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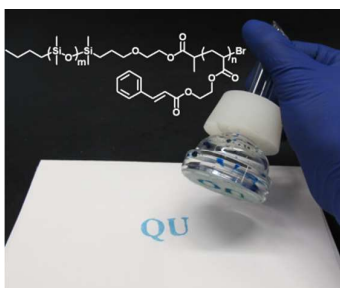
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## Hydrophilically-Patterned Superhydrophobic Cotton Fabrics and Their Use in Ink Printing

Yu Wang, Xiaoyu Li, Heng Hu, Guojun Liu\* and Muhammad Rabnawaz

Department of Chemistry, Queen's University, 90 Bader Lane, Kingston, Ontario, Canada K7L 3N6 Email: [guojun.liu@chem.queensu.ca](mailto:guojun.liu@chem.queensu.ca)

**Abstract.** Poly(dimethylsiloxane)-*block*-poly(2-cinnamoyloxyethyl acrylate), (PDMS-*b*-PCEA), has been synthesized and characterized. The copolymer formed micelles in mixtures of tetrahydrofuran and hexane. Treating cotton swatches by soaking them in the micellar solutions, removing them, and annealing them at 120 °C after solvent evaporation yielded swatches with their fibers covered by the copolymer. Our X-ray photoelectron spectroscopy (XPS) and surface wetting property analyses indicated that the PDMS block topped the polymer coating. Photolyzing the cotton swatches under a mask crosslinked the anchoring PCEA layer around the fibers in the unmasked regions. While the crosslinked copolymer was not removed by dichloromethane extraction, polymer in the non-irradiated regions was readily extracted, regenerating the cotton fibers. Since PDMS-coated regions were superhydrophobic and the regenerated cotton was hydrophilic, these treatments yielded hydrophilically-patterned superhydrophobic cotton fabrics. While water-based solutions such as ink readily permeated the hydrophilic regions, they were blocked in the superhydrophobic regions. Thus, inverted ink or dye reservoirs held by these cotton swatches were used as stamps for ink or dye printing, reproducing the original lithographic mask pattern. The pattern has been printed onto fabrics, cardboard, paper, wood, and aluminum foil.

## I. Introduction

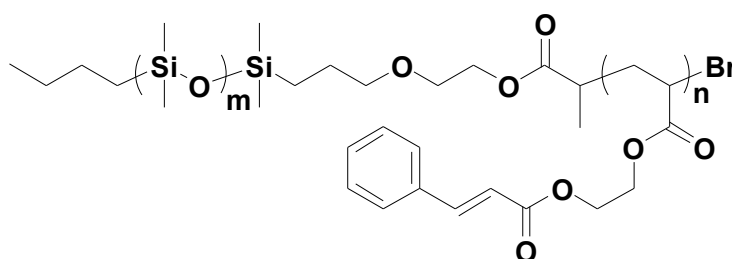
Coating a hydrophilic cotton fabric with hydrophobic moieties may turn the fabric superhydrophobic.<sup>1-9</sup> Superhydrophobic cotton fabrics strongly repel water because they possess water contact and shedding angles exceeding  $150^\circ$  and below  $10^\circ$ , respectively.<sup>10-12</sup> Superhydrophobic fabrics have a wide range of applications.<sup>13, 14</sup> For example, they can be used for waterproof tents, canvas, or umbrellas. If the fabrics still possess good hand (feel) and breathability, they can be used for waterproof outerwear.

The simplest method to coat cotton is to polymerize a hydrophobic monomer and crosslink the resultant polymer around the cotton fibers.<sup>1, 7, 15-18</sup> An alternative method is to graft an alkyl compound onto cotton fibers.<sup>19-21</sup> The coating obtained from the latter process may be a thin monolayer, with a thickness less than 1 nm. To increase the monolayer thickness to the scale of nanometers or tens of nanometers, block copolymers can be used to coat cotton fabrics. A suitable block copolymer for such a coating would bear an anchoring block that becomes covalently linked to or crosslinked around the cotton fibers and another block that renders the desired water-repellency (and sometimes also oil-repellency) to the textile.<sup>4, 22-24</sup>

A coating provides water and sometimes also oil repellency because it reduces the surface tension of the cotton substrate. While alkyl compounds can reduce surface tensions down to 25 - 30 mN/m, a fluorinated compound reduces the surface tension down to  $\sim 6.7$  mN/m.<sup>25, 26</sup> These values are substantially smaller than the surface tension of water, which is 72.8 mN/m at room temperature.<sup>27</sup> High water contact angles and low shedding angles are possible on coated fabrics also because of their intrinsic roughness.<sup>28-31</sup> Fabrics are woven from threads that are composed of bundles of fibers and void spaces thus exist between the different threads and the different fibers. A water droplet that is in the Wenzel state<sup>30</sup> (droplet bottom in full contact with the

substrate) does not spread as much on a rough but inherently hydrophobic surface as on a flat surface because the same degree of spreading on the former surface creates a larger water/substrate contact area and costs more energy. Analogously, a water droplet that is in the Cassie state<sup>31</sup> (hanging over protrusions and trapping air in the cavities) does not readily spread so that it can minimize the free energy.

Unimolecular block copolymer coatings have so far been applied onto cotton fabrics by grafting one block of a copolymer onto cotton fibers or crosslinking the block around them or by using the grafting and crosslinking mechanisms simultaneously.<sup>4, 22-24</sup> The trigger for these coating reactions has included catalysts or heat. In principle, light can also be used to trigger these reactions. This paper reports the synthesis of a diblock copolymer poly(dimethylsiloxane)-*block*-poly(2-cinnamoyloxyethyl acrylate) (PDMS-*b*-PCEA, Scheme 1), and the subsequent use of this copolymer to coat cotton fabrics. The PCEA block wraps around cotton fibers during cotton coatings and crosslinks during UV photolysis via the dimerization of the pendant CEA double bonds of different PCEA chains.<sup>32-34</sup> In addition, the PDMS block has a low surface tension of ~20 mN/m at room temperature<sup>26</sup> and thus provides the water-repellency.



**Scheme 1.** Chemical structure of PDMS-*b*-PCEA.

The photo-crosslinking of PCEA offers the possibility for creating patterned coatings. After the cotton textile fibers are wrapped by PCEA after coating by the diblock copolymer, one can protect certain regions of the fabric with a mask and subsequently irradiate the fabric. While the

polymer in the exposed regions becomes crosslinked and cannot be removed by solvent extraction, the coating can be readily removed from the non-irradiated regions to re-generate the hydrophilic fibers. Thus, we also report the use of the above method to create a superhydrophobic cotton fabric that bears a hydrophilic pattern.

Patterns possessing different wettability have so far been prepared on substrates of inorganic materials,<sup>35, 36</sup> polymers,<sup>37, 38</sup> paper,<sup>19, 39-41</sup> electrospun fibers,<sup>42</sup> and woven silk.<sup>43</sup> These patterned surfaces can be used to regulate liquid transport,<sup>39, 44-46</sup> liquid evaporation and condensation,<sup>47, 48</sup> as well as the self-assembly of molecules or nanoparticles.<sup>37, 42</sup> For example, the wings of the *Stenocara* beetles of the Namib Desert consist of hydrophilic bumps surrounded by a hydrophobic matrix. These hydrophilic bumps collect water droplets from the morning fog. Once the condensed droplets become large enough so that their gravitational force overcomes the van der Waals force between the droplets and the hydrophilic bumps, the droplets roll down the hydrophobic regions into the beetle's mouth.<sup>48</sup> In addition, patterned wettability has been used to encode chemical information.<sup>49</sup>

Hydrophilically-patterned cotton fabrics have also been prepared and have even been used as inexpensive microfluidic devices for facile medical diagnostic tests or biofluidic transport.<sup>50, 51</sup> To prepare hydrophobic patterns on cotton fabrics, the traditional batik painting technique can be used.<sup>50</sup> In batik painting, molten wax is first infused into regions to create hydrophobic patterns that do not need to be dyed. The hydrophilic regions are then dyed to produce a colored pattern. Hydrophilic patterns have also been prepared by stitching hydrophilic cotton yarn into a hydrophobic fabric substrate.<sup>51</sup> However, we are not aware of reported use of block copolymers in the fabrication of hydrophilically-patterned superhydrophobic cotton fabrics.

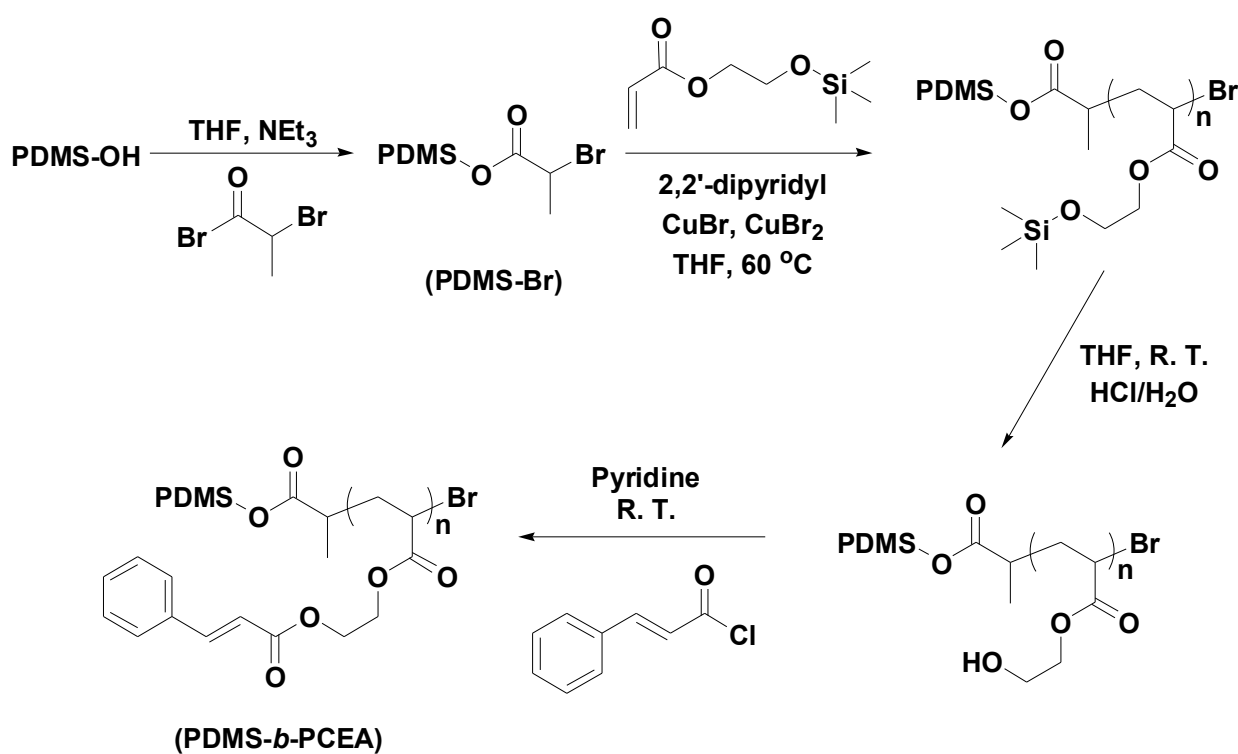
In this paper, we report in addition the use of hydrophilically-patterned superhydrophobic cotton fabrics as a stamp for ink printing. To build the stamp, we attach the fabric to the base of an assembly filter funnel (see TOC or Scheme 4). An aqueous ink is then added into the funnel that faces downwards. Since the ink only permeates the hydrophilic regions and is blocked by the superhydrophobic regions, the permeated liquid forms a pattern on the receiving substrate that resembles the original lithographic mask. Since both the substrate and the water-based printing liquid can be diversified, this represents a convenient promising method for printing patterns onto T-shirts or jerseys, for example.

## II. Results and Discussion

**Polymer Synthesis and Characterization.** PDMS-*b*-PCEA was synthesized via atom transfer radical polymerization (ATRP).<sup>52, 53</sup> The macroinitiator (PDMS-Br) was obtained by reacting hydroxyl-terminated PDMS (PDMS-OH, degree of polymerization or DP = 58, and  $M_w/M_n = 1.10$ ) with 2-bromopropionyl bromide (Scheme 2, first step).<sup>54-56</sup> PDMS-OH was obtained through the fractionation of a commercially available PDMS-OH sample (DP = 60, and  $M_w/M_n = 1.21$ ).

The synthesized PDMS-Br macroinitiator and its PDMS-OH precursor were characterized by <sup>1</sup>H NMR using CDCl<sub>3</sub> as the solvent. Figure 1a compares the spectra of the two samples in the region where the end group protons displayed signals. By comparing the signal integrations of the end groups with the integration of the signal at 0.08 ppm corresponding to the dimethylsiloxane polymer backbone (not shown here), we obtained for these polymers the repeat units numbers of 58. The key observation in the spectral region ranging from 3.0 to 4.8 ppm was that the signals corresponding to the *b* and *c* protons of the original PDMS-OH polymer were

completely replaced by the new peaks denoted as  $b'$  and  $c'$  after the polymer had been reacted with 2-bromopropionyl bromide. In addition, a new peak denoted as  $d'$  corresponding to the methyne group of the attached 2-bromopropionyl group appeared. The integration ratio between  $b'$ ,  $c'$ , and  $d'$  was 1.99:1.93:1.00, which was consistent with the theoretical values of 2:2:1. These results suggest that PDMS-OH had been quantitatively end-capped by 2-bromopropionyl bromide.

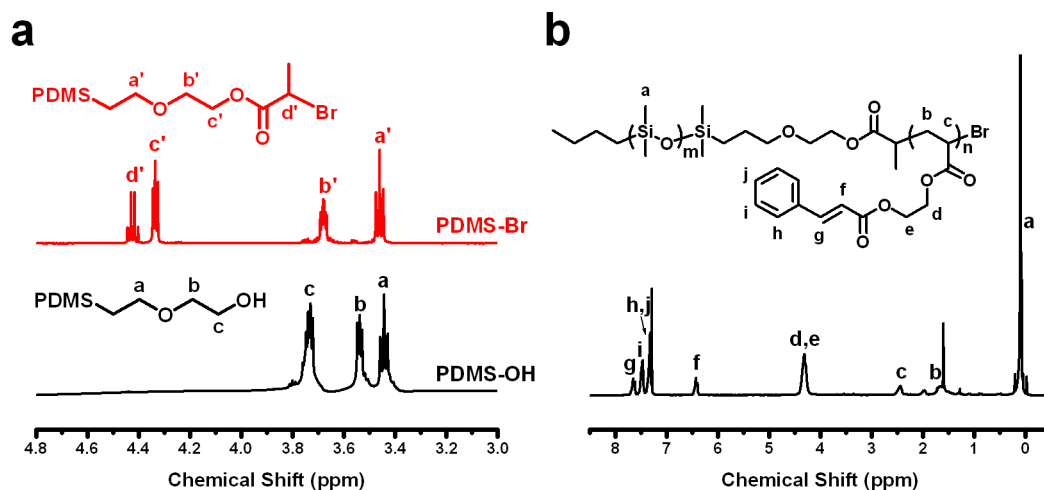


**Scheme 2.** Synthesis of the macroinitiator PDMS-Br and diblock copolymer PDMS-*b*-PCEA.

PDMS-Br was then used as a macroinitiator to polymerize 2-trimethylsilyloxyethyl acrylate (HEA-TMS). This was followed by the removal of the trimethylsilyl protecting groups under



acidic conditions and the cinnamation of the resultant poly(2-hydroxyethyl acrylate) block by cinnamoyl chloride to yield PDMS-*b*-PCEA (Scheme 2).



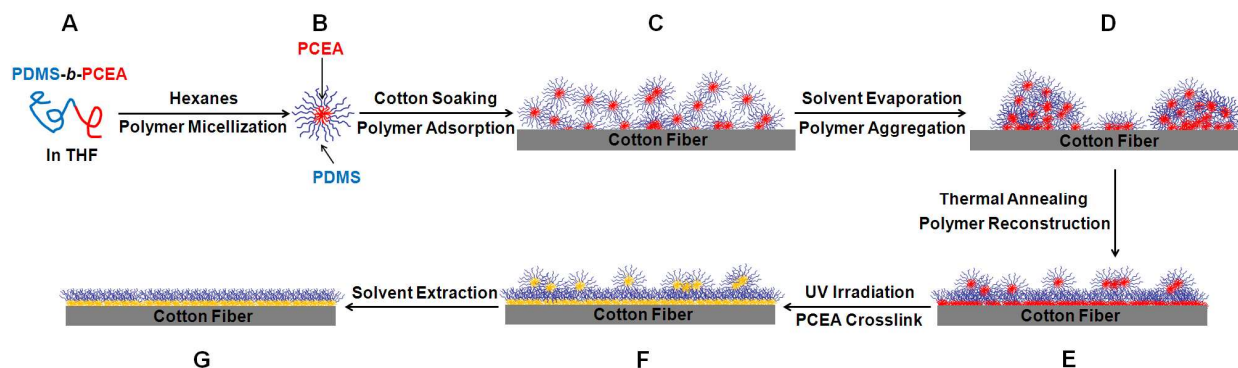
**Figure 1.** <sup>1</sup>H NMR spectra of PDMS-Br (a-top) and PDMS-OH (a-bottom) in the 3.0-4.8 ppm region and the diblock copolymer PDMS-*b*-PCEA (b).

The final product PDMS-*b*-PCEA was analyzed by <sup>1</sup>H NMR using CDCl<sub>3</sub> as the solvent, as shown in Figure 1b. The integration ratio between the signal denoted as *a* corresponding to the PDMS backbone and the signals corresponding to the PCEA block (labeled as *f*, *g*, *i* etc.) suggested that the repeat unit ratio between PDMS and PCEA was 3.6:1.0. Thus, the PCEA block was 16 units long based on a PDMS repeat unit number of 58.

The copolymer was also analyzed by size-exclusion chromatography (SEC) using CHCl<sub>3</sub> as the eluent. The SEC trace recorded for the diblock copolymer shifted to the higher-molecular weight side relative to its PDMS-Br precursor. Additionally, there was little overlap between the copolymer and the PDMS-Br peak (See the ESI, Figure S1). Thus, the initiation efficiency of PDMS-Br was high. In terms of polystyrene standards the diblock copolymer had a polydispersity index of 1.19, which was reasonable for a polymer that had been synthesized via ATRP.<sup>53</sup>

**Cotton Coating.** To coat cotton, a micellar solution was first prepared by dissolving the copolymer in THF and then adding hexanes to a volume fraction  $f_{\text{HX}}$  (A→B, Scheme 3). Since only PDMS was soluble in such mixtures, the micelles would have a PCEA core and PDMS corona. Subsequently, a cotton swatch was immersed in the micellar solution for 3 min. We hoped that the polymer micellar solution would have infiltrated the cotton matrix by this stage and some micelles would have deformed and adsorbed on the cotton fiber surfaces via their insoluble PCEA core (B→C). The cotton swatch was next withdrawn, dried in the air to remove most of the solvent (C→D). We anticipated that more polymer would have deposited during this process, yielding clustered or aggregated micelles on the fiber surfaces. In a further step, the dried cotton was annealed at 120 °C for 15 min to facilitate coating smoothing due to the increased polymer chain mobility at 120 °C (D→E). We further anticipated that the rubbery PDMS block would migrate to the polymer/air interface to reduce the surface tension of the coating and the PCEA block would wrap around the fiber to form an underlying layer (D→E).<sup>57</sup>

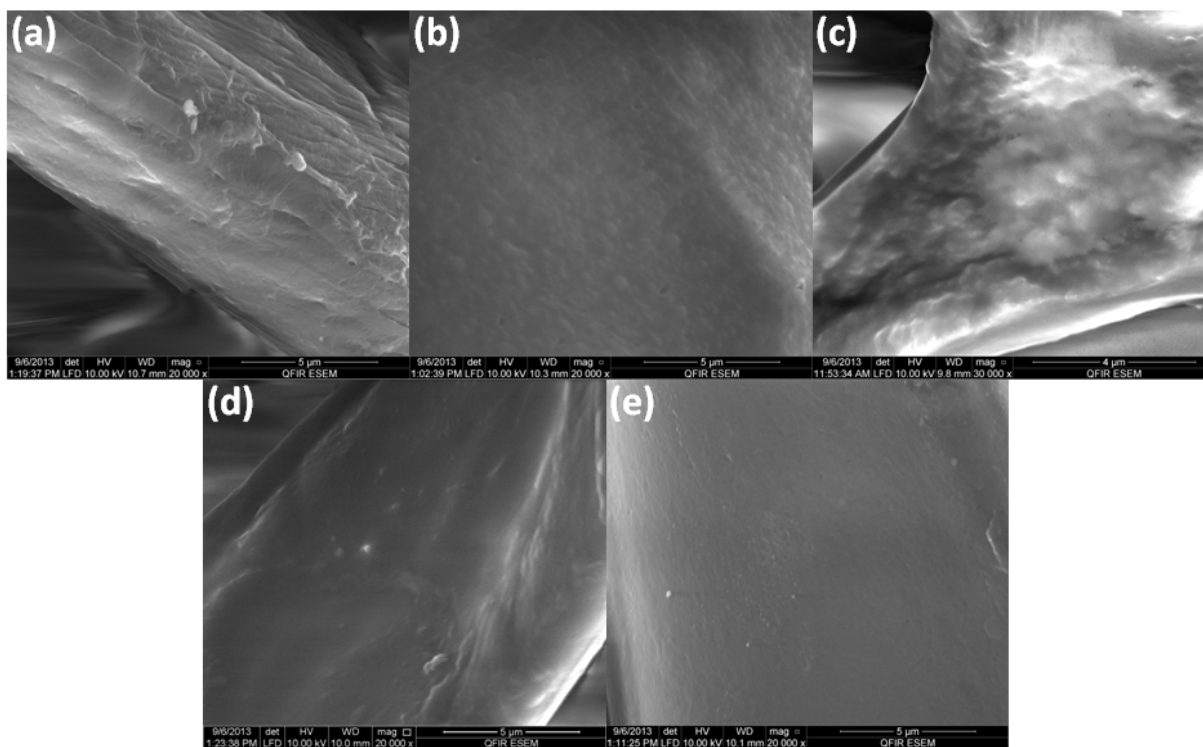
<sup>58</sup> Evidently, the deposited polymer amount on the fiber would increase with the concentration of coating polymer solution. At low polymer concentrations, the deposited polymer would form a sub-saturated diblock copolymer unimolecular layer. Above a critical concentration, a saturated unimolecular layer together with excess surface micelles would form on the fiber surfaces (E). After this, we photolyzed the cotton with a focused UV beam that was from a 500-W Hg lamp and passed a 270 nm cut-off filter to crosslink the PCEA anchoring layer via a [2 + 2] cycloaddition among CEA units<sup>32</sup> of different chains to yield an encasing stable PCEA network around cotton fibers (E→F). In the last step, the swatch was rinsed with  $\text{CH}_2\text{Cl}_2$ , a good solvent for both PDMS and uncrosslinked PCEA, to remove the crosslinked micelles that were expelled from the crosslinked unimolecular layer (F→G).



**Scheme 3.** Illustration of steps involved in the preparation of cotton coatings from micellar PDMS-*b*-PCEA solutions.

To gain evidence supporting this hypothesized coating mechanism, cotton samples were taken at different stages during coating and were then analyzed via scanning electron microscopy (SEM). Figure 2 shows SEM images of these specimens. The cotton fibers that had been soaked in a coating solution for 3 min and subsequently dried in the air for 5 min (Figure 2b) or for 2 h (Figure 2c) exhibited new semi-spherical or spherical structures. These new structures indicated that the polymers had been successfully adsorbed onto the cotton fibers. By comparing the diameters of these (semi)spherical structures (300-400 nm) with the calculated length of 18 nm for the fully stretched polymer chain of 74 repeat units, we conclude that these (semi)spherical structures were not individual micelles, but instead were aggregates of micelles. These micellar aggregates were formed probably during solvent evaporation as we hypothesized in Scheme 3 from step C to D. However, after thermal annealing was performed at 120 °C for 15 min, the large aggregates disappeared (Figure 2d). This result supported the possibility of surface smoothing and reconstruction at 120 °C. Finally, after UV irradiation and extraction with dichloromethane the surfaces of the cotton fibers exhibited no further changes (Figure 2e)

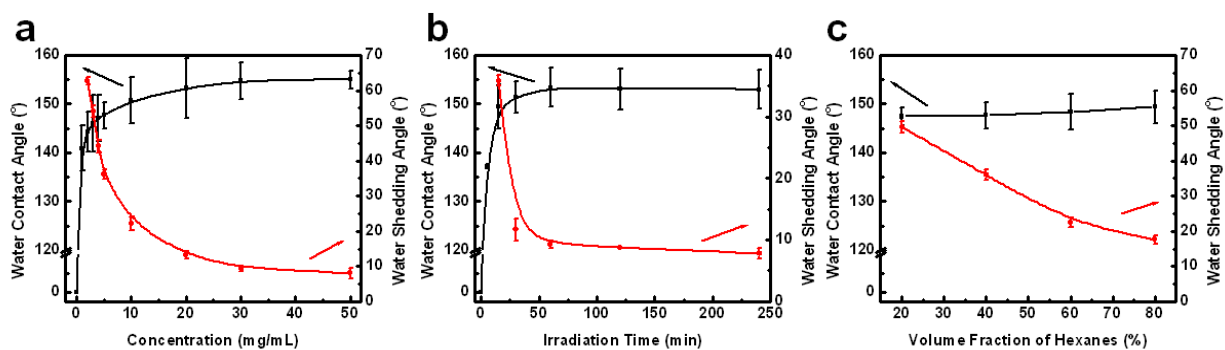
because our SEM could not resolve the small spherical micelles. Therefore, our SEM results supported our hypothesized coating formation mechanism.



**Figure 2.** SEM images recorded for specimens prepared from cotton samples taken at different stages during the coating procedure. Image (a) shows an uncoated cotton fiber. Meanwhile, samples (b)-(e) had been soaked in the coating solution for 3 min and subsequently removed and dried for 5 min (b) or 2 h (c-e) in the air. In addition, sample (d) was annealed at 120 °C for 15 min and samples (b)-(d) were all irradiated with UV light to lock in their structures prior to SEM analysis. Sample (e) was not only irradiated but also extracted by dichloromethane.

**Coating Optimization.** According to the hypothesized coating mechanism, the concentration of the polymer coating solution ( $C$ ), the UV irradiation time ( $IT$ ), and the hexane volume fraction ( $f_{HX}$ ) in the coating solution should affect final performance of the coating. Thus, we investigated the effect of varying these parameters on the water contact angles (WCAs) and water shedding angles (WSAs) on the coated cotton fabrics.

When other factors were fixed ( $IT = 30$  min on each side and  $f_{HX} = 40\%$ ), increasing the concentration of the coating solution increased the WCAs and decreased the WSAs on the coated cotton (Figure 3a) after the cotton had undergone the standard treatments including coating, air drying, thermal annealing, and solvent extraction. While an uncoated cotton sample absorbed water immediately, cotton swatches that were coated at  $C = 10.0$  mg/mL had  $WCA = 151 \pm 5^\circ$  and  $WSA = 22 \pm 2^\circ$ . A low WSA of  $9 \pm 1^\circ$  was obtained when  $C = 30.0$  mg/mL or at this point the coated cotton were superhydrophobic. In addition, the trend of an enhanced water-repellency with increases in  $C$  diminished when  $C$  was increased beyond  $\sim 30.0$  mg/mL. This trend agreed our hypothesized coating mechanism. As we discussed above, increasing the concentration of the polymer coating solution would increase the amount of copolymer deposited on the cotton fibers. The increased polymer amount would have helped build an increasingly dense unimolecular layer around the fibers until the layer got saturated. After saturation, the excess deposited polymer might not incorporate into the crosslinked first layer but exist as crosslinked spherical micellar particles. These particles would get extracted by  $CH_2Cl_2$  and would not help improve water repellency. A leveling-off behavior in water repellency with coating solution concentration has been observed by others as well.<sup>4, 22, 23</sup>



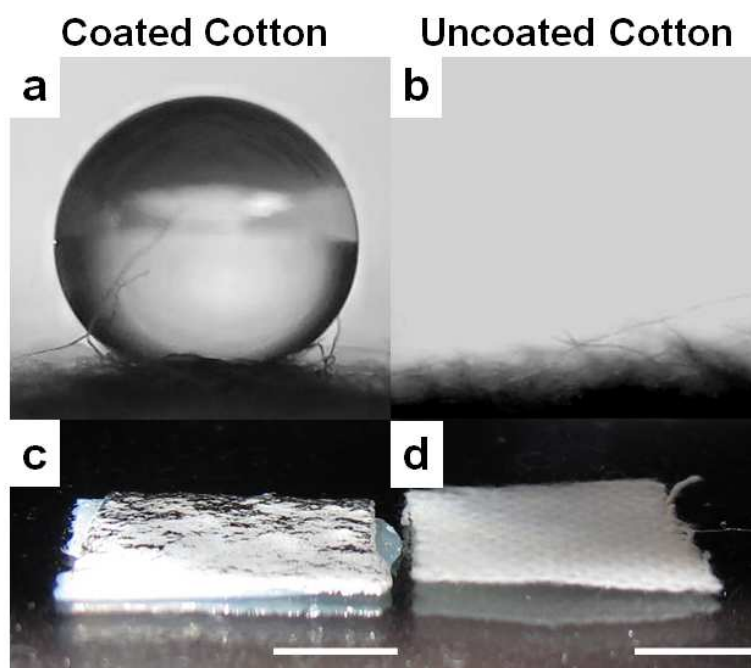
**Figure 3.** Variation of the WCAs and WSAs of cotton surfaces with changes in the copolymer concentration of the coating solution (a), UV irradiation time (b) and  $f_{HX}$  (c).

When other factors were fixed ( $C = 20.0$  mg/mL and  $f_{\text{HX}} = 80\%$ ), prolonging the irradiation time yielded higher WCAs and lower WSAs (Figure 3b) on coated and  $\text{CH}_2\text{Cl}_2$ -extracted cotton. Irradiating the sample for 30 min provided both a high WCA ( $151 \pm 3^\circ$ ) and a low WSA ( $12 \pm 2^\circ$ ). Increasing the irradiation time on each side of the cotton swatches to 1 h improved the water-repellency further, providing the fabric with superhydrophobic properties (WCA =  $153 \pm 4^\circ$  and WSA =  $9 \pm 1^\circ$ ). This influence of the irradiation time on the water repellency can be explained upon consideration that the photo-crosslinkable PCEA block needs a particular length of time to become crosslinked enough to resist extraction by  $\text{CH}_2\text{Cl}_2$ . We also tested a sample that was not irradiated ( $IT = 0$  min). In this case, the resultant fibers were hydrophilic after  $\text{CH}_2\text{Cl}_2$  extraction. Instead of beading up, an applied water droplet was immediately absorbed by this cotton sample, giving an apparent WCA of  $0^\circ$ . Thus, polymer chains deposited around the cotton fibers but were not irradiated could be removed from the cotton, regenerating the original hydrophilic cotton. On the other hand, coated cotton samples that were irradiated for more than 60 min and extracted by  $\text{CH}_2\text{Cl}_2$  were superhydrophobic.

When the other factors were fixed ( $C = 5.0$  mg/mL and  $IT = 30$  min), varying the volume fraction of hexanes ( $f_{\text{HX}}$ ) from 20% to 80% did not affect the WCAs significantly but decreased the WSAs (Figure 3c). Increasing  $f_{\text{HX}}$  would decrease solubility of PCEA. This might have helped increase the interaction between the insoluble PCEA and the cotton fibers during the cotton soaking and solvent evaporation stages and helped push more PDMS chains to the surface. An increasing density of PDMS chains on the surface would provide the cotton fibers with a lower surface tension ( $\sim 20$  mN/m)<sup>26</sup> than that provided by PCEA ( $\sim 35$  mN/m)<sup>59</sup>. The

difference in surface energy between these two chains may not be large enough to significantly influence the WCAs but only the WSAs.

We have also coated the cotton fabric with a homopolymer of poly(2-cinnamoyloxyethyl methacrylate) (PCEMA, DP = 75,  $M_w/M_n = 1.06$ ), which had similar properties as those of PCEA, under similar conditions ( $C = 5$  mg/mL in THF and  $IT = 30$  min on each side). This coated cotton sample exhibited a high WCA ( $145 \pm 3^\circ$ ). However, the water droplet could not roll off the cotton surface, even as the tilting angle was set to  $70^\circ$  in the standard WSA measurement.<sup>11</sup> Therefore, exposed PCEMA homopolymer could provide a high WCA but not a low WSA. To achieve a relatively low WSA, more of the PDMS chains from this particularly diblock copolymer-based coating need to be exposed on the surface.

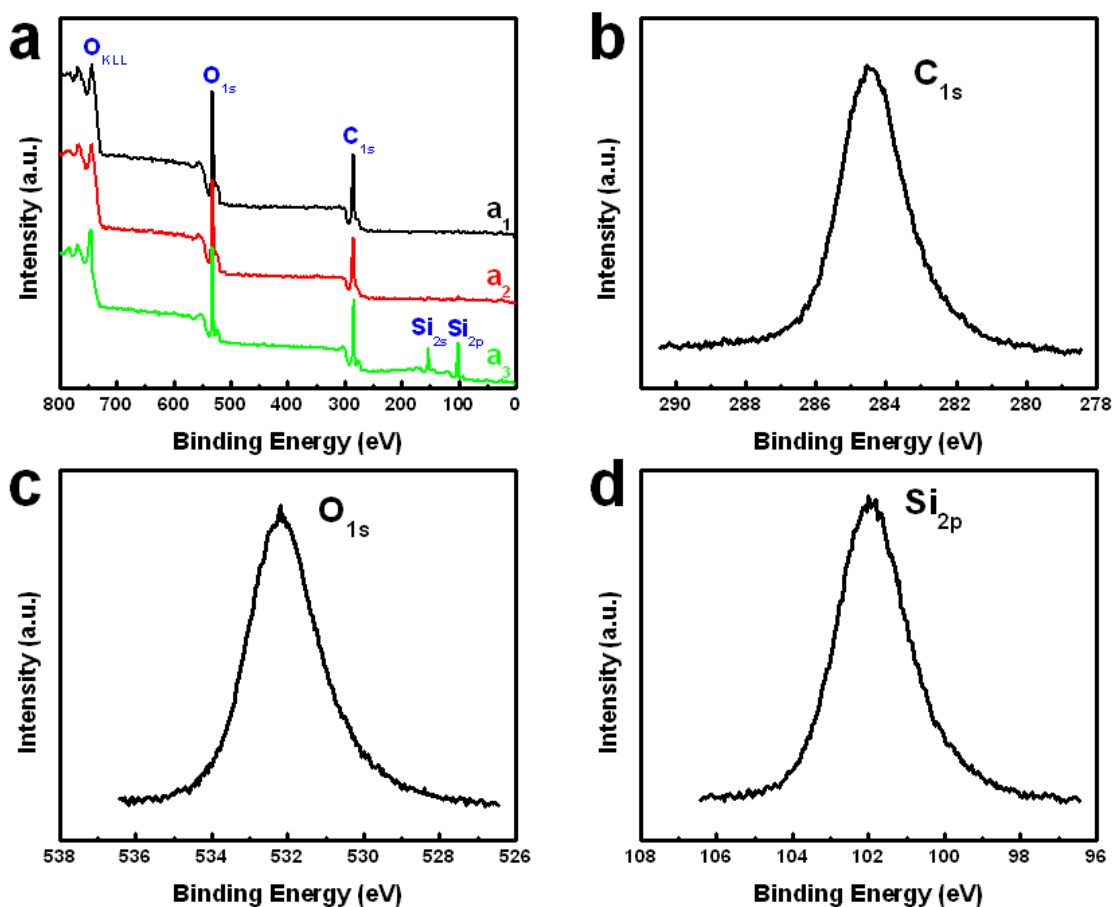


**Figure 4.** Photographs of water droplet dispensed on (a) coated and (b) uncoated cotton as well as of (c) coated and (d) uncoated cotton swatch submersed under water. The dispensed water was immediately absorbed by the uncoated cotton and the double-sided tape was used to glue the cotton swatches upon the glass substrates. The scale bars represent 5.0 mm.

Based on results of the above systematic study we have chosen the following standard coating conditions: a copolymer concentration of 20.0 mg/mL, 1 h of irradiation time on each side of a coated cotton swatch, and an  $f_{\text{HX}}$  of 80%. Figure 4 shows a comparison of the water-repellency exhibited by a cotton sample that had been coated under these conditions and by an uncoated cotton sample. The coated cotton sample exhibited a WCA of  $153 \pm 4^\circ$  (Figure 4a) and a WSA of  $9 \pm 1^\circ$ , while the uncoated cotton swatch absorbed the water droplet immediately (Figure 4b). The coated cotton swatch did not wet even when it was pushed into water. In particular, when the coated sample was submerged into water a layer of air (a plastron layer) became trapped between the water and the coated cotton swatch, giving rise to a reflective sheen (Figure 4c). In contrast, no such reflective plastron layer was observed when the uncoated cotton sample was submerged underwater (Figure 4d).

**Coating Characterization by XPS.** X-ray photoelectron spectroscopy (XPS) was used to characterize the diblock copolymer coating prepared under the standard conditions. After UV irradiation and extraction by dichloromethane, the coated cotton surface exhibited  $\text{Si}_{2s}$  and  $\text{Si}_{2p}$  peaks at 154.0 and 102.0 eV, respectively (Figure 5a<sub>3</sub>). These signals were not observed from the uncoated cotton (Figure 5a<sub>1</sub>). They were absent also from the XPS spectrum of the coated cotton that was not irradiated by UV but was extracted by  $\text{CH}_2\text{Cl}_2$  (Figure 5a<sub>2</sub>).





**Figure 5.** XPS spectra of (a<sub>1</sub>) uncoated cotton, (a<sub>2</sub>) coated cotton that were not irradiated but extracted by CH<sub>2</sub>Cl<sub>2</sub>, and (a<sub>3</sub>) coated cotton that were irradiated and extracted by CH<sub>2</sub>Cl<sub>2</sub>. High-resolution (b) C<sub>1s</sub>, (c) O<sub>1s</sub> and (d) Si<sub>2p</sub> XPS spectra of coated and extracted cotton.

The PDMS Si peaks (Figure 5a<sub>3</sub>) demonstrated the stability of the photolyzed coating. The absence of these Si peaks in Figure 5a<sub>2</sub> confirmed that the non-crosslinked polymers were rinsed away by CH<sub>2</sub>Cl<sub>2</sub>. The XPS results again confirmed the possibility for fabricating hydrophilically-patterned superhydrophobic cotton fabrics by photolithography and CH<sub>2</sub>Cl<sub>2</sub> extraction.

In addition, high resolution C<sub>1s</sub>, O<sub>1s</sub> and Si<sub>2p</sub> XPS spectra were obtained. All the C<sub>1s</sub>, O<sub>1s</sub> and Si<sub>2p</sub> peaks were single and symmetric (Figure 5b, 5c and 5d respectively), suggesting the

presence of a single C, O, or Si species on the cotton fiber surface. These three peaks at 284.5, 532.2 and 102.0 eV were attributed to C<sup>\*</sup>-Si-O, C-Si-O<sup>\*</sup>, and C-Si<sup>\*</sup>-O, respectively. Therefore, XPS only detected PDMS on the coated cotton surfaces. Further, the calculated C/O/Si atomic ratio (48.2/26.5/25.2) based on these high resolution spectra were close to the theoretical value of PDMS (C/O/Si = 50/25/25). These XPS results indicate that the cotton fiber surface was completely covered by a layer of polymer and only PDMS block was exposed on the outer surface. Therefore, the PCEA block must have anchored on the cotton fiber surfaces.

**Grafted Polymer Amount.** To determine the grafting density  $x$  or the mass fraction of polymer in the coated cotton, a literature method<sup>4</sup> based on thermogravimetric analysis (TGA) was initially used. Three different kinds of samples, including uncoated cotton, the diblock copolymer itself, and the diblock copolymer-coated cotton were analyzed by TGA (See the ESI, Figure S2). The  $x$  was determined based on the weight residue values (%) of these samples. If the polymer weight fraction in the coated cotton was  $x$ , then the following equation applied:

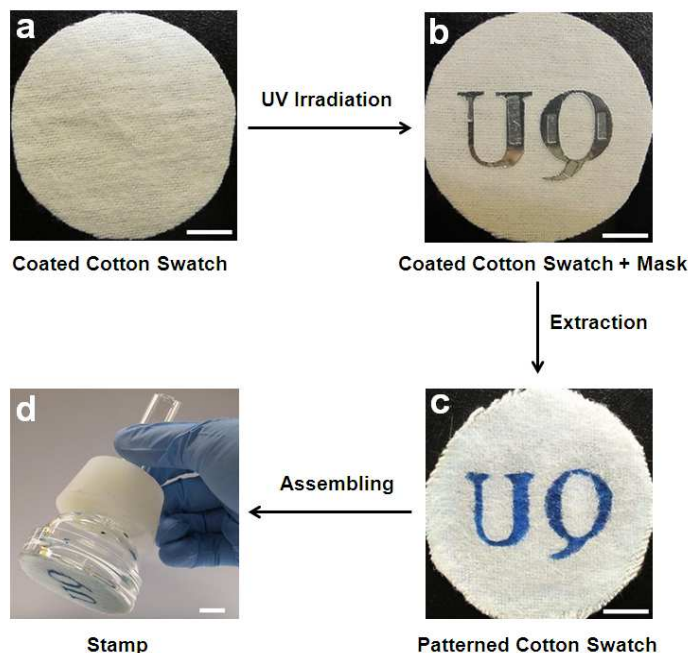
$$(1 - x)R_C + xR_P = R_{PC} \quad (1)$$

where  $R_C$ ,  $R_P$ , and  $R_{PC}$  are the weight residues of uncoated cotton, the polymer, and the polymer-coated cotton. The polymer-coated cotton samples that were characterized in this TGA study were prepared under standard conditions ( $C = 20.0$  mg/mL,  $IT = 1.0$  h on each side and  $f_{HX} = 80\%$ ) and extracted with  $\text{CH}_2\text{Cl}_2$ . Based on the  $R_C$ ,  $R_P$  and  $R_{PC}$  of  $(5.991 \pm 0.039)\%$ ,  $(2.615 \pm 0.041)\%$  and  $(5.869 \pm 0.054)\%$  from TGA analysis for each sample run in triplet,  $x$  was calculated as  $(3.6 \pm 2.8) \%$  from equation (1). The uncertainty in  $x$  was large because of error propagation, although the uncertainty of each residue value ( $R_C$ ,  $R_P$  and  $R_{PC}$ ) was small.

We double checked the  $x$  value using a simple gravimetric analysis method that relied on measuring the weight difference between the coated and uncoated cotton fabrics, using a

microbalance.<sup>17</sup> This analysis indicated that the coated quadruple samples analyzed had an average  $x$  value of  $(4.6 \pm 0.2)\%$ , which was the same, within experimental error, as  $(3.6 \pm 2.8\%)$ , the value determined from TGA. Thus, the grafted copolymer amount under the standard coating conditions was relatively low.

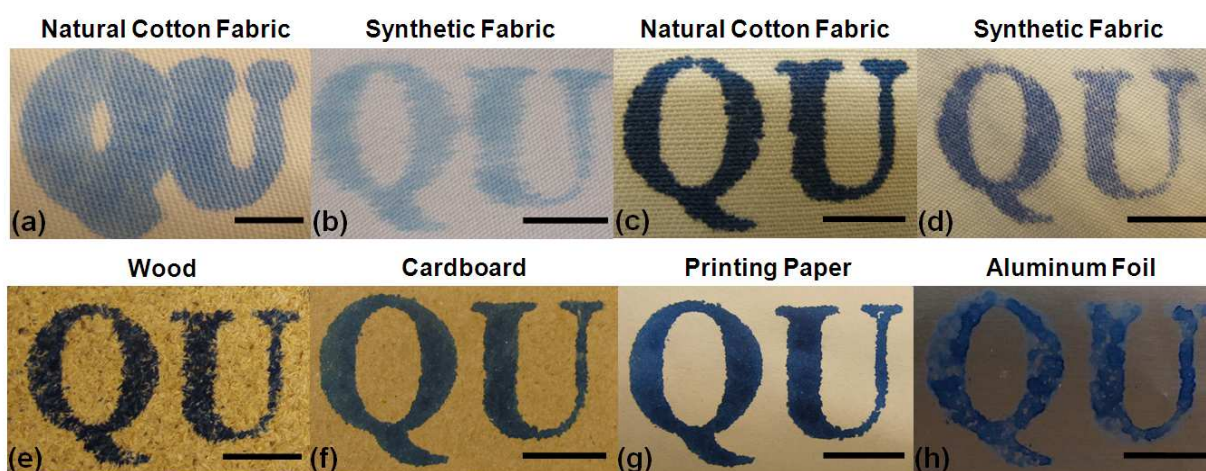
**Ink Stamp.** Our approach to prepare hydrophilically-patterned superhydrophobic cotton fabrics and to use these fabrics as the cotton-based stamps is illustrated in Scheme 4. First, a cotton swatch was coated using the standard protocol involving cotton soaking, solvent evaporation and coating annealing (Scheme 4a). Then, one side of the coated cotton fabric was irradiated for 1 h by UV light under a photo-mask made of sculpted aluminum foil glued to a quartz plate (Scheme 4b). The photolysis caused the anchoring PCEA block of the copolymer in the exposed region to crosslink around the cotton fibers. This was followed by extracting the cotton swatch with  $\text{CH}_2\text{Cl}_2$  to remove polymer that was initially masked, yielding in an otherwise superhydrophobic cotton swatch a hydrophilic pattern that resembled the original aluminum mask (Scheme 4c). Finally, the swatch was glued to the support base of a filter funnel (Scheme 4d) and the funnel was filled with ink to yield a stamp.



**Scheme 4.** Process for preparing the cotton-based stamp. Immersing a cotton swatch in a polymer micellar solution, taking it out to evaporate solvent, and then annealing the cotton yielded a polymer-coated cotton swatch (a). The coated cotton swatch is subsequently covered with an aluminum mask and irradiated (b). After extracting with  $\text{CH}_2\text{Cl}_2$ , a hydrophilically-patterned cotton swatch is obtained (c, the patterned region was dyed by blue ink). This hydrophilically-patterned cotton fabric is subsequently attached to a funnel to make a stamp for ink-printing (d). The scale bars represent 1.0 cm.

**Ink Printing.** As depicted in Scheme 4, we prepared a cotton-based stamp bearing hydrophilic pattern “QU” and then printed the letters “QU” on various substrates including cotton fabric, semi-synthetic fabric (65% polyester/35% cotton), wood, cardboard, printing paper and aluminum foil. We also tested the effect of changing the viscosity of the aqueous ink by adding water or poly(ethylene oxide) (PEO,  $M_w = 100,000$  g/mol) into a commercially available ink. For the mixtures consisting of water/ink at  $v/v = 20/1$  and ink containing PEO at 10.0 mg/mL, their relative viscosities with respect to that of water were 1.04 and 2.47, respectively. The relative viscosity of the ink was 1.28. Figure 6 shows photographs of the patterns printed using the PEO-containing ink on different substrates. Also included are photographs of the

patterns printed on cotton and semi-synthetic cotton fabrics using the diluted ink. Photographs of the patterns printed on other substrates using the diluted and the commercial ink are shown in the ESI as Figures S3 and S4.



**Figure 6.** Patterns of “QU” that had been printed using the diluted ink onto (a) cotton fabric and (b) semi-synthetic cotton fabric (65% polyester/35% cotton). The rest of the photographs were taken of the pattern printed using the PEO-containing ink onto (c) cotton, (d) semi-synthetic cotton, (e) wood, (f) cardboard, (g) printing paper and (h) aluminum foil. The scale bars represent 1.0 cm.

While the patterns printed using the PEO-containing ink looked reasonable on all of the tested substrates except on aluminum foil. On aluminum foil, the dried ink pattern was not uniform. This was caused by the non-wetting property of the aluminum foil and the inability of the ink to spread uniformly on the foil. Rather, the ink beaded up. After the solvent water evaporated, a non-uniform trace was left behind.

At the other end of the spectrum, the letters printed using the diluted ink bulged out because of the good wetting properties of the cotton. As mentioned before, cotton absorbed water. This water uptake caused the dye to spread beyond the master pattern. This spreading evidently

became less severe for the semi-synthetic cotton because of the reduced hydrophilicity of the substrate.

The pattern bulging effect was reduced by increasing the viscosity of the ink used. As is seen in Figure 6, the use of PEO-containing ink eliminated this effect and a sharp pattern was produced on both cotton and semi-synthetic cotton.

### III. Conclusions

Diblock copolymer PDMS-*b*-PCEA consisting of 58 DMS units and 16 CEA units was synthesized and characterized. The copolymer formed micelles in THF/hexanes containing 80 vol% of hexanes. Soaking cotton swatches in this micellar solution, taking them out to evaporate the solvent, and annealing at 120 °C yielded uniform copolymer coatings on cotton fibers. Our XPS and water contact and shedding angle data suggested that these coatings were topped by the PDMS layer. After UV irradiation for 1 h on each side of the coated cotton, the anchoring PCEA crosslinked around the cotton fibers and could not be removed by CH<sub>2</sub>Cl<sub>2</sub> extraction. On the other hand, the polymer could be readily extracted from non-irradiated coated cotton. Therefore, we irradiated coated cotton under an aluminum foil pattern and extracted the resultant cotton fabric with CH<sub>2</sub>Cl<sub>2</sub> to produce hydrophilically-patterned superhydrophobic cotton fabric. The patterned fabric allowed selective permeation of water-based reagents through the hydrophilic regions. This represented the first report on the use of lithography and solvent extraction to produce patterned cotton fabrics and this method should be useful in the future for the preparation of cotton-based inexpensive microfluidic devices.

Sealing the base of a filtration funnel with the patterned cotton swatch and filling the funnel with an aqueous ink produced a stamp. Pressing the stamp against substrates with different

wetting properties produced ink patterns that resembled the original mask. The fidelity of the reproduced pattern was the best on substrates that were wetted by the ink but were not too hydrophilic so as to readily absorb and spread the ink. The pattern fidelity improved on highly hydrophilic substrate such as cotton by increasing the viscosity of the aqueous ink. This printing technique may be useful for printing T-shirts and jerseys in the future.

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