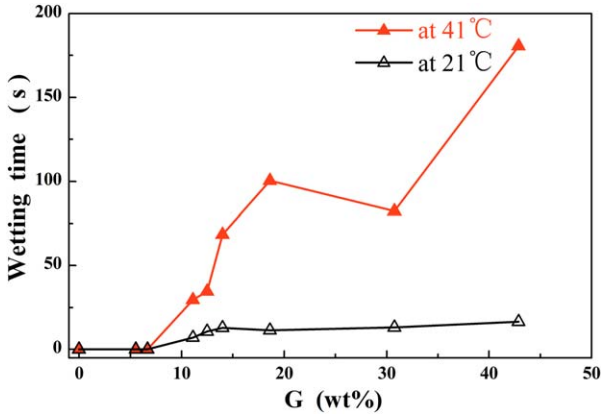

Figure 7. Wetting time of CF-*g*-PNIPAAm with various *G*s at 41 and 21°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

So, the thermoresponse shown by the CF-*g*-PNIPAAm and the relationship between the thermoresponse of CF-*g*-PNIPAAm and the corresponding *G* were confirmed by the MDSC analysis, CA analysis, and the wetting time at the same time. In addition, Figures 5–7 simultaneously show that with the growth of *G*, the thermoresponse of the CF-*g*-PNIPAAm with the *G* of 30.7 wt % was not better than that of the CF-*g*-PNIPAAm with the *G* of 18.4 wt %. This may have been caused by the nonuniform distribution of the grafted PNIPAAm layer.

CONCLUSIONS

The grafting reaction system, consisting of simply CF, NIPAAm (monomer), APS (initiator), and water (solvent), was effective. APS could successfully initiate CF to be grafted onto PNIPAAm. The SEM analysis shows that the grafted PNIPAAm layer covered the CF surface. By the adjustment of the initiator concentration and grafting polymerization temperature, the *G* values of CF-*g*-PNIPAAm were distributed near several values, and its maximum was 42.8 wt % at 0.06 mol/L and 60°C. MDSC, water CA analysis, and wetting time analysis all manifested that only the CF-*g*-PNIPAAm samples with *G* values of greater than 10 wt % showed thermoresponse functions near about 33°C. Moreover, the higher the *G* was, the more obvious the thermoresponse of CF-*g*-PNIPAAm was. So, the thermoresponse of the CF-*g*-PNIPAAm with a *G* value of 42.8 wt % was the most obvious.

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