Dear Author/Editor,
Greetings, and thank you for publishing with SAGE. Your article has been copyedited and typeset, and we have a few queries for you. Please address these queries when you return your proof corrections. Thank you for your time and effort.

Please ensure that you have obtained and enclosed all necessary permissions for the reproduction of artistic works, (e.g. illustrations, photographs, charts, maps, other visual material, etc.) not owned by yourself, and ensure that the Contribution contains no unlawful statements and does not infringe any rights of others, and agree to indemnify the Publisher, SAGE Publications Ltd, against any claims in respect of the above warranties and that you agree that the Conditions of Publication form part of the Publishing Agreement.

Any colour figures have been incorporated for the on-line version only. Colour printing in the journal must be arranged with the Production Editor, please refer to the figure colour policy outlined in the e-mail.

Please assist us by clarifying the following queries:

1. The corresponding author details have been copied from SMART. Please check that they are as intended.
2. The homopolymer was not too much: Please clarify this sentence.
Surface-initiated atom transfer radical polymerization on cotton fabric in water aqueous

Tieling Xing, Jie Liu and Shiwei Li

Abstract
In this work, 2-bromoisobutyryl bromide was first reacted with the hydroxyl groups on the surface of cotton fabric to obtain cotton macroinitiator (C-Br) for surface-initiated atom transfer radical polymerization (ATRP) of (2-dimethylamino)ethyl methacrylate (DMAEMA). Then C-Br was grafted with DMAEMA via the ATRP method in water aqueous. The tertiary amino groups of immobilized DMAEMA polymer on the cotton fabric were quaternized with bromomethane to produce the antibacterial function. The structure of cotton-grafted-PDMAEMA (C-g-PDMAEMA) was characterized by attenuated total reflection–Fourier transform infrared spectroscopy, scanning electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. The results show that DMAEMA was grafted onto the surface of cotton and the tertiary amino groups were quaternized. The C-g-PDMAEMA has good thermostability. The whiteness and strength of C-g-PDMAEMA decreased slightly, but the wrinkle recovery angle increased distinctly compared with the control sample. The quaternized grafted cotton has the great antibacterial property and good laundry resistance.

Keywords
surface modification, finishing, structure properties, atom transfer radical polymerization, cotton fabric

Cotton is the most abundant polymeric raw material in the world. This inexpensive, biodegradable, and renewable resource has been widely studied during the past decades. Cotton fabric has many useful properties, but for some applications, it lacks advantages of synthetic fabrics, such as the wrinkle recovery property and chemical stability. Modification of cotton fabric by graft polymerization provides a significant route to alter the physical and chemical properties, including heat resistance, elasticity, resistance to abrasion and wear, oil and water repellency, ion-exchange capabilities, and antibacterial activity. 1–3

Grafted copolymerization of cotton fabric using various conventional techniques has been studied quite extensively. Conventional grafting of cotton fabric has usually been conducted by a “grafting-from” technique, where radicals are generated along the cellulose backbone, followed by chemical means or by irradiation. 4–7 Using this method, it is almost impossible to predetermine the molecular weight of the polymer and the molecular weight distributions are very broad. If, instead, the cotton fabric is grafted via a living/controlled polymerization technique, the properties of the grafts can be accurately controlled and thereby also tailored. 8,9 Atom transfer radical polymerization (ATRP) is one of the most broadly applied methods of living/controlled polymerization technique because it has an easy experimental setup, is readily accessible, and has inexpensive catalysts and a simple initiator. 10 ATRP relies on the reversible reaction of a low-oxidation-state metal complex with alkyl
halide-generating radicals and the corresponding high-oxidation-state metal complex with a coordinated halide ligand.\textsuperscript{11} In 2003, Carlmark and Malmstrom\textsuperscript{1} first demonstrated the controlled growth of poly(methacrylate/poly 2-hydroxyethylmethacrylate (PHEMA) brushes from cellulose filter paper using ATRP. Lindqvist and Malmstrom\textsuperscript{8} grafted methacrylate and styrene onto filter paper, microcrystalline cellulose, lyocell fibers, and chitosan films. A recent study reported that ATRP of many hydrophilic monomers could be carried out in aqueous media.\textsuperscript{11,12} Our group has previously reported the use of ATRP for silk grafting in aqueous media.\textsuperscript{13,14} So far, there is no literature about cotton fabric grafting using the ATRP method.

In the present work, (2-dimethylamino)ethyl methacrylate (DMAEMA) monomer was grafted on the surface of cotton fabric through ATRP in water aqueous. The tertiary amino groups of immobilized DMAEMA polymer on the cotton fabric were quaternized with bromomethane to obtain cotton fabric with an antibacterial property.

**Experimental details**

**Materials**

Desized cotton fabric (twill weave, 138 g/m$^2$) was purchased from the market. DMAEMA was purchased from Wuxi Xinyu Chemical Co. Ltd and was distilled under reduced pressure prior to polymerization. Triethylamine (TEA) and tetrahydrofuran (THF) were dried by CaH$_2$ overnight, and then distilled under reduced pressure before use. CuBr, N,N,N',N'-pentamethyldiethylenetriamine (PMDETA), 4-(dimethylamino) pyridine (DMAP), nitromethane, and bromomethane were used as received. 2-bromoisobutyryl bromide (BriB-Br) (98%, Alfa Aesar) and all other reagents were used without further purification.

**Synthesis of the macroinitiator**

Cotton macroinitiator(C-Br) was prepared by reacting BriB-Br with the hydroxyl groups present on cotton in the presence of TEA and DMAP catalysis at room temperature. Typically, 50 ml of THF, 2 ml of TEA and 0.5 g of DMAP were mixed in a 100 ml Erlenmeyer flask under oscillation. The flask was cooled down to 10$^\circ$C with an ice bath and 1.0 ml of BriB-Br was added into the flask. Then 1 g of dried cotton sample was added into the mixed solution. The reaction mixture was stirred at the same temperature for an additional 1 h, then left to warm up to room temperature before being mixed for 24 h. The sample was thereafter thoroughly washed with THF, then water and finally dried at 80$^\circ$C in a vacuum oven. Thus, C-Br was prepared.

**Surface-initiated ATRP of DMAEMA**

The procedure of ATRP grafting cotton with DMAEMA was as follows: the C-Br was immersed into a reaction mixture containing DMAEMA, CuBr/PMDETA (the mole ratio was 1:2), and deionized water in a 100 ml round-bottom flask. After sealing it with a polytetrafluoroethylene three-way stopcock, the flask was evacuated and flushed with nitrogen, which was repeated three times. The mixture was placed in a water bath and polymerized under oscillating at 80$^\circ$C for 2 h. After the reaction finished, the sample was rinsed with methanol and water, and then dried under a vacuum oven. Thus the cotton-grafted-DMAEMA (C-g-PDMAEMA) sample was obtained. The grafting condition was as follows: the monomer concentration was 0.25 mol/l, the concentration of the catalyst CuBr was 0.376 mmol/l, the molar ratio of the catalytic system was 2:1, the reaction temperature was 80$^\circ$C, and the reaction time was 2 h.

The weight gain was calculated as

$$\text{Weight gain} = \frac{w_2 - w_1}{w_1} \times 100\%,$$

where $w_1$ and $w_2$ denote the weight of C-Br and C-g-PDMAEMA, respectively.

**Quaternization of C-g-PDMAEMA**

The C-g-PDMAEMA was immersed into a reaction mixture containing nitromethane and bromomethane in a sealed 100 ml round-bottom flask at -20$^\circ$C. The mixture was placed in a low-temperature reactor and reacted at 0$^\circ$C for 3 h, then left to warm up to 30$^\circ$C for 24 h. The sample was thereafter thoroughly washed with water for three times, and then dried at 80$^\circ$C for 2 h in a vacuum oven. Finally, the quaternized grafted cotton fabric with antibacterial property (C-q-PDMAEMA) was obtained. The synthetic pathway is shown in Scheme 1.

**Characterization and measurements**

The infrared spectra of cotton fabric were recorded on a Nicolet 5700 Fourier transform infrared (FTIR) spectrometer equipped with a single-reflection attenuated total reflection (ATR) system. X-ray photoelectron spectroscopy (XPS) analysis of the cotton fabric was carried out on an AEM PHI 5300X spectrometer. The X-ray source was run at a power of 150 W.
The samples were attached to the spectrometer probe with double-sided adhesive tape and analyzed with an Al Ka X-ray source (1486.6 eV photons) with pass energy of 20 eV. The surface of the grafted and control sample was examined, after gold coating, with a Hitachi S-4700 scanning electron microscope (SEM) at an acceleration voltage of 3 kV. Differential scanning calorimetry (DSC) measurements were performed on a Diamond 5700 thermal analyzer at a heating rate of 10°C/min. The temperature range was from 40 to 500°C. The open aluminum cell was swept with N2 during the analysis. X-ray diffraction (XRD) patterns were obtained at a scanning rate of 1°C/min using a D/Max-III C X-ray diffractometer. The voltage and current of the X-ray source were 40 kV and 30 mA, respectively. Tensile properties were measured in standard conditions with a Model YG026A electricity fabric tester machine (ISO 13934-1: Textiles Tensile Properties of Fabrics Part 1: Determination of Maximum Force and Elongation at Maximum Force Using the Strip Method, 1999). Air permeability was measured using an MO21A Air Permeability Tester in the standard conditions at 20°C and 65% relative humidity (RH) according to ISO 9237-1995(Textiles – Determination of the permeability of fabrics to air). Test pressure and test area were 200 Pa and 20 cm². The whiteness index was measured using the WSD III whiteness instrument. The result was the average of eight measurements. The wrinkle recovery angle (WRA) of the treated samples was measured according to AATCC66-2003(Wrinkle Recovery of Woven Fabrics: Recovery Angle). The WRA of specimens in the warp (W) and fill (F) directions was measured separately. The urgent WRA had a value of 30 s and the slow WRA had a value of 5 min. The WRA (W + F) values of specimens were evaluated. The moisture regain of samples was measured to characterize the hygroscopic properties of cotton fabric according to ASTM D2654-1989. Samples were dried in an oven at 105°C for 2 h and put into a vacuum desiccator containing silica gel for 24 h and then weighed. This process was repeated, if necessary, until the weight became constant. This was termed the dry weight ($G_0$). The samples were then conditioned at 25°C and 65% RH and reweighed until the weight became constant. This weight was termed the conditioned weight ($G$). Moisture regain ($MR$, %) was calculated as

$$MR = \frac{G - G_0}{G_0} \times 100\%.$$  

The antibacterial properties of C-q-PDMAEMA were tested against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) according to the modified testing method for antibacterial activity of textiles (AATCC 100). The reductions of bacteria (*inhibition rate*)...
Inhibition rate were calculated according to the following equation:

$$Inhibition\ rate = \frac{B - A}{B} \times 100\%.$$  \hspace{1cm} (3)

where \(A\) and \(B\) are the surviving bacterial cells for the plates containing quaternized grafted cotton fabrics and the control (pristine cotton fabric), respectively.

**Results and discussion**

**FTIR spectra**

FTIR analysis was used to demonstrate the presence of polymer grafted onto the cotton surface. Obviously, in the case of C-g-PDMAEMA samples there were additional characteristic peaks of carbonyl of ester groups at about 1724.1 cm\(^{-1}\) compared with the spectrum of C-Br sample, and the strength of peaks at about 1152.2 cm\(^{-1}\) attributed to C-O stretching vibration of ester increased with increasing of weight gain (Figure 1). Thereby, DMAEMA was confirmed to be grafted onto cotton fabric. A new adsorption peak at about 950 cm\(^{-1}\), a characteristic peak of quaternary ammonium groups, presents in the spectrum of the C-q-PDMAEMA sample. However, there was no adsorption peak in the spectra of the C-Br and C-g-PDMAEMA sample. This proved that quaternary ammonium groups were obtained by the quaternization of tertiary amino groups of immobilized DMAEMA polymer on cotton fabric.

**Surface morphology**

Figure 2 shows the surface of the C-g-PDMAEMA with different weight gain values. At low weight gain, the cotton surface was similar to that of the untreated
sample, while at higher gain a thin polymeric film partly covered the fibers. As the weight gain further increased, the thicker film occurred on the surface of the cotton fabrics, which attributed to the homopolymerization. However, the homopolymer was supposed to establish strong interactions with cotton by means of physical forces or chemical bonds, because it was resistant to methanol treatments. The homopolymer was not too much. Because in the ATRP grafting system there was no initiator in the grafting solution, theoretically the monomer could only react with the macroinitiator.

**XRD**

XRD intensity curves of the cotton fabrics are shown in Figure 3. The C-g-PDMAEMA samples with different weight gain all exhibited the characteristic peaks of

![Figure 3](image)

**Figure 3.** X-ray diffraction intensity curves of cotton with different weight gain values: (a) 0%; (b) 9.5%; (c) 21.2%; (d) 30.4%.

![Figure 4](image)

**Figure 4.** X-ray photoelectron spectroscopy wide-scan and C1s core-level spectra of untreated cotton ((a) and (b)) and cotton-g-PDMAEMA ((c) and (d)).
cotton fiber that appeared at $2\theta = 15.5^\circ$ and $2\theta = 22.5^\circ$, which represented the crystallization and non-crystallization regions. The position and intensity of the major XRD peak did not change regardless of the introduction of DMAEMA. The results indicated that the crystalline structure was not directly modified by the graft-copolymerization reaction using the ATRP method. This was reasonable because ATRP only modified the surface of the fibers and it could not change the crystal orientation of the whole fiber, regardless of where the polymer chains were grafted.

**XPS**

The chemical compositions of the C-Br and C-g-PDMAEMA were determined by XPS. The respective XPS wide-scan and C1s core-level spectra ((a) and (b)) of the C-Br, and the respective XPS wide-scan and C1s core-level spectra((c) and (d)) of C-g-PDMAEMA are shown in Figure 4. The C1s core-level spectrum of the C-Br showed that untreated cotton contained three distinct peaks at 284.5 ($-\text{C} - \text{C}$), 286.2 ($-\text{C} - \text{OH}$), and 289.3 eV ($-\text{COOH}$). These peaks were attributed to the bonds present in the cellulose and any residual surface contaminants (including assistant). A comparison of the wide-scan spectra of C-Br(Figure 4(a)) and C-g-PDMAEMA(Figure 4(c)) surface indicated that the N1s signal, the characteristic peak of nitrogen, appeared on the C-g-PDMAEMA surface. After grafting treatment, the C1s spectra showed the peaks of nitrogen groups at 285.3 eV ($-\text{C} - \text{N}$), and ester groups at 288.5 eV ($-\text{O} - \text{C} = \text{O}$), which further confirmed that the DMAEMA monomer was grafted on the cotton surface.

**Thermal properties**

Figure 5 shows the DSC curves of grafted cotton with different weight gain values. The untreated sample displayed an intense endothermic peak at 369°C, attributed to the thermal decomposition of cotton with cellulose I crystal structure. In addition, a new endothermic peak appeared at about 427°C in the curve of C-g-PDMAEMA, which was attributed to specific thermal transitions of the poly (DMAEMA) chain. It can be seen from Figure 5 that C-g-PDMAEMA and C-Br had similar heat flow behavior. The DSC results showed that cotton-g-PDMAEMA had good thermostability.

**Physical properties**

It can be seen from Table 1 that the whiteness and tensile strength of C-PDMAEMA slightly decreased compared with the untreated sample. The urgent and slow WRA increased with the increase of weight gains, which meant the wrinkle resistance of the cotton was improved after grafting with DMAEMA. With the increase of weight gain, the breaking strength, whiteness, and air permeability of the cotton decreased. This was because the pore size between the interstices of cotton fibers became smaller, which derived from the grafting of DMAEMA monomer onto the cotton fabric and the homopolymer formation. The moisture regain of the grafted cotton fabric firstly decreased then increased. The grafting occurred mainly in the amorphous region of cotton fabric, and PDMAEMA might block certain hydrophilic groups of cotton macromolecules, which decreased the hygroscopic properties of cotton fabrics. However, with the weight gain continuously increased, the tertiary amine groups also increased with the introduction of PDMAEMA, which increased the hygroscopic properties of cotton fabric. In general, under the circumstances of less affecting the intrinsic properties of cotton fabric, cotton with an antibacterial property could be obtained by properly controlling the weight gain.

**Antibacterial property**

From Table 2 it can be seen that C-q-PDMAEMA with different weight gains had a good antibacterial property to both *S. aureus* and *E. coli*. The bacterial inhibition rate increased with increasing weight gain. In addition, the inhibition rate of grafted cotton to *S. aureus* was better than to *E. coli*. With the washing times extended, the bacterial inhibition rate just slightly decreased. Consequently, quaternized C-g-PDMAEMA had a
great antibacterial property and perfect laundry resistance.

**Conclusions**

The results reported in this study showed that the ATRP method for producing cotton fabric grafted DMAEMA was successfully developed. FTIR, SEM, and XPS results confirmed that DMAEMA was grafted onto the cotton fabric surface. FTIR characterization of the C-q-DMAEMA indicated that grafted cotton was quaternized. The bacterial inhibition rates of quaternized grafted cotton to *S. aureus* and *E. coli* were both over 88%, and just slightly decreased after 50 times of washing. The whiteness, breaking strength, and air permeability of grafted cotton slightly decreased, which had little effect on the intrinsic properties of cotton fabric.

**Funding**

This work was supported by the National Natural Science Foundation of China (grant number 50973079, 51003071), the Natural Science Foundation of Jiangsu Province (grant number BK 2010254, BK 2011353), and a project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

**References**


