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Electronic Supplementary Information

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

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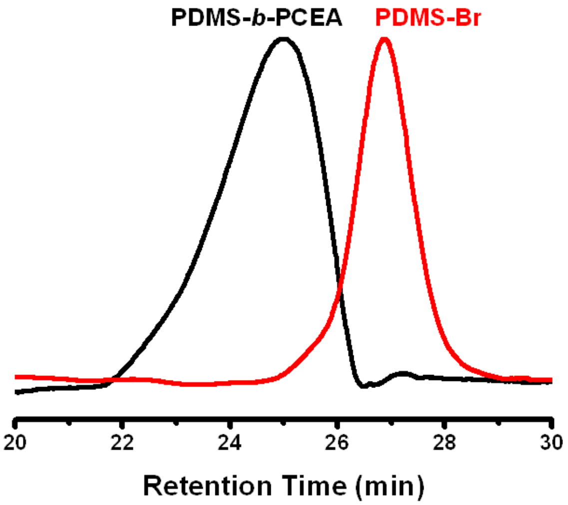

Figure S1. Comparison of SEC traces of PDMS-*b*-PCEA and the macroinitiator PDMS-Br.

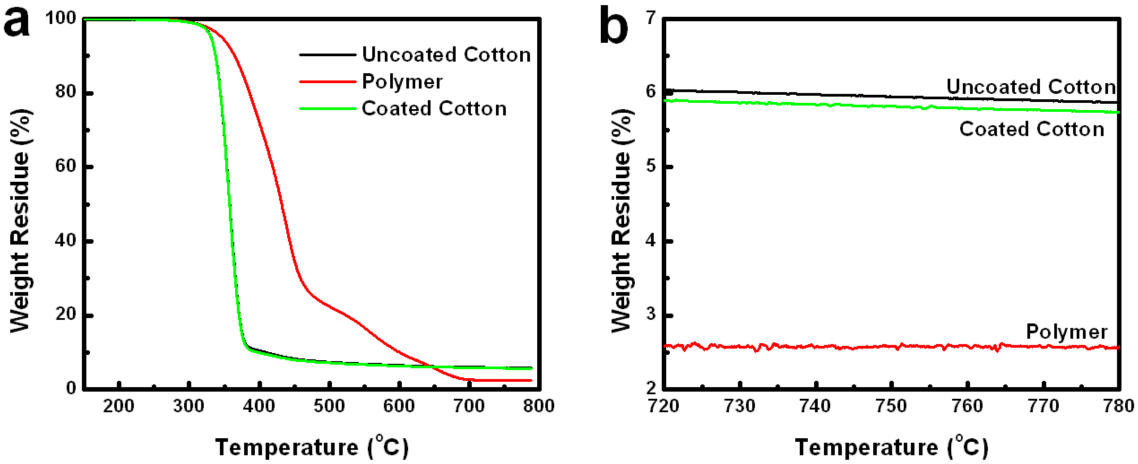

Figure S2. TGA traces of uncoated cotton, the diblock copolymer itself, and coated cotton in the range of (a) 150-800 °C and (b) 720-780 °C.

Coating Thickness Estimation. To further estimate the thickness of the grafted polymer layer, a calculation was performed based on the surface area of the cotton fabrics (*A*) and density of the diblock copolymer (ρ). The specific surface area of the same type of cotton was estimated in our previous work, and was found to be 1.3 ± 1.0 m^2/g.[1] The density of the diblock copolymer was estimated to be 1.09 g/mL using:

$$1/\rho = f_1/\rho_1 + f_2/\rho_2 \qquad (1)$$

where f_1 and ρ_1 were the respective mass fraction (52.2 %) and density (0.97 g/mL)[2] of the PDMS block, while f_2 and ρ_2 were the respective mass fraction (47.8 %) and density (1.25 g/mL)[3] of the PCEA block. If we used the grafting density x that were determined via gravimetric analysis (x = 4.6 ± 0.2%), the thickness (d) of the grafted polymer layer that would be anticipated after the samples had been subjected to irradiation/extraction treatment was found to be 32 ± 26 nm. However, some issues should be noted for the thickness calculation. First, the final estimated value would reflect an average thickness of the grafted polymer layer since the more deeply buried regions of the cotton swatch may have lost more polymer during the extraction, rather than the regions that were close to the surfaces of cotton swatch and had greater exposure to the UV irradiation. Therefore, the actual grafted thickness in these relatively deeply buried regions of the fabric may have been lower than those that were close to the surface. Another issue that should be noted was the estimation of the surface area (A = 1.3 ± 1.0 m^2/g) of the cotton fabrics, which was based on an assumption of cylindrical cotton fibers with smooth surfaces. However, the actual A may be somewhat larger due to the rough surfaces of the cotton fibers. Therefore, the actual thickness of the grafted polymer layer should be lower than the calculated value. The thickness, of the grafted polymer layer, which was on the scale of tens of nanometers, was sufficiently thin to allow the cotton fabrics to retain their desirable intrinsic properties, such as softness and breathability.

Ink Printing. Patterns of “QU” had been printed onto various substrates using the diluted ink and commercial ink.

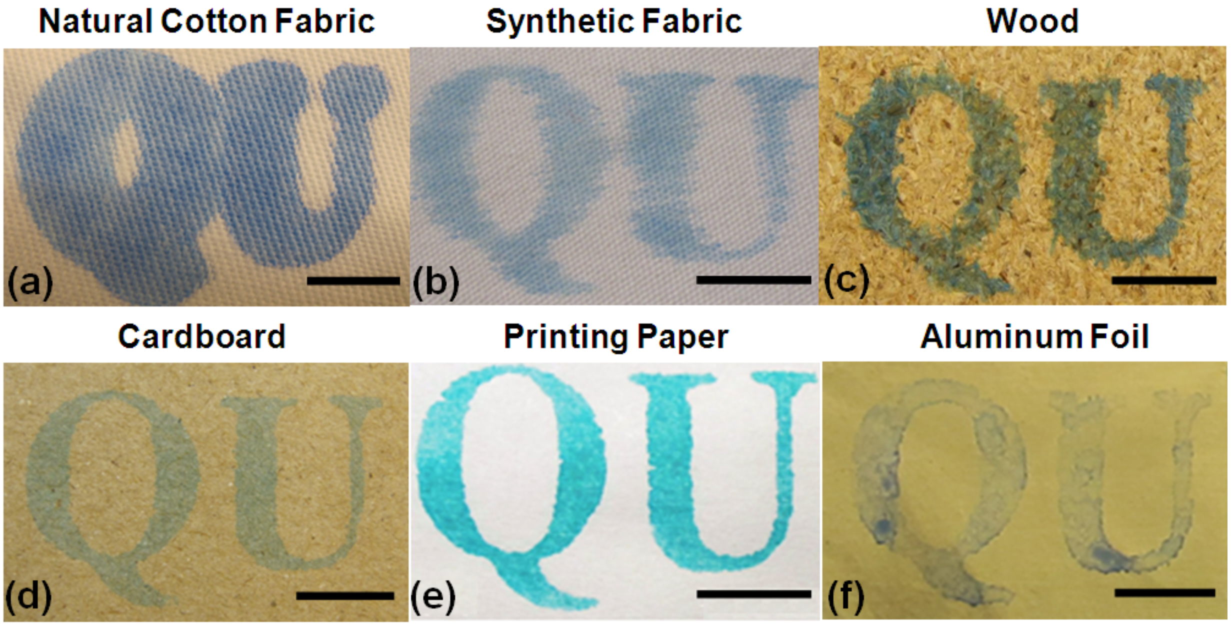

Figure S3. Patterns of “QU” that had been printed using the diluted ink onto (a) cotton fabric, (b) semi-synthetic fabric (65% polyester/35% cotton), (c) wood, (d) cardboard, (e) printing paper and (f) aluminum foil. The scale bars represent 1.0 cm.

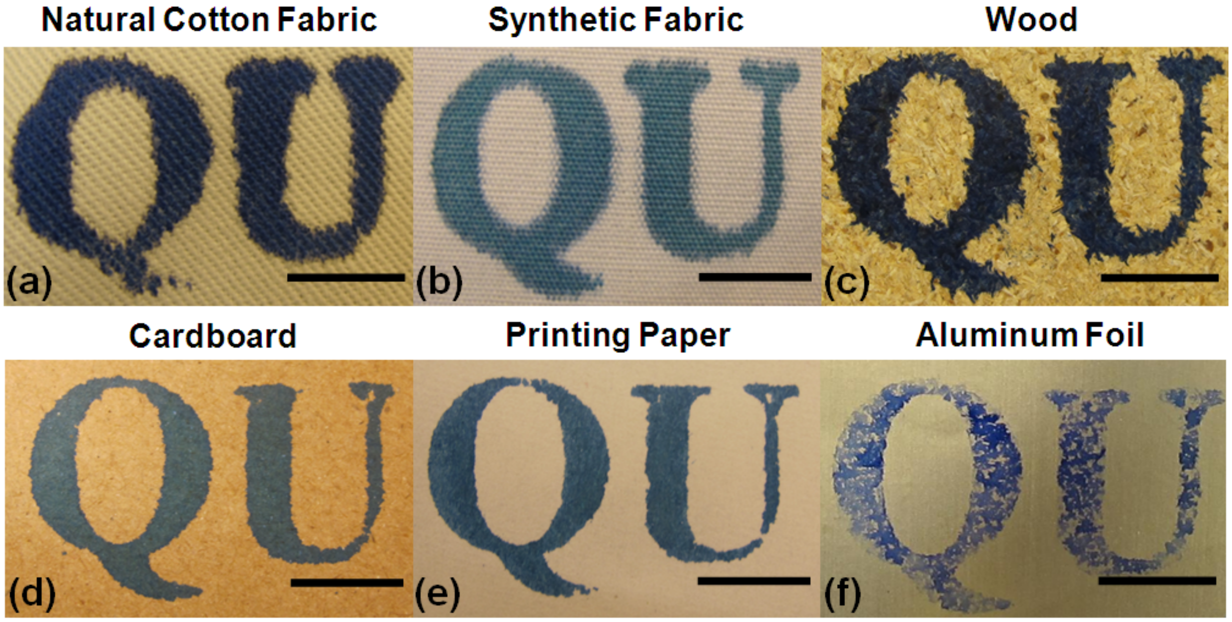

Figure S4. Patterns of "QU" that had been printed using commercial ink onto (a) cotton fabric, (b) semi-synthetic fabric (65% polyester/35% cotton), (c) wood, (d) cardboard, (e) printing paper and (f) aluminum foil. The scale bars represent 1.0 cm.

Fluorescent Dye Printing. A fluorescent polymer solution (C = 10.0 mg/mL) was applied as the dye to fabricate fluorescent patterns on cotton fabrics using the cotton-based stamp. The polymer used for this pattern printing was pyrene-terminated PEO (PEO-Py, M_w = 2000 g/mol), which was synthesized in our lab previously.

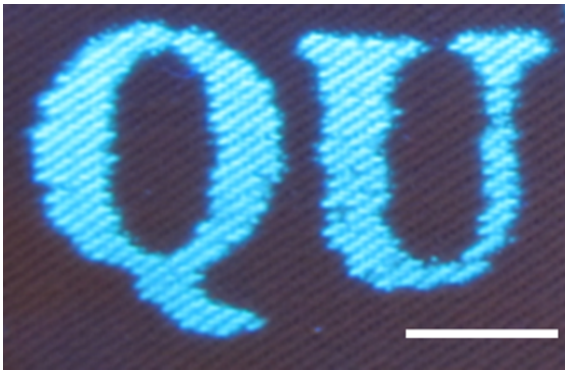

Figure S5. Fluorescent pattern of "QU" that had been printed using an aqueous PEO-Py solution as the dye onto cotton fabric. The scale bar represents 1.0 cm.

AFM Study of Micellar Films Deposited on Silicon Wafers and Then Treated Under Different Experimental Conditions. To provide insight into the behavior of PDMS-*b*-PCEA micelles during the cotton coating process, we employed the procedures that were used to coat cotton to coat flat silicon wafers. The structures of the coatings at different stages were imaged by atomic force microscopy (AFM). The AFM height images are shown in Figure S6.

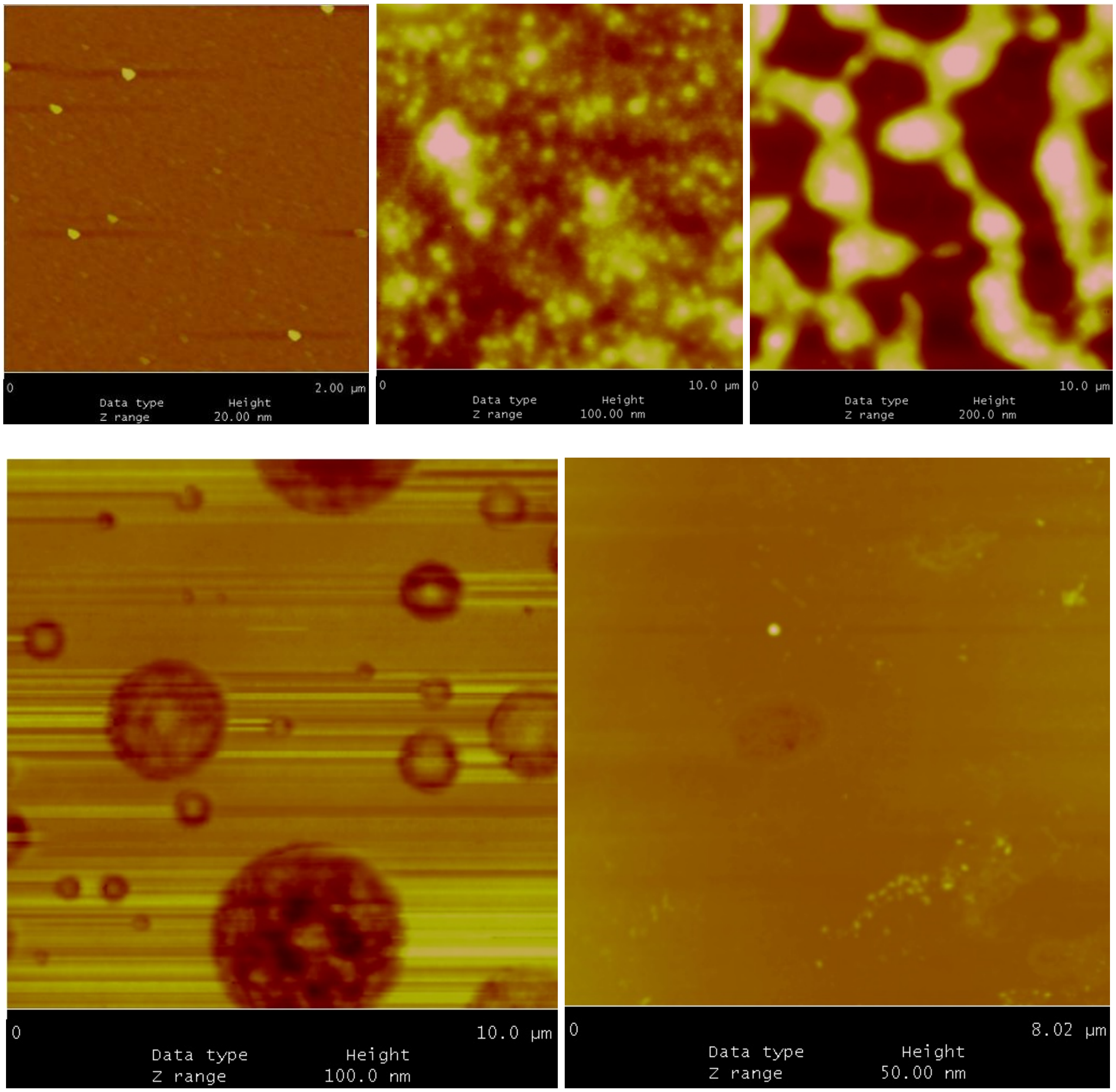

Figure S6. AFM topography images of silicon wafers bearing PDMS-*b*-PCEA coatings that were treated differently. From left to right, from row 1 to row 2, and then from left to right are images for bare silicon wafer, coating that was air-dried for 5 min and then photolyzed, coating that was air-dried for 2 h and then photolyzed, coating that was air-dried for 2 h, annealed at 120 ^{o}C for 15 min, and then irradiated, as well as coating that was annealed at 120 ^{o}C for 15 min, photolyzed, and then extracted with CH_2Cl_2.

Due to the totally different adsorption properties of silicon wafer and cotton, we do not know if the polymer would behave identically on the two surfaces. Despite this caution, we note that the behavior observed on cotton surfaces was mostly mirrored on silicon wafer surfaces.

Before annealing, micellar aggregates were observed on the silicon plates. Thermal annealing smoothed out the background. Patches were, however, left in different regions of the annealed film. These patches were probably aggregates formed from excess polymer that was not needed for brush formation. After extraction by CH_2Cl_2, the coating appeared smooth. However, the water contact angle on it was low at 74 ± 1°. This value, smaller than the reported value of 107°,[4] suggested that the extracted layer was either not dense or not intact. The last property differed from that of the coating on cotton fibers probably due to the shape difference between the coated substrates. The formation of a perfect brush layer on a silicon wafer which has a much larger surface area than a single cotton fiber is probably much more challenging.

Experimental Section

Materials. Plain-weave cotton fabric used was purchased from a local store. Based on our previous characterization (optical, scanning electron and atomic force microscopy), the fabrics had warp and weft thread diameters of 270 ± 10 and 620 ± 10 μm, respectively.[1] In addition, the fibers were imperfect cylinders with rough surfaces. Before use, a 20 cm x 20 cm swatch of the fabric was stirred at 300 rpm in 500 mL of an aqueous 5.0 wt% Fisher Sparkleen detergent at room temperature for 15 min before it was transferred into 500 mL of distilled water and was stirred at 300 rpm for 15 min. This rinsing process was repeated thrice before the swatch was dried at 120 °C for 20 min. The sample was subsequently cut into small pieces with various sizes to be used for various experiments. The substrates used for ink printing included cotton fabrics, semi-synthetic fabric (65% polyester/35% cotton), cardboard, printing paper, wood and aluminum foil. All of these substrates were purchased from local stores and used as received.

Tetrahydrofuran (THF, Fisher) was distilled over sodium and a trace amount of benzophenone. Pyridine (Fisher) was refluxed and distilled over CaH_2. 2-Trimethylsiloxyethyl acrylate (HEA-TMS) was synthesized according to a literature method[5] and distilled over CaH_2 before use. CuBr (Aldrich, 99.999%) was stirred with glacial acetic acid and washed with pure ethanol. Chloroform (Fisher, 99.9%) was passed through a membrane filter (Durapore, 0.45μm) before it was used as a SEC eluent. 2-Bromopropionyl bromide (Aldrich, 97%), cinnamoyl chloride (Acros, 98%), triethylamine (Alfa Aesar, 99%), $CuBr_2$ (Aldrich, 99.999%), 2,2'-dipyridyl (Acros, 99+%), hydrochloride acid (Fisher, 37%), acetonitrile (Fisher, 99.96%), hexanes (Caledon, 98.5%), methanol (Caledon, 99.8%), ethanol (Commercial Alcohols), dichloromethane (ACP, 99.5%), poly(ethylene oxide) (PEO, Polysciences Inc., M_w = 100,000 g/mol), and blue ink (Parker Quink) were used as received. In addition, chloroform-*d* (Aldrich, 99.8%) was purchased for NMR analysis and was used as received.

The fluorescent polymer PEO-Pyrene was synthesized previously by reacting poly(ethylene glycol) methyl ether (M_w = 2000 g/mol) with 1-pyrenebutyric acid, in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and 4-dimethylaminopyridine (DMAP), in CH_2Cl_2 at room temperature.

PDMS-OH. The crude PDMS-OH sample was purchased from Sigma-Aldrich. Based on ^1H NMR analysis, the crude polymer had 60 repeat units, which was consistent with the calculated value obtained based on the provided molecular weight (M_n = ~4670 g/mol). SEC analysis indicated that the polymer had a polydispersity index of 1.21 in terms of polystyrene standards.

To fractionate the polymer, 9.70 g of the crude polymer was dissolved in 98.5 mL of THF (10.0 wt. %) before enough methanol (155 mL) was slowly added to just turn the solution cloudy.

The resultant solution was left idle overnight at 4 °C to yield two phases. The top layer was collected and the solvent was removed via rotary evaporation to yield an oil. This oil was dried under vacuum for 24 h to yield 7.52 g of the polymer (yield ≈ 78%).

PDMS-Br. A modified literature method was followed to prepare PDMS-Br.[6-8] Fractionated PDMS-OH (7.52 g, 1.65 mmol), triethylamine (0.83 g, 8.24 mmol) and 2-bromopropionyl bromide (1.78 g, 8.24 mmol) were dissolved in 10.3 mL of THF. This mixture was stirred for 72 h at room temperature and then for 1 h at 60 °C. The final mixture was centrifuged at 3600 rpm to remove the insoluble salt and the solvent was subsequently removed via rotary evaporation. The resulting oil was washed three times with 30.0 mL of ethanol, centrifuged, and subsequently collected. The light yellow crude product was dissolved in 20.0 mL of hexanes and filtered through a silica gel column. Finally, most of the solvent was removed via rotary evaporation and the oil was dried under vacuum for 48 h to yield 5.20 g of PDMS-Br (yield ≈ 70%).

PDMS-*b*-PHEA. The copolymer PDMS-*b*-PHEA was prepared according to a modified literature procedure,[9] in which PDMS-Br (0.51 g, 0.12 mmol) and HEA-TMS (0.61 mL, 3.00 mmol) were initially mixed together in a two-necked round-bottom flask. Subsequently, THF (1.10 mL), 2,2'-dipyridyl (56.2 mg, 0.36 mmol) and $CuBr_2$ (4.1 mg, 0.018 mmol) were added to the mixture. The flask was then purged with N_2 before CuBr (25.8 mg, 0.18 mmol) was added and the contents of the flask were degassed by three freeze-pump-thaw cycles. The final N_2-filled flask was immersed in a preheated oil bath that was kept at 60 °C. The reaction was stopped after 19 h by quenching with liquid nitrogen and subsequently introducing air. The crude mixture was warmed to room temperature, diluted with THF (8.0 mL) and filtered through a neutral alumina column using THF as the eluent. Subsequently, a 1.0 M of HCl solution (a

13.0 M aqueous HCl solution that had been diluted with THF) was slowly added into the collected polymer solution under vigorous stirring to hydrolyze the TMS group. After this HCl solution had been added to the polymer solution, the final HCl concentration was 0.025 M. After 10 min, the polymer solution was concentrated to 1.0 mL and poured into 30.0 mL of acetonitrile. The precipitated polymer was collected after it had been centrifuged and was subsequently re-dissolved into 1.0 mL THF. This dissolution-precipitation-centrifugation purification treatment was repeated twice before the product PDMS-*b*-PHEA was air dried in a fume hood for 48 h. Finally, 0.78 g of the product was obtained (yield ≈ 90%).

PDMS-*b*-PCEA. To 15.0 mL of dry pyridine were added 0.78 g of PDMS-*b*-PHEA and 0.52 g of cinnamoyl chloride. After the mixture had been stirred in the dark at room temperature for 13 h, it was subsequently added dropwise into 100 mL of ethanol to precipitate the final polymer PDMS-*b*-PCEA. The polymer was collected after centrifugation and re-dissolved in 5.0 mL THF. Subsequently, 45.0 mL of ethanol was added slowly under stirring to precipitate the polymer again. This dissolution-precipitation-centrifugation purification treatment was repeated three times and the final product was dried under vacuum in the dark for 24 h to obtain 0.72 g of PDMS-*b*-PCEA (yield ≈ 70%).

Characterization. Size exclusion chromatography (SEC) was performed at 25 °C using a Wyatt Optilab rEX refractive index detector. The three columns were packed by MZ-Analysentechnik with 5 μ AM 500, 10,000 and 100,000 Å gels. The system was calibrated with monodisperse polystyrene (PS) standards. Chloroform was used as the eluent with a flow rate of 1.0 mL/min. The solution samples were filtered by syringe filters (Dikma, PTFE, 0.22 μm) before they were injected into the SEC system. ^{1}H NMR characterization was performed using a

Bruker Avance-500 instrument at 25 °C using chloroform-*d* ($CDCl_3$) as the solvent and a 3 s relaxation delay time.

Cotton Coating. The general protocol for coating the cotton samples involved the following steps. First, the copolymer was dissolved in THF. Second, hexane was added to a particular hexane volume fraction, denoted as f_{HX}. Third, 1.0 cm x 1.0 cm cotton swatches were immersed in the coating solution for 3.0 min. Fourth, the cotton swatches, which had become saturated with the polymer solution, were withdrawn from the solution and dried in the air for 2 h. Fifth, the dried cotton samples were subsequently annealed at 120 °C for 15 min. Sixth, the coated swatches were irradiated for a particular length of time on each side with a focused UV beam that was generated by a 500 W Hg lamp that was housed in an Oriel 6140 lamp case. The UV beam was passed through a 270-nm cut-off filter before it reached the cotton samples. Seventh, the polymers that had not become grafted around the fibers were subsequently removed via solvent extraction treatment. This extraction treatment involved immersing the coated cotton samples in 5.0 mL of CH_2Cl_2 at 35 °C for 2 h and subsequently rinsing them three times with 5.0 mL of CH_2Cl_2 at room temperature for 15 min. Lastly, the coated cotton samples were completely dried at 120 °C for 15 min before they were evaluated.

To investigate the effect of changing the polymer concentration (C) on the wetting properties of the coated cotton, f_{HX} was set at 40% and the irradiation time was set at 30 min for each side of the cotton samples. The copolymer concentrations were varied between 1.0 and 50.0 mg/mL, with concentrations of 1.0, 2.0, 3.0, 4.0, 5.0, 10.0, 20.0, 30.0, and 50.0 mg/mL being employed. In addition, uncoated cotton samples were also investigated for comparison.

To examine the effect of varying the irradiation time (*IT*) on the stability of the coating layer, f_{HX} was set at 80% and the copolymer concentration was set at 20.0 mg/mL. The irradiation times on the side of the cotton whose wetting properties would be evaluated were varied between 0 and 240 min. In particular, these irradiation times included 0, 5, 15, 30, 60, 120, and 240 min.

The effect of varying f_{HX} was examined by fixing the copolymer concentration to 5.0 mg/mL and the irradiation time to 30 min on each side. The f_{HX} values investigated included 20%, 40%, 60% and 80%. For the controlled experiment in which the PCEMA homopolymer was applied as a coating on the cotton sample, the coating procedure was identical to that applied for the diblock copolymer-based cotton coating. The conditions used for this PCEMA-based coating were C = 5.0 mg/mL, IT = 30 min and f_{HX} = 0% (pure THF) respectively.

Hydrophilic Pattern Preparation. To prepare a hydrophilically-patterned cotton fabric, a circular cotton swatch with a diameter of 5.0 cm was immersed into 5.0 mL of a 20.0 mg/mL micellar copolymer solution (THF/hexane at f_{HX} = 80%) for 3 min. After the cotton swatch had been removed from the coating solution and air-dried for 2 h, it was annealed at 120 °C for 15 min. Subsequently, one side of the swatch was irradiated for 1 h while it was covered with a photo-mask to allow selective photo-crosslinking of the unmasked regions. To remove the polymers that had not become crosslinked, the swatch was subsequently washed with 20.0 mL of CH_2Cl_2 at 35 °C for 2 h and then rinsed three times with 20.0 mL of CH_2Cl_2 at room temperature for 15 min. Finally, the patterned cotton sample was completely dried at 120 °C for 15 min before it was used as the face of the stamp.

Aqueous Ink Solutions. A diluted ink solution was prepared by adding distilled water into the commercial ink, so that the volume ratio between the ink and the distilled water was 1:20 (ink:water). A viscous ink solution, PEO-containing ink, was prepared by adding PEO (M_{w} = 100,000 g/mol) into the commercial ink at a concentration of 10.0 mg/mL. A fluorescent polymer dye solution was prepared by dissolving PEO-Pyrene into distilled water at a concentration of 10.0 mg/mL.

Pattern Printing. The hydrophilically-patterned superhydrophobic cotton fabric that served as the stamp face was attached to the support base of a commercially available filter funnel. This funnel served as both the stamp handle and also as the ink reservoir, and the edges of the fabric were affixed to the support base of this funnel with tape. Thus, the support base of the funnel was inverted, with the cotton fabric-covered head of the base (the face of the stamp) facing downward and the stem of the base facing upward. In addition, a sealed-in coarse porosity fritted disc was placed inside the base (between the cotton-covered head and the stem) to serve as a sieve. Various aqueous ink solutions (with volumes ranging between 1.0 and 3.0 mL) were loaded into the reservoir of cotton-based stamp through the stem of the funnel support base using a plastic syringe. Subsequently, the ink-filled stamp was pressed onto various substrates for ~2 s to imprint patterns from the cotton template onto these substrates.

Contact Angle Measurements. Images of 5 μL water (Milli-Q) droplets were captured at room temperature (21 °C) with a Canon PowerShot A700 camera and processed with the ImageJ software package to yield the contact angles. The contact angle reported for each sample represented the average of five measurements together with the calculated standard deviations.

Shedding Angle Measurements. Water shedding angles (WSAs) were measured at room temperature (21 °C) according to a literature method.[10] First, a coated cotton swatch was attached to a glass plate with double-sided adhesive tape. This glass plate was then placed on a custom-built tilting stage, and a syringe containing water was mounted 1.0 cm above the testing spot (Figure S7). To determine the WSA, measurements were started at a tilting angle of 70°. Water droplets (10 μL in volume) were dispensed onto five different spots on the coated cotton samples. If all of the water droplets bounced or rolled off the sample, the tilting angle was reduced by ~1° via reducing the height of the adjustable end of the tilting stage. This procedure was repeated until one or more of the water droplets would not completely roll off the surface. The lowest tilting angle at which all of the drops completely bounced or rolled off the sample surface was noted as the WSA. The WSA reported for each sample represented the average of five measurements together with the calculated standard deviations.

Gravimetric Analysis. To determine the polymer grafting density x on the cotton fabrics, four cotton samples with weights ranging between 4.0 and 20 mg were prepared for gravimetric analysis. First, the weights of all of the uncoated cotton samples were recorded using a microbalance (± 0.002 mg) after they had been dried under vacuum at 100 °C until their weights reached constant values. These weights were denoted as W_0. Subsequently, all of these samples were immersed into 2.0 mL of a 20 mg/mL micellar copolymer solution (THF/hexane at $f_{\mathrm{HX}} = 80\%$) for 3 min. These samples were withdrawn from the coating solution and dried in air for 2 h followed by thermal annealing at 120 °C for 15 min. Subsequently, all of the samples were irradiated for 1 h on each side, extracted with CH_2Cl_2 and dried under vacuum at 100 °C until the weights reached constant values. These final weights observed after the solvent extraction treatment were also recorded using the microbalance and they were denoted as W_1. The polymer grafting density x was determined as the weight increases exhibited by the samples, as determined by equations (2):

$$x = (W_1 - W_0)/W_0 \text{ x } 100\% \qquad (2)$$

The reported x value represented the average values for all four samples together with the calculated standard deviations.

SEM Sample Preparation and Characterization. Five 1.0 cm x 1.0 cm cotton samples denoted as S1-S5, respectively, were prepared for SEM characterization. S1 was an uncoated cotton sample, while S2-S5 were coated with the copolymer. To coat samples S2-S5, they were immersed into 3.0 mL of a 20 mg/mL micellar copolymer solution (THF/hexane at $f_{\mathrm{HX}} = 80\%$) for 3 min. After the samples had been withdrawn from the coating solution and air-dried for 5 min, S2 was irradiated for 1 h on one of its sides to photo-crosslink the copolymer before it was characterized via SEM. Meanwhile, samples S3-S5 were dried in the air for 2 h after they were removed from the coating solution. Subsequently, S3 was irradiated for 1 h on one side to crosslink the polymer. Meanwhile, after S4-S5 had been air-dried, they were annealed at 120 °C for 15 min. After these samples had been annealed, both S4 and S5 were irradiated for 1 h on one side. Finally, S5 was subjected to extraction treatment under similar conditions as described in the cotton coating section. SEM images of the cotton samples were recorded using a FEI-MLA Quanta 650 FEG-ESEM instrument that was operated at 10 kV. In the case of samples S2-S5, the irradiated side was recorded via SEM. The samples were not coated with Au prior to SEM observation.

Viscosity Measurements. The relative viscosities (η_r) of various aqueous ink solutions used for the pattern printing experiments were measured with an Ostwald viscometer at 25 °C using water as a reference.

AFM Study of Micellar Films Deposited on Silicon Wafers and Then Treated Under Different Experimental Conditions. PDMS-b-PCEA micelles were deposited on four ~0.5 × 0.5 cm^2 Si wafers and treated differently to yield samples S2-S5 for AFM analysis. S1 was an uncoated Si wafer. To coat samples S2-S5, they were immersed into 2.0 mL of a 20 mg/mL micellar copolymer solution (THF/hexane at $f_{\mathrm{HX}} = 80\%$) for 3 min. After the samples had been withdrawn from the coating solution and air-dried for 5 min, one sample was irradiated for 1 h to photo-crosslink PCEA to yield S2. Meanwhile, samples S3-S5 were dried in the air for 2 h after they were removed from the coating solution. Irradiating a sample at this stage for 1 h yielded S3. The left two samples were annealed at 120 °C for 15 min. The sample not treated further was denoted as S4. S5 was obtained after the annealed and irradiated sample was extracted with CH_2Cl_2. The samples were analyzed by a Veeco Multimode instrument that was equipped with a Nanoscope IIIa controller and operated in the Tapping Mode. Rectangular-shaped silicon probes (AppNano, ACT) with a 300 kHz resonance frequency and a spring constant of 40 N/m were used for the AFM characterization.

Other Techniques. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Instruments Microlab 310F surface analysis system (Hastings, U.K.). Thermogravimetric analysis (TGA) was performed using a TA Q500 instrument under nitrogen. A typical TGA measurement involved heating the samples from room temperature to 150 °C at 10 °C/min, holding the temperature at 150 °C for 15 min, and increasing the temperature further to 800 °C at 10 °C/min. Each residual weight reported was normalized relative to that determined at 150 °C and represented the average of three measurements.

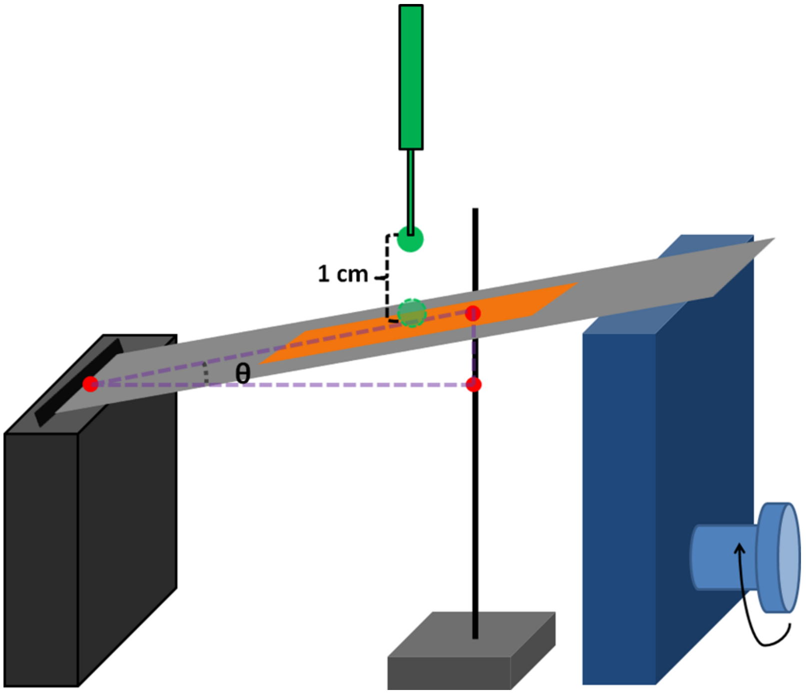

Figure S7. Setup used for the water shedding angle measurements.

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