

Polymer-grafted Modification of Cotton Fabrics by SI-ARGET ATRP

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Abstract: Cotton fabrics with sophisticated surface-specific properties were obtained by grafting poly(tert-butyl acrylate) (PtBA), poly(acrylic acid) (PAA), poly(oligo(ethylene oxide) monomethyl ether methacrylate) (POEOMA), poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) and quaternized PDMAEMA (QPDMAEMA) bushes on cotton surfaces using surface-initiated activators regenerated by electron transfer atom transfer radical polymerization (SI-ARGET ATRP) of three rather different monomers in a water-ethanol solvent. Due to the different physical properties and chemical composition of grafted polymers, the properties of such obtained cotton fabrics can be tailored including mechanical properties from enhanced tensile strength to increased breaking elongation, hydrophilic/hydrophobic characteristics from superhydrophilic to hydrophobic, varied water absorption abilities, different dye adsorption capabilities and charge properties. This work presents a high potential surface modification route towards functional textiles which are expected to play an important role in the future applications.

Keywords: Cotton fabric, Graft polymerization, SI-ARGET ATRP, Surface modification, Properties

Introduction

Cotton fibers and fabrics are amongst the most and widely used commodities throughout the world and have a wide variety of applications in apparel, home furnishings, and industrial products. This inexpensive, biodegradable, and renewable resource has been widely studied during the past decades. Efforts to improve the wrinkle recovery properties and handle of cotton fabrics have never stopped [1-3], and many attempts have been made to enhance functionalities of cotton fabrics such as antimicrobial ability [4-6], superhydrophobicity or/and superoleophilicity [7,8], self-cleaning property [9,10], UV radiation protection ability [11], flame retardancy [12,13], electrical conductivity or capacitive performance [14,15]. Textile products with multiple functionalities or stimuli-responsive (smart) property have generated great interest in recent years [16-18]. These functions can be added to textiles via surface modification, and surface properties play an important role in the performance of fabrics with tailored properties.

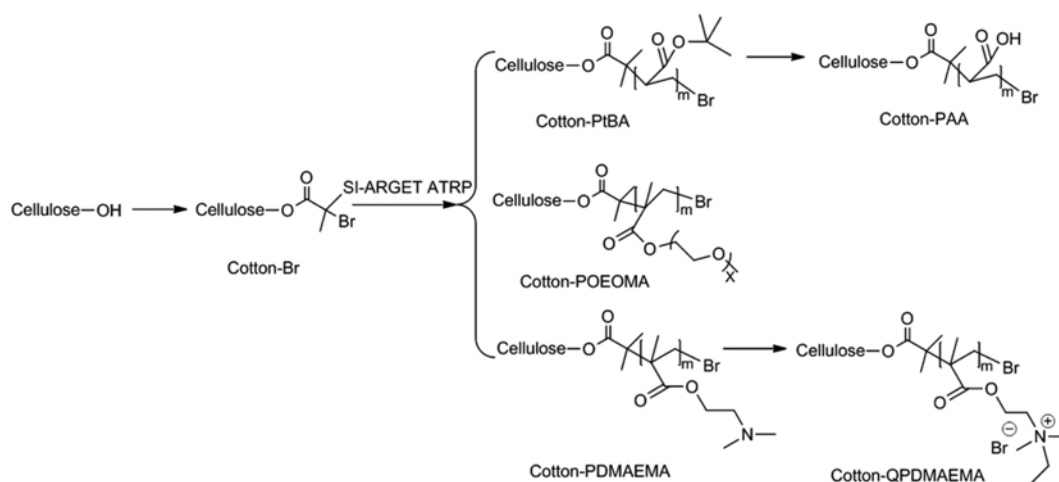
Various techniques are available for the surface modification of cotton fabrics mainly including gas treatments (such as plasma treatments [19,20], ozonation [21], UV or γ Radiation [22,23], and vapor deposition [24]) and wet modifications (such as enzymatic treatment [25], chemical etching [26], in-situ introduction or adsorption of nanoparticles [27,28], layer-by-layer deposition [29,30], sol-gel process [31,32], and deposition or grafting of polymers or macromolecules [33-35]). Comparing with gas treatments, wet modification

of fabrics does not need special equipment or affect bulk properties of fiber, and thus is more suitable for industrial applications. Among the wet modification processes, graft polymerization is one of the most promising methods because the modified surface is mechanically and chemically robust, and structurally designable for multi-functionality [36].

Graft polymerization can be performed via grafting-from and grafting-to approaches. Comparing with grafting-to technique, in which the polymer bearing a functional group(s) reacts with the fiber surfaces to form chemically attached chains, grafting-from method can get higher surface graft densities because the polymerization of monomer is initiated by the initiators who are initially anchored on the surface and the monomer can diffuse freely between the existing grafted polymer chains. The recent development of improved polymerization techniques including controlled radical polymerization (CRP), ionic polymerization and ring-opening polymerization (ROP) makes it possible to provide considerable control over both the structure of the polymer to be grafted onto the fiber surface and surface graft densities. These polymerization methods with polymer grafting techniques have been successfully used as an approach to modify the surface of cotton fibers or fabrics with a variety of functional polymers [37-39]. As one of CRP techniques, atom transfer radical polymerization (ATRP) method is recognized as a green chemical approach for polymer synthesis, and this method has been used to graft polymer chains from the surface of cotton fabrics, resulting in thermo-responsive property and enhanced antimicrobial ability [39-41]. However, ATRP is especially sensitive to oxygen and requires relatively large amounts of transition metal complex. These drawbacks can be overcome by an improved ATRP technique, activators

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Scheme 1. SI-ARGET ATRP of various monomers from cotton fabric.

regenerated by electron transfer for ATRP (ARGET ATRP) process, which has been developed by Matyjaszewski's group more recently and greatly reduced sensitivity to oxygen by the introduction of an excess of reducing agent in the reaction [42,43]. Surface modification of solid cellulose and related materials, such as filter paper, cellulose membranes and wood, has been already investigated by several researchers [44-47], but information concerning grafted cotton fabric is rather scarce in the literature [48].

This paper presents a straightforward method for preparing polymer-grafted cotton fabrics with a range of various monomers including N,N-dimethylaminoethyl methacrylate (DMAEMA), tert-butyl acrylate (tBA) and oligo(ethylene glycol) monomethyl ether methacrylate (OEOMA) using surface-initiated ARGET ATRP (SI-ARGET ATRP) (Scheme 1). DMAEMA is an interesting monomer containing tertiary amino group that offers water solubility and excellent adhesion properties, and can induce the antimicrobial activity by quaternization after polymerization [41]. The t-butyl groups of hydrophobic PtBA can be hydrolyzed to give acidic PAA for further surface functionalization [49,50]. Hydrophilic OEOMA monomer has been widely utilized in the field of anti-fouling surface protection [51]. Despite the different natures of the three monomers, the only parameters that need to be altered are monomer concentration and temperature. By grafting these functional polymers from the surface of cotton fabrics, the physical and chemical properties of the fabrics would be modified, with the purpose of obtaining high-tech and high-added-value textiles and increasing the application area of cotton-based materials.

Materials and Experimental Methods

Materials

Cotton plain woven fabrics, with a weight of 201 g/m² and a density of 20 threads/cm in the warp direction and

14 threads/cm in the weft direction, were offered by Jiangsu Lianfa Textile Co., Ltd. (Nantong, Jiangsu Province, China) and thoroughly rinsed with ethanol and distilled water, dried at 60 °C in a vacuum oven before use. Triethylamine (TEA, Sinopharm 99 % purity), 4-(dimethylamino)pyridine (DMAP, Sinopharm 99 %), 2-bromoisobutyl bromide (BiBB, J&K 97 %), copper(II) bromide (CuBr₂, J&K 99 %), N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA, J&K 99 %), ascorbic acid (AsAc, TCI 99 %), trifluoroacetic acid (TFA, J&K 99 %), ethyl bromide (TCI 99 %), Astrazon Red FBL 250 % (Dystar), Astrazon Blue GRL 300 % (Dystar), Evercion Red H-E3B (Everlight Chemical Industrial Corporation), Evercion Navy Blue H-ER (Everlight Chemical Industrial Corporation) and all other solvents (analytical grade) were used as received. DMAEMA and tBA were purchased from Aldrich and purified by distillation under reduced pressure before use. OEOMA (number average molecular weight M_n 300 and ca 5 pendant EO units) was also purchased from Aldrich and purified by passing through a column filled with basic alumina to remove inhibitors before use.

Preparation of Polymer-grafted Cotton Fabrics

Preparation of Cotton Macroinitiator (Cotton-Br)

Typically, 100 ml dry tetrahydrofuran (THF), 5.00 ml of TEA and 0.6 g of DMAP was mixed in a 250 ml round-bottom flask under oscillating. The flask was cooled down to 0-5 °C and 2.22 ml of BiBB was added into the flask. And then 2 g of dried cotton fabric was added into the mixed solution. The reaction mixture was stirred at 0-5 °C for 2 h, then left to warm up to room temperature (25 °C) and reacted for 24 h. The fabric sample was thereafter thoroughly washed sequentially with THF, distilled water and ethanol, and then dried at 60 °C in a vacuum oven.

SI-ARGET ATRP Grafting Cotton with Monomers

The general procedure for batch ARGET ATRP of tBA to create PtBA-grafted cotton fabric (Cotton-PtBA) was as

follows. CuBr₂ (11.2 mg, 0.08 mmol), PMDETA (34 μ l, 0.16 mmol), tBA (3.2 g, 25 mmol), 40 ml water-ethanol mixture (50/50 v/v) and Cotton-Br (1.5 g) were added sequentially into a 100 ml round-bottom flask. The flask was evacuated and flushed with nitrogen, and then immersed into a water bath preheated at 60 °C. A solution of AsAc (10 mg/ml, 5 ml, 0.28 mmol) was added to the flask to reduce the Cu (II) complex to the activator Cu (I) complex and start the polymerization under oscillating. After a predetermined time, the polymerization was stopped by exposing the solution to air. The obtained sample was ultrasonic rinsed sequentially with THF, distilled water and ethanol (30 minutes per solvent), and then dried at 60 °C in a vacuum oven. The ATRP POEGMA-grafted cotton fabric (Cotton-POEGMA) and PDMAEMA-grafted cotton fabric (Cotton-PDMAEMA) with OEGMA and DMAEMA respectively was conducted following similar procedure as that of tBA, and the reaction conditions were listed in Table 1. The weight uptake of fabrics and graft yield of monomers were calculated as:

$$\text{Weight uptake} = (w_2 - w_1)/w_1 \quad (1)$$

$$\text{Graft yield} = (w_2 - w_1)/n \quad (2)$$

where w_1 and w_2 denote the weight of cotton fabric before and after grafting, respectively, and n represent the mass of monomer which were initially inserted into the reaction flask.

Hydrolysis of Cotton-PtBA to Prepare Cotton-PAA

The prepared Cotton-PtBA (1.0 g) was soaked in a solution of 50 ml of dichloromethane and 1 ml of TFA at room temperature under stirring for 48 h. After hydrolysis, the sample was ultrasonic rinsed with water twice to remove the residues of TFA, and subsequently with ethanol for 30 min, and then dried at 60 °C in a vacuum oven. The hydrolysis ratio (HR) of PtBA was obtained according to an equation as following:

$$\text{HR} = ((w_2 - w_3)/(57.07 - 1.01))/((w_2 - w_1)/128.1) \quad (3)$$

where w_3 is the weight of poly(acrylic acid)-grafted cotton fabric (Cotton-PAA), 128.1 is the molecular weight of tBA unit, 57.07 is the molecular weight of tert-butyl group, and 1.01 is the atomic weight of hydrogen. In the current study, the HR of PtBA was 0.81.

Quaternization of Cotton-PDMAEMA to Prepare Cotton-QPDMAEMA

The obtained Cotton-PDMAEMA (1.0 g) was immersed in a mixture of ethyl bromide and isopropanol (1/2, v/v, 60 ml) at room temperature under stirring for 48 h. The sample was thereafter thoroughly ultrasonic washed with water twice and then ethanol for 30 min, and subsequently dried at 60 °C in a vacuum oven. The quaternization ratio (QR) of PDMAEMA was obtained according to an equation as following:

$$\text{QR} = ((w_4 - w_2)/108.97)/((w_2 - w_1)/157.2) \quad (4)$$

where w_4 is the weight of Cotton-PDMAEMA, 157.2 is the molecular weight of DMAEMA unit, and 108.97 is the

molecular weight of ethyl bromide. In the current study, the QR of PDMAEMA was 0.58.

Materials Characterization

The infrared spectra of cotton fabric were recorded on a Varian 640-IR Fourier transform infrared (FTIR) spectrometer fitted with ATR (Attenuated Total Reflectance) accessories.

The surface morphology of the polymer-grafted and native cotton was examined with a Hitachi TM-1000 scanning electron microscope (SEM) at acceleration voltage of 15 kV.

For tensile testing, all samples were conditioned at 21 °C and 65 % relative humidity for 48 h. Tensile strength and percentage elongation at the breaking point of the rectangular-shaped samples (70 mm×10 mm) were evaluated using a universal material tester (H5K-S, Hounsfield, UK) equipped with a 50-N load cell, at a crosshead speed of 10 mm/min. At least five samples in both warp and weft directions, selected from three separate fabrics, were tested for each condition and the average±one standard deviation was reported.

The water contact angles (CA) were measured with 2 μ l deionized water droplet at room temperature using an contact angle goniometer (KRÜSS GmbH, DSA30), which contains an optical system to capture the profile of the droplet on a solid substrate, and a computer with a program to analyze the angle. The image was captured immediately (within 5 s) and 10 min later, and the CA was determined using the circle or the Young-Laplace equation fitting method by averaging the measurements taken from at least five different positions on fabric samples.

Moisture regain (MR) was measured as follows: samples were dried at 105 °C for 2 h and put into a vacuum desiccator containing silica gel for 24 h and then weighed (G_0). The dried sample was then conditioned at 25 °C and 65 % relative humidity (RH) and reweighed until the weight became constant (G_1), and the moisture regain was calculated according to:

$$\text{MR} = (G_1 - G_0)/G_0 \quad (5)$$

The degree of swelling (SD) was also measured gravimetrically. Briefly, preweighed samples (G_0) were immersed in water at 25 °C. The samples were weighed at different time intervals (G_2) until no change in weight was observed, which allowed the samples to reach equilibrium swelling. SD was calculated based on the difference between the two readings [52]:

$$\text{SD} = (G_2 - G_0)/G_0 \quad (6)$$

Preliminary sorption experiments were conducted in order to examine the adsorption ability of the samples to different kinds of dyes. 0.05 g rectangular-shaped samples was immersed in two kinds of cationic dye solutions (60 mg/l Astrazon Red FBL, 30 mg/l Astrazon Blue GRL) and two kinds of anionic dye solutions (100 mg/l Evercion Red H-

E3B, 77 mg/l Evercion Navy Blue H-ER), respectively. The volume of dye solutions was 5 ml. The solutions were stood for 3 days at room temperature, and then analyzed by UV-Visible spectroscopy (Hitachi, Japan) to determine their concentrations with the help of a calibration plot measured from reference solutions.

Zeta potential measurements were carried out on a zeta-Potential analyzer (Nano ZS, Malvern Instruments Ltd.). Specifically, 10 mg native or polymer-grafted cotton was cut into small pieces and put into 1 mmol/l KCl solution (pH=6.7), and the solution was sonicated for 30 min in an ultrasonic bath and then kept at room temperature overnight. The supernatant with small particles was used to conduct zeta potential measurements, and all data were determined 10 times, and the average values were adopted.

Results and Discussion

Preparation and Mechanical Properties of Polymer-grafted Cotton Fabrics

ARGET ATRP is regarded as an industrially friendly method to prepare polymers and grow polymer chains directly from a substrate because just a few ppm of Cu(II) is required and the system is less sensitive to oxygen. The concentration of Cu(II) was relatively low in this study, and the grafted cotton fabrics were essentially colorless after washing. During SI-ARGET ATRP of different monomers, the weight uptake increases linearly with reaction time at fixed monomer concentration and temperature, and the time is varied to achieve a similar weight uptake. The results are given in Table 1.

Figure 1 shows the FTIR spectra of native cotton, Cotton-Br and polymer-grafted cotton fabrics. The modified fabrics reveal the appearance of the peak at 1730 cm^{-1} where the stretching vibration of the ester carbonyl group except Cotton-Br, of which the ester group was undetectable due to the molecular-level-thickness of bromo-ester groups and the spectra from FTIR measurements originate from a layer thickness in the micrometer scale [53]. The fact that the polymers are covalently attached but physisorbed to the surface can be confirmed by replacing Cotton-Br with native cotton during polymerization and FTIR of as-prepared sample revealing no traces of carbonyl content.

The native and polymer-grafted cotton fabrics were also analyzed by SEM, Figure 2. It can be observed that the woven structure of cotton fabric did not change after graft

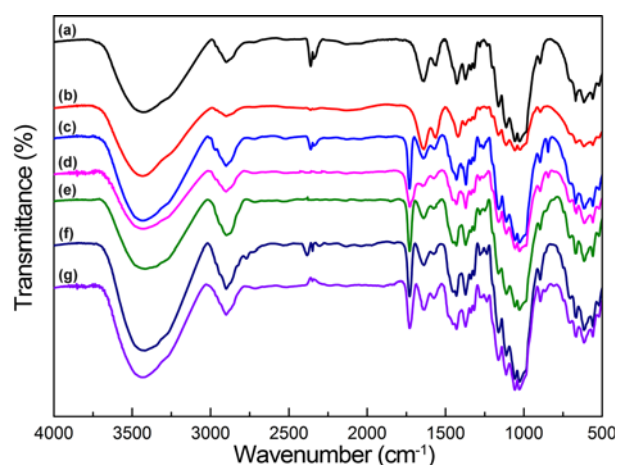


Figure 1. FTIR spectra of the polymer-grafted cotton fabrics; (a) Native cotton, (b) Cotton-Br, (c) Cotton-PtBA, (d) Cotton-PAA, (e) Cotton-POEOMA, (f) Cotton-PDMAEMA, and (g) Cotton-QPDMAEMA.

polymerization, which indicates the good preservation of fabric softness and air-breathing properties that are important for clothing comfort. Inset images show the surface of the polymer-grafted cotton fibers appear to be covered because it is no longer smooth comparing with that of native cotton fibers. The formation of granules on the polymer-grafted fiber surface might attribute to the coiled (aggregated) configuration or small amounts of physisorbed polymer on the substrate [40,41].

The results of tensile strength and breaking elongation of polymer-grafted cotton fabrics are shown in Figure 3. The mechanical properties of textiles depend on many parameters, including fiber properties, yarn properties, fabric structure and surface properties, etc. When the fiber surface was covered by a layer of grafted polymer, the fabric mechanical behavior could be changed due to the varied elasticity and surface properties of the fiber, which is highly depended on the polymer properties. As shown in Figure 3, when the cotton fabric was modified with BiBB, the tensile strength and break elongation became lower probably attributed to the reduced hydroxyl groups on the fiber surface and decreased interfacial molecular interactions. The fabric became more rigid after PtBA grafting, and it exhibited increased tensile strength and decreased break elongation as compared to native cotton, probably because of the increased elasticity and surface roughness, or the enhanced fiber weak

Table 1. Reaction conditions and weight uptake percentages of the polymer-grafted cotton fabrics

Sample	[Monomer] (mol/l)	Temperature (°C)	Time (h)	Weight uptake <i>m</i> (%)	Grafting yield <i>y</i> (%)
Cotton-PtBA	0.51	60	2	17.7	8.3
Cotton-POEOMA	0.37	25	4	20.3	3.0
Cotton-PDMAEMA	0.63	60	4	16.3	4.9

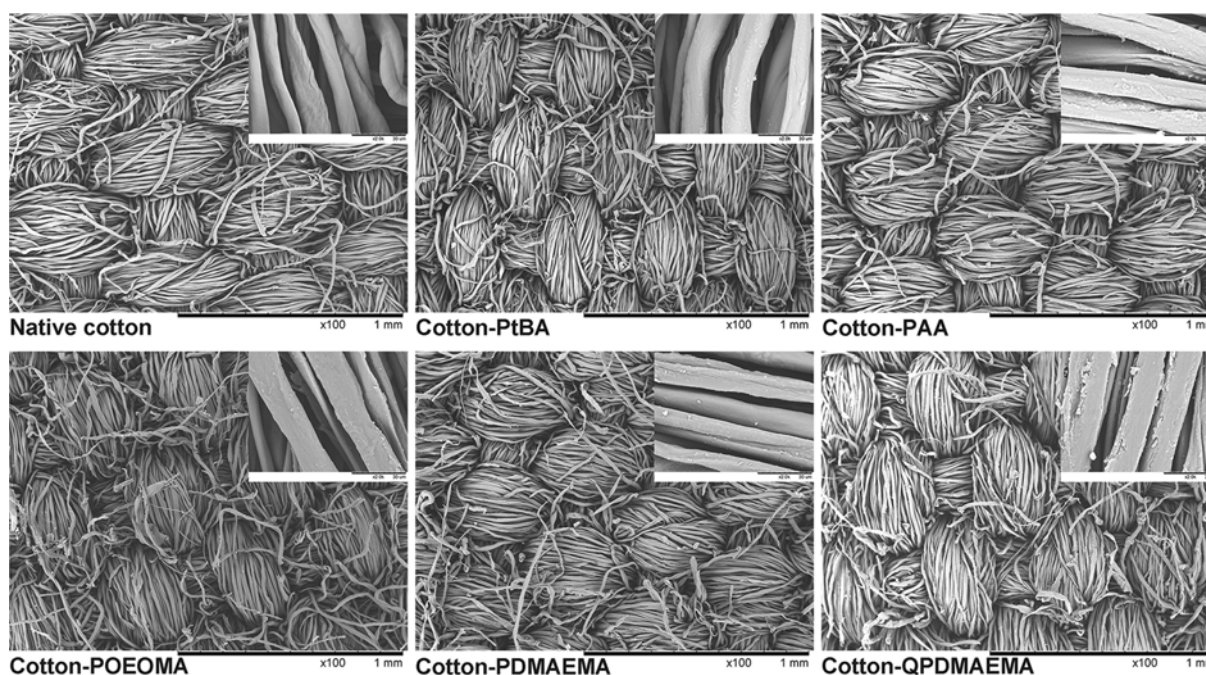


Figure 2. SEM micrograph of the native and polymer-grafted cotton fabrics. The scale bars are 1 mm and 30 μm in the insets.

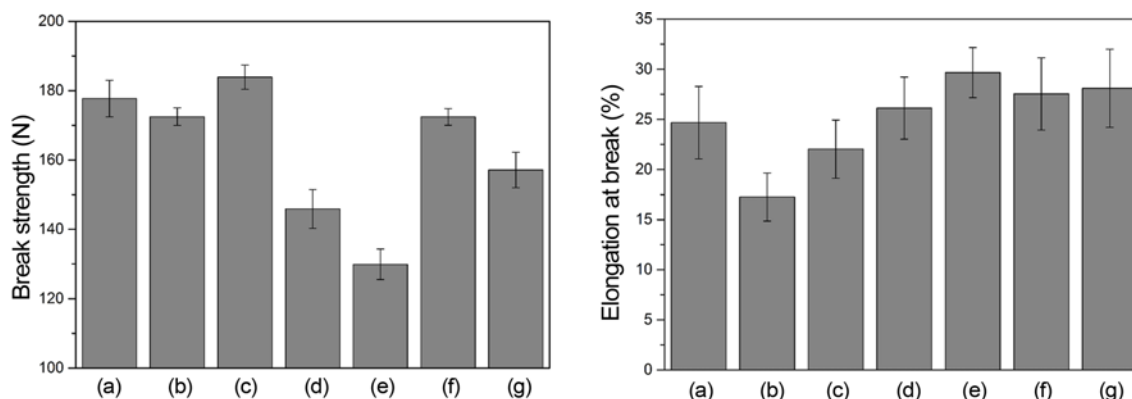


Figure 3. The strength and elongation of the polymer-grafted cotton fabrics; (a) native cotton, (b) Cotton-Br, (c) Cotton-PtBA, (d) Cotton-PAA, (e) Cotton-POEOMA, (f) Cotton-PDMAEMA, and (g) Cotton-QPDMAEMA.

links. However, the different results were found when the surface was grafted with POEGMA, which has higher elongation at break but lower tensile strength. An explanation for this could be that POEGMA has a very low glass transition temperature (T_g) (between -56 and -59 °C) and T_g of PtBA reported in literature is 36 °C [54,55]. The soft POEGMA segment increases the inter yarn slippage and sliding effect, the tensile strength decreased. T_g of PDMAEMA is reported at 5 °C [56], which is between that of POEGMA and PtBA, and thus the tensile strength and break elongation of Cotton-PDMAEMA is between that of Cotton-PtBA and Cotton-POEOMA. Although PAA and QPDMAEMA have higher T_g compare with PtBA and PDMAEMA, respectively (T_g of PAA is above 95 °C, and fully quaternized PDMAEMA

is ca. 140 °C) [57,58], their grafted fabrics has lower tensile strength and higher elongation at break than their counterpart respectively, probably due to the increased hydrophilicity and the plasticizer effect exerted by the adsorbed water.

Wetting Properties of Polymer-grafted Cotton Fabrics

The wetting properties of the native and polymer-grafted cotton fabrics was investigated by determining surface contact angle, moisture regain and swelling degree, as shown in Figure 4 and Table 2. Water contact angle measurements showed that on the fabric before and after initiator grafting, the initial CA increased from 0° to $134 \pm 6^\circ$, which also proved the successful grafting of BiBB. However, the CA of Cotton-Br decreased to $104 \pm 7^\circ$ due to the water permeated

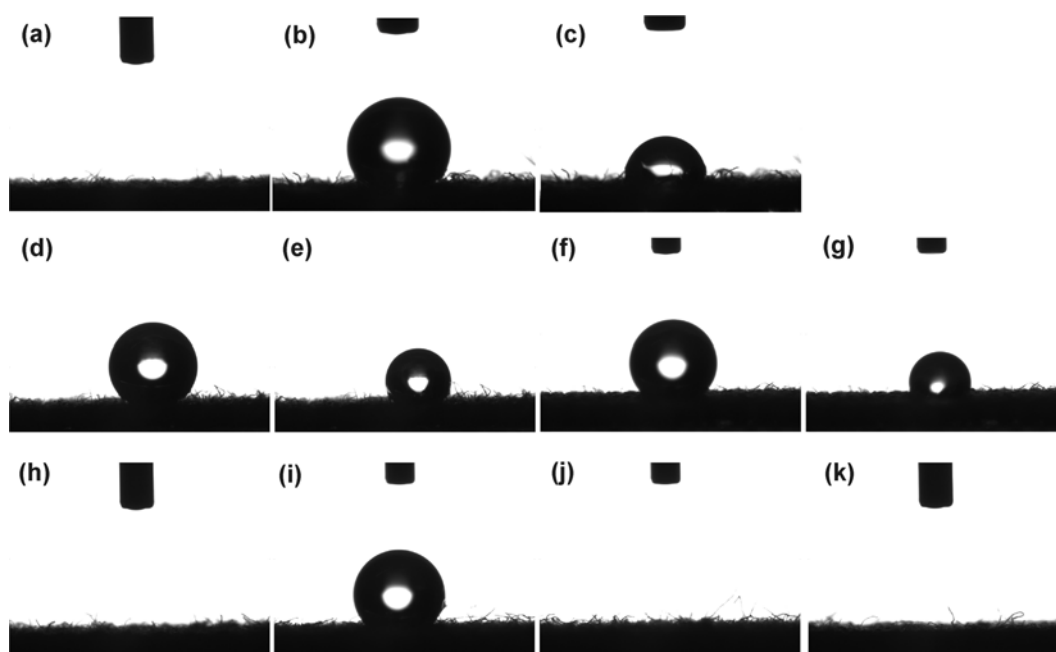


Figure 4. Photographs of water droplets placed on textiles: native cotton (initial) (a), Cotton-Br (initial) (b), Cotton-Br (10 min later) (c), Cotton-PtBA (initial) (d), Cotton-PtBA (10 min later) (e), Cotton-PAA (initial) (f), Cotton-PAA (10 min later) (g), Cotton-POEOMA (initial) (h), Cotton-PDMAEMA (initial) (i), Cotton-PDMAEMA (45 s later) (j), and Cotton-QPDMAEMA (initial) (k).

Table 2. Wetting properties of the native and polymer-grafted cotton fabrics

Sample	Moisture regain (%)	Swelling degree (%)	CA (initial) (°)	CA (10 min) (°)
Native cotton	7.8	100	0	0
Cotton-Br	6.5	80	134±6	104±7
Cotton-PtBA	4.6	47	139±4	119±2
Cotton-PAA	6.5	56	132±3	106±5
Cotton-POEOMA	6.1	80	0	0
Cotton-PDMAEMA	4.7	76	123±7	0
Cotton-QPDMAEMA	8.6	87	0	0

into the internal structure of the hydrophilic cotton fiber, which can be found in Figure 4(c). Attribute to the hydrophobic nature of PtBA polymer chain, cotton fabric grafted by PtBA displayed increased CA compared with Cotton-Br, and it also exhibited the phenomenon of water penetration into the fiber. The plausible explanation for this observation is that the exposure of unmodified areas of the cotton fabric caused by the damage of the interfibrillar structure during the modification of cotton fabric with large density polymer chains [59]. The cleavage of the tert-butyl ester groups of PtBA produce PAA chain, which has been considered to a hydrophilic polymer. However, the CA of Cotton-PAA was close to that of Cotton-PtBA in this study. This can be explained by the pH-responsive property of PAA, who is virtually undissociated and exists as a neutral chain at a low pH (pK_a of PAA is in the range 4.5-5.5 [60]). When the deionized water droplet was placed on the fabric surface,

local acid-base balance would lower the pH of water droplet and inhibit the further ionization of PAA chain. The high T_g of PAA is probably another reason for the hydrophobic behavior of Cotton-PAA. As for PDMAEMA-grafted cotton fabric, the initial CA was relatively high as well, but the applied droplet was adsorbed into the substrate within 45 s. The lower T_g of PDMAEMA benefit the penetration of water into the fiber, and the pK_a of PDMAEMA (in the range 7.0-7.5) [61], which is close to that of deionized water (6.7), contribute the wetting properties of Cotton-PDMAEMA as well. The cotton fabric grafted by quaternized PDMAEMA was superhydrophilic because of the positively-charged strong polyelectrolyte brush on the surface. Cotton-POEOMA has good hydrophilic property due to the outmost layer of hydrophilic PEG segments on fiber.

Moisture regain and swelling degree represent long-time wetting properties of fabrics. Consistent with the CA results,

hydrophobic Cotton-PtBA has the lowest moisture regain and swelling degree. As listed in Table 2, the swelling degree of all modified fabrics is lower than that of native cotton, probably because the encapsulated polymer matrix inhibits the swelling of fibers and tightly woven fabrics. The moisture regain of Cotton-QPDMAEMA is higher than that of the native cotton, contrary to that of other modified fabrics.

Adsorption and Charge Properties of Polymer-grafted Cotton Fabrics

Dyes can adsorb onto fabrics through attractive forces including hydrogen bonding, Van der Waals forces and ionic bonding, and the dye affinity of a fabric highly depends on the dye chemical structure and fabric properties. Two cationic dyes (Astrazon Red FBL and Astrazon Blue GRL) and two anionic dyes (Evercion Red H-E3B and Evercion Navy Blue H-ER) with different concentrations were applied in this study to reveal the interactions between the dyes and the fabrics, as shown in Figure 5 and Table 3.

It is not surprising to observe that Cotton-PAA adsorbed most of the cationic dyes in the solutions, and Cotton-

PDMAEMA and Cotton-QPDMAEMA adsorbed most of the anionic dyes in the solutions due to their negatively charged or positively charged properties respectively, which is also revealed by the zeta potential measurements listed in Table 3. The results not only confirmed that the specific charge properties have been successfully introduced to the cotton fabric, but also opened the way to prepare functional cotton fabrics for new and advanced applications such as extraction of heavy metals or dyes from wastewater, in-situ grown of nanoparticles for advanced functionalities, stimuli-responsive materials. As a sequel to the present study, an extensive report on the advanced applications of polymer-grafted fabrics and their related materials will be reported in the future.

The adsorption ratio of cationic dyes by native cotton is higher than that of anionic dyes because of the negatively charged nature of cotton fiber. Besides the charge properties of the fabrics, its hydrophobicity affects the dyes adsorption as well, as demonstrated by the results of Cotton-Br and Cotton-PtBA. Hydrophilic Cotton-POEOMA, however, has lower dye adsorption ability largely due to its anti-fouling

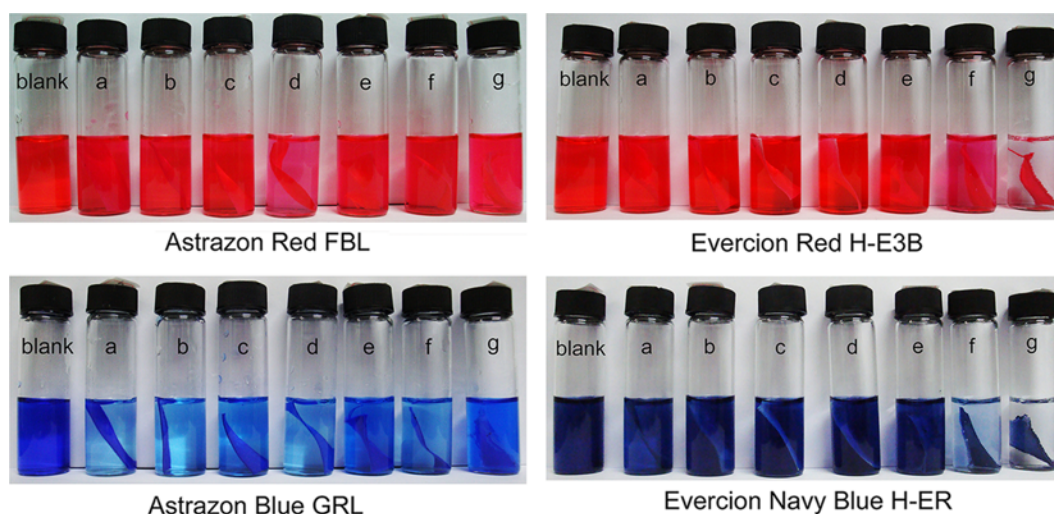


Figure 5. Appearance of the dye solutions after adsorption by native cotton (a), Cotton-Br (b), Cotton-PtBA (c), Cotton-PAA (d), Cotton-POEOMA (e), Cotton-PDMAEMA (f), and Cotton-QPDMAEMA (g).

Table 3. Adsorption and charge properties of the polymer-grafted cotton fabrics

Sample	Adsorption (Astrazon Red FBL, %)	Adsorption (Astrazon Blue GRL, %)	Adsorption (Evercion Red H-E3B, %)	Adsorption (Evercion Navy Blue H-ER, %)	Zeta potential (mV)
Native cotton	31.3	91.4	29.2	42.6	-10.1
Cotton-Br	33.5	89.0	10.2	15.5	-8.2
Cotton-PtBA	32.9	84.4	1.1	1.3	-7.9
Cotton-PAA	84.0	92.9	2.0	5.2	-17.1
Cotton-POEOMA	22.7	65.7	23.7	31.0	-8.9
Cotton-PDMAEMA	9.8	87.6	82.2	93.7	12.4
Cotton-QPDMAEMA	4.1	33.6	99.6	99.1	30.6

properties on the surface. It also can be found in the experiment that the dyes are evenly adsorbed on all the fabrics, meaning that the polymers are uniformly grown from the fabric surface.

Conclusion

SI-ARGET ATRP, a robust and versatile synthetic technique, was used to prepare PtBA, POEOMA and PDMAEMA bushes on cotton fabric surface. Only minor adjustments to the reaction conditions were required to get similar weight uptake. Grafted PtBA on the fabric surface was further hydrolyzed to PAA, and PDMAEMA was quaternized to QPDMAEMA. The chemical structure of the polymer grafted cotton fabrics were investigated by SEM and FTIR, and the results verified the successful grafting of polymer on cotton fabrics. Due to the different structures of grafted polymers, the surface properties of the fabrics can be tailored. Compared with native cotton, PtBA-grafted cotton fabric exhibited increased tensile strength and decreased break elongation while POEGMA-grafted fabric had higher elongation at break but lower tensile strength, probably because these polymers have different T_g . Also, attribute to their different hydrophilicity, Cotton-POEOMA, Cotton-PDMAEMA and Cotton-QPDMAEMA could be wetted by water within a few seconds, but Cotton-Br, Cotton-PtBA and Cotton-PAA were hydrophobic and had relatively lower moisture regain and wet swelling. It was also observed that Cotton-PAA had the enhanced capability towards cationic dyes adsorption, while Cotton-PDMAEMA and Cotton-QPDMAEMA exhibits a high adsorption capability on anionic dyes, because of the different charge properties gained by the fabrics. Further studies are underway to fabricate novel functional fabrics and investigate their advanced applications on the textile and related industries.

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