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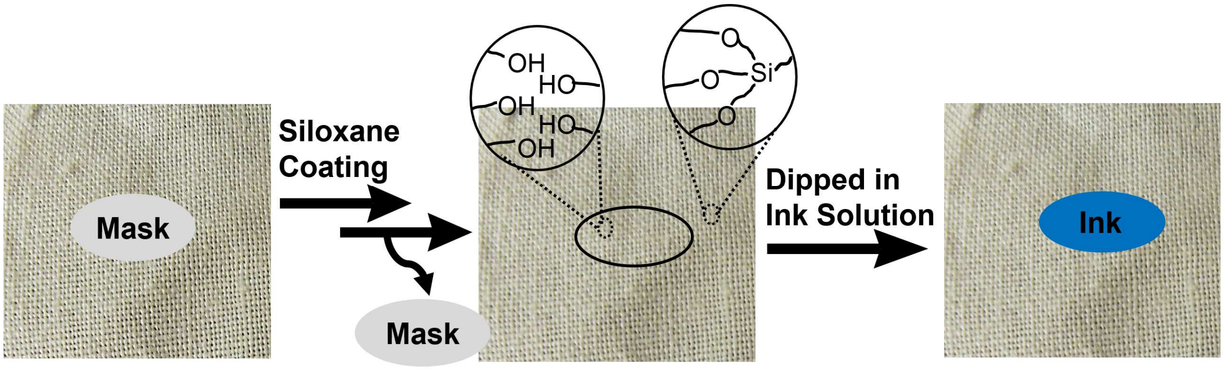
Graphical Abstract



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ARTICLE TYPE

Synthesis of Poly(dimethylsiloxane)-*block*-Poly[3-(triisopropyloxysilyl) propyl methacrylate] and its use in the Facile Coating of Hydrophilically Patterned Superhydrophobic Fabrics

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ABSTRACT. We report the synthesis and applications of a novel poly(dimethylsiloxane-*block*-poly[3-(triisopropyloxysilyl)propyl methacrylate] (PDMS-*b*-PIPSMA) diblock copolymer. PDMS-*b*-PIPSMA was synthesized via atom transfer radical polymerization (ATRP), and was characterized by ^{1}H NMR and SEC analysis. This block copolymer was successfully grafted onto cotton fabrics via sol-gel chemistry using the PIPSMA block as an anchor to generate superhydrophobic fabrics. These superhydrophobic cotton fabrics coatings were tested as membranes for oil-water separation, where water was retained on the surface of the hydrophobic cotton, while organic solvents permeated through this coated fabric. In addition, the batik technique was used to prepare superhydrophobic cotton fabrics that bore hydrophilic patterns. We demonstrated that water-based ink solutions readily wet the hydrophilic regions, but they were repelled by the superhydrophobic regions. These patterned fabrics may thus find applications as stamps for the imprinting of aqueous ink solution-based patterns onto other fabrics.

Introduction

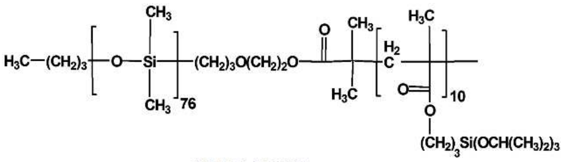
Superhydrophobic surfaces display water contact angles >150°.[1,2] Fabrics with water repellent properties are very useful.[3,4] Two methods are used to prepare superhydrophobic cotton fabrics, which can be accomplished either by forming a thin layer (< 1 nm) by grafting small hydrophobic molecules onto fibers,[5] or by forming a thick hydrophobic polymer layer of several nm that surrounds the fibers.[6-8] One way in which thick polymer films can be applied onto cotton substrates is by the polymerization of hydrophobic monomers from a fabric surface bearing polymer initiation sites.[9,10] However, the *in situ* growth of polymer chains from cotton surfaces is not considered as a viable strategy for large scale production. Alternatively, premade polymers can be grafted onto fabrics. This method requires a polymer bearing both an active anchoring functionality to graft onto the fabrics, and hence form stable covalent bonds, as well as a low surface energy polymer chain to render water/oil repellency.[11,12] Recently, the use of a photo-crosslinkable anchoring block that surrounds the cotton fibers has been reported.[13,14] For example, poly(dimethylsiloxane)-*block*-poly[2-(cinnamoyloxy)ethyl acrylate] (PDMS-*b*-PCEA) was used to coat cotton substrates, where the PCEA block was photo-crosslinked around the cotton fibers. Meanwhile, the PDMS block provided the desired water repellency, because PDMS has a low surface energy of $\sim$20 mN m^{-1} at room temperature.[15]

Various oil-water separation strategies have been reported, which have used a diverse range of water-repellent materials including superhydrophobic mesh films,[16] gels,[17] and polymer membranes.[18] Despite the fact that superhydrophobic cotton fabrics[3] that were modified with small molecules have been used as sorbents to separate oils from oil-water mixtures, we are not aware of any reports describing the use of block copolymer-coated superhydrophobic cotton fabrics for oil-water separation.

Patterned surfaces having domains with different wettabilities have various potential applications.[19-23] For example, they are used to regulate liquid transport,[24,25] liquid evaporation and condensation,[26] as well as the self-assembly of molecules or nanoparticles.[20] Similarly, fabrics bearing hydrophilic patterns have numerous applications.[27,28] There are several methods to generate patterns on hydrophobic cotton fabrics, including the batik painting method as well as the stitching of hydrophilic cotton yarn onto hydrophobic fabrics.[28] Recently, we reported the use of a block copolymer for the fabrication of superhydrophobic cotton fabrics bearing hydrophilic patterns via photo-masking methods. However, there have been no reports on the preparation of hydrophilically patterned superhydrophobic fabrics from block copolymer solutions.

Herein we report the synthesis and characterization of a novel diblock copolymer, poly(dimethylsiloxane)-*block*-poly[3-(triisopropyloxysilyl)propyl methacrylate] (PDMS$_{76}$-*b*-PIPSMA$_{10}$), where the subscripts denote the repeat unit numbers. A wide variety of PDMS-bearing block copolymers have been previously synthesized, including polydimethylsiloxane-*block*-polystyrene (PDMS-*b*-PS),[29,30] dimethylsiloxane-*block*-poly(ethylene oxide) (PDMS-*b*-PEO),[31] polydimethylsiloxane-*block*-poly(methyl methacrylate) (PDMS-*b*-PMMA),[32] poly(butyl methylacrylate)-*b*-poly(dimethylsiloxane)-*b*-poly(butyl methylacrylate) (PBMA-*b*-PDMS-*b*-PBMA),[33] and poly(dimethylsiloxane)-*block*-poly[2-(cinnamoyloxy) ethyl acrylate] (PDMS-*b*-PCEA).[13] Similarly, PIPSMA-bearing block copolymers such as poly[3-(triisopropyloxysilyl)propyl methacrylate]-*block*-poly[2-(perfluorooctyl)ethyl methacrylate] (PIPSMA-*b*-PFOEMA), and poly(perfluoropropylene oxide)-*block*-poly[3-(triisopropyloxysilyl)propyl methacrylate] (PFPO-*b*-PIPSMA) have been reported by our group.[34] Chen and coworkers reported poly(3-(triethoxysilyl)propyl methacrylate) (PTESPMA) as sol-gel block in poly(ethylene oxide)-*block*-poly(3-(triethoxysilyl)propyl methacrylate) copolymer.[35] However, there have been no reports describing the synthesis of PDMS-*b*-PIPSMA.

The block copolymer PDMS-*b*-PIPMSA was successfully grafted onto cotton fabrics via sol-gel chemistry, thus rendering these fabrics superhydrophobic. These superhydrophobic coatings were successfully tested for their ability to promote oil-water separation, where water was retained on the surface of hydrophobic cotton, while chloroform permeated through the coated fabric. In addition, hydrophilic patterns were created on superhydrophobic fabrics using the batik approach. These patterned fabrics were subsequently used as printing stamps for the application of aqueous ink onto other cotton fabrics. The ink was readily absorbed in the regions bearing the hydrophilic patterns, but not in the superhydrophobic regions.



PDMS-*b*-PIPSMA

Figure 1. Chemical structure of PDMS-*b*-PIPSMA.

Experimental

Materials. Copper(I) chloride (CuCl, Acros, 99.99%), copper(II) bromide (CuBr$_2$, Aldrich, 99.999%), 2,2′-bipyridine (Acros, 99%), α,α,α-trifluorotoluene (TFT, 99+%, Acros), and *p*-toluenesulfonic acid monohydrate (Sigma-Aldrich 98%) were used as received. Isopropanol and THF were purchased from Caledon Laboratories Ltd. (Canada) and used without further purification. 3-(Trimethoxysilyl)propyl methacrylate (Aldrich, 98%) was also used as received. Poly(dimethylsiloxane)monohydroxy terminated (PDMS$_{62}$-OH, M_n ~4670 g/mol, Sigma-Aldrich) was fractionated prior to use. Aqueous hydrogen chloride (HCl, 13 M, Fisher) was diluted with THF before use.

Characterization

^{1}H NMR

^{1}H NMR measurements were performed using a Bruker Avance-400 instrument at room temperature. Prior to ^{1}H NMR analysis, the samples were prepared at ~5 mg/mL in CDCl$_3$, and recorded with a relaxation delay (d_1) of 3 s.

Size Exclusion Chromatography

Polymer samples were characterized via size exclusion chromatography (SEC) using trifluorotoluene (TFT) as the eluent. The samples were recorded at 40 °C using a Waters 515 system equipped with a Waters 2410 refractive index (RI) detector, at a flow rate of 1.0 mL/min. The SEC column was calibrated with narrowly dispersed polystyrene (PS) standards using TFT as the eluent.

Synthesis

Synthesis of 3-(triisopropyloxysilyl)propyl methacrylate (IPSMA)

3-(Triisopropyloxysilyl)propyl methacrylate (IPSMA) was prepared according to a previously reported procedure, with slight modifications.[36] Detail synthesis and ^{1}H NMR characterization of IPSMA are shown in the Supporting Information (SI).

Fractionation of PDMS-OH

Commercial PDMS$_{62}$-OH (8.0 g, M_n = 4670 g/mol) was dissolved in 7.0 mL of THF. Methanol (34.0 mL) was subsequently slowly added to this solution. The resultant turbid solution was transferred into a separatory funnel and was cooled to 4 °C for 2 h. Two layers appeared. The top layer was collected and dried via rotary evaporation. The obtained polymer was further dried under vacuum overnight at room temperature. The polymer recovered from top layer was characterized as PDMS$_{50}$-OH (M_n = 3800 g/mol). ^{1}H NMR (in CDCl$_3$ at 400 MHz): δ 3.55 (*t*, J = 5.6 Hz, -OCH_2, 2H), 3.66 (*q*, J = 4.8 Hz, HOCH$_2$$CH_2$-, 2H), 3.49 (*t*, J = 7.2 Hz,-CH$_2$$CH_2$OH, 2H), 2.00 (*t*, *J* = 6 Hz, -CH$_2$, 2H), 1.7 (*q*, *J* = 6.4 Hz, -CH$_2$, 2H), 0.6 (*q, J* = 4.8 Hz -CH$_2$, 2H), 0.1 (*br*,- CH$_3$ of PDMS, 6H) ppm.

Synthesis of PDMS-Br

PDMS-OH (2.00 g, 5.26 × 10^{-4} mol) was dissolved in THF (2.0 mL). An acid scavenger, triethylamine (TEA, 0.18 mL, 1.3 × 10^{-3} mol) and 2-bromoisobutyryl bromide (0.11 mL, 0.9 × 10^{-3} mol) were added sequentially to this solution. The reaction mixture was stirred for 12 h at room temperature. The resultant crude polymer solution was washed with acetonitrile (20 mL) and centrifuged at 3900 rpm for 3 min. This polymer was dissolved again in THF (0.2 mL), and poured into acetonitrile (20 mL), and centrifuged at 3900 for 3 min. The last step of involving the precipitation from acetonitrile was repeated once again. The precipitate was allowed to settle, subsequently collected, and then dried under vacuum for 24 h at room temperature. ^{1}H NMR (in CDCl$_3$ at 500 MHz): δ 4.35 (*t*, *J* = 5.0 Hz, -CO$_2$C*H*$_2$, 2H), 3.70 (*t*, *J* = 4.5 Hz, -CO$_2$CH$_2$C*H*$_2$-, 2H), 3.45 (*t*, *J* = 6.5 Hz -CH$_2$C*H*$_2$-O, 2H), 2.00 (*s*, -(CH$_3$)$_2$, 6H), 1.6 (*m*, -CH$_2$, 2H), 0.6 (*t*, *J* = 8.5 Hz -CH$_2$, 2H), 0.1 (*br*,- CH$_3$ of PDMS, 6H) ppm.

Synthesis of PDMS-*b*-PIPMSA

PDMS-Br (0.90 g, M_n = 5600 g/mol, 1.6 × 10^{-1} mmol, 1.0 equiv.), and IPSMA (0.77 mL, 2.1 mmol, 13 equiv.) were mixed together in a two-neck flask. Bipyridine (84 mg, 5.3 × 10^{-1} mmol), CuCl (17.4 mg, 1.78 × 10^{-1} mmol mmol), CuBr$_2$ (3 mg, 0.01 mmol), and TFT (3.0 mL) were added to this reaction mixture before it was degassed via freeze-pump-thaw treatment. This degassing procedure was repeated three more times. After the degassing treatment, the flask was placed into a pre-heated oil bath at 80 °C and the reaction was monitored via ^{1}H NMR spectroscopy. After 2.5 h, ~80% conversion was reached. The polymerization was stopped immediately by cooling the reaction mixture to room temperature and allowing air to enter the flask. The crude polymer mixture was diluted with TFT (8.0 mL), and passed over an alumina column. The solution was concentrated to ~2 mL via rotary evaporation. The concentrated crude polymer solution was added dropwise into acetonitrile (20 mL), and centrifuged at 3900 rpm for 3 min. The polymer was dissolved again in THF (0.9 mL), and poured again into acetonitrile (20 mL). The sample was centrifuged at 3900 rpm and the polymer was allowed to settle as a dense viscous material. The last step of the precipitation from acetonitrile was repeated once again. After the polymer was dried under vacuum overnight at room temperature, the product was obtained as semi-solid wax-like material. ^{1}H NMR (in CDCl$_3$ at 500 MHz): δ 4.25 (*br*, -C*H*(CH$_3$)$_2$, 3H), 3.90 (*br*,-CO$_2$C*H*$_2$, 2H of PIPSMA), 1.95 (*br*, -C*H*$_2$, 2H), 1.70 (-CH$_2$C*H*$_2$CH$_2$, 2H), 1.3 (*br*, -CH(C*H*$_3$)$_2$, 6H), 1.1-0.8 (*br*, -CH$_3$, 3H), 0.60 (*br*, -SiC*H*$_2$, 2H), 0.10 (*br*, -CH$_3$ of PDMS), 6H) ppm.

Preparation of the PDMS-*b*-PIPSMA-Coated Cotton Fabrics

In a typical procedure, the diblock copolymer PDMS-*b*-PIPSMA was dissolved into 2.0 mL of THF at concentrations of 0.50, 1.0, 5.0, and 20 mg/mL. Subsequently, a 1.0 mL HCl solution (0.30 M in THF) was added into each polymer solution. After the solutions were stirred for 30 min, 0.05 mL of TEA was added into each polymer solution to neutralize the HCl. Three pieces of small cotton fabrics (~ 1.0 cm × 1.0 cm) or one large piece of cotton fabric (3.0 cm × 3.0 cm) were subsequently immersed into each solution at room temperature and kept immersed for 1 h. All of the cotton swatches were subsequently withdrawn from the coating solution and heated at 105 °C under vacuum for 24 h to remove the solvent and complete the condensation of the PIPSMA block. Finally, the coated cotton fabrics were washed three times with THF at room temperature to remove any non-grafted copolymer before they were dried at 105 °C for 30 min. Finally, the coated cotton fabrics were extracted with THF (15.0 mL at 60 °C for 20 min. This extraction step was repeated two more times. After extraction, these samples were dried at 105 °C for 30 min before any properties measurements.

Oil-Water Separation.

A coated cotton swatch of 3.0 cm × 3.0 cm (coated with a 5.0 mg/mL coating solution) was tightly sandwiched as a filter membrane between the top and bottom sections of a glass funnel. In total 30.0 mL solution of water and chloroform was prepared in 1:1 v/v mixture. For this purpose, 15.0 mL of chloroform (containing with the red dye "Red Oil O") and 15.0 mL of water (containing 0.050 M AgNO$_3$) was vigorously stirred, and immediately poured into the funnel. An Erlenmeyer flask was placed beneath this funnel in order to collect the filtrate. The dye containing chloroform component permeated through the membrane and was collected in the Erlenmeyer flask, while the colorless water layer was retained in the funnel above the membrane. Once the separation was completed, 1.5 mL of HCl solution (4.0 M in dioxane) was added into the filtrate to determine if white AgCl precipitate was formed.

Selective Oil Absorption by Coated Fabric

In a plastic petri dish, 30.0 mL of water and 0.50 mL of hexane (dyed with "Red Oil O") were taken. A piece of coated cotton (coated from 5.0 mg/mL coating solution, 2.0 cm × 2.0 cm) was used to absorb oil selectively. The cotton piece was gently dragged on the oil spilled regions on the liquid surface for ~10 s. As a controlled experiment, one piece of uncoated cotton (2.0 cm × 2.0 cm) was also used for oil absorption under identical conditions.

Application of Hydrophilic Patterns onto Hydrophobic Cotton

Initially, PDMS-*b*-PIPSMA was dissolved in an HCl solution (0.1 M in THF) at a concentration of 5 mg/mL, and this solution was subsequently neutralized with TEA (0.05 mL).

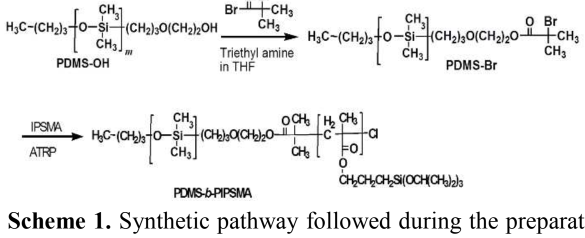
DMF (2.5 mL) was added to this solution, and the THF was subsequently removed via rotary evaporation to yield the final coating solution in which DMF served as the solvent. A piece of cotton fabric was then partially masked by the infusion of melted wax. The partially masked cotton fabric was subsequently immersed into the DMF coating solution at room temperature for 10 min. Therefore, the unmasked domains of the cotton fabric became coated by the copolymer, while the copolymer was unable to graft onto the wax-bearing regions. The cotton fabric was subsequently removed from this solution, and kept under vacuum for 24 h at room temperature. The wax-bearing mask was scratched before it was heated at 105 °C for 24 h to avoid wax flow during the heating. Finally, the coated cotton fabrics were washed with THF (3 × 10 mL) at room temperature to remove any non-grafted copolymer chains. The coated fabric was washed with hexane (3 × 10 mL) to remove any residual wax from the patterned cotton fabric before it was heated at 105 °C for 30 min.

Ink-Stamping Tests

An aqueous ink solution was prepared by mixing Parker ink (1.0 mL) with water (20.0 mL). The hydrophilically patterned cotton fabric was fixed onto a stamp using a piece of double-sided tape. The stamp was immersed into the dilute ink solution, and the stamp was used to imprint the ink onto an uncoated cotton fabric. The ink permeated through the hydrophilic pattern, but did not penetrate the hydrophobic domains of the coated fabric to thus yield a reproduction of the pattern on the uncoated cotton substrate. This process of immersing the stamp into the ink solution and applying the stamp pattern onto a new uncoated cotton substrate was repeated over 20 times without any noticeable deterioration in the clarity of the resultant images.

Results and Discussion

Scheme 1 depicts the synthetic pathway followed during the synthesis of the diblock copolymer PDMS-*b*-PIPSMA. The first step involved the preparation of the ATRP macroinitiator PDMS-Br. In the next step, the PDMS-Br macroinitiator was used to induce the polymerization of the IPSMA monomer, which thus yielded the targeted block copolymer PDMS-*b*-PIPSMA.



Scheme 1. Synthetic pathway followed during the preparation of PDMS-*b*-PIPSMA-Br.

Commercial PDMS$_{62}$-OH exhibits a bimodal SEC peak and has a relatively wide molecular weight distribution. Therefore, PDMS$_{62}$-OH was first fractionated via fractional precipitation using THF and methanol as the solvent and precipitant, respectively to yield narrowly distributed PDMS$_{50}$-OH chains. In the next step, the fractionated PDMS$_{50}$-OH was modified with 2-bromoisobutyryl bromide to obtain PDMS$_{50}$-Br. PDMS-Br is a non-polar polymer, and therefore was purified by precipitation from acetonitrile, which is an aprotic but highly polar solvent. SEC traces of PDMS-Br were recorded in TFT, as shown in Figure 2. A negative maximum peak was observed because of the lower refractive index of PDMS-Br relative to that of the TFT eluent. The M_n, M_w and PDI of PDMS-Br were found to be 18.7 kg/mol, 20.5 kg/mol and 1.09, respectively, based on SEC measurements that were calibrated using polystyrene standards.The product was also characterised by ^{1}H NMR and SEC analysis. Figure 3 (bottom) shows the ^{1}H NMR spectrum of PDMS-Br, along with the peak assignments. The integration ratios of each proton were quantified, and these calculations indicated that the macroinitiator had 76 repeat units (PDMS$_{76}$-Br). This repeat unit number suggested that the M_n value was higher than that of the starting material, PDMS$_{50}$-OH. This discrepancy arose because the longer polymer chains precipitated from acetonitrile more readily than the shorter chains during the fractionation process, thus causing the purified macroinitiator to have a higher molecular weight.

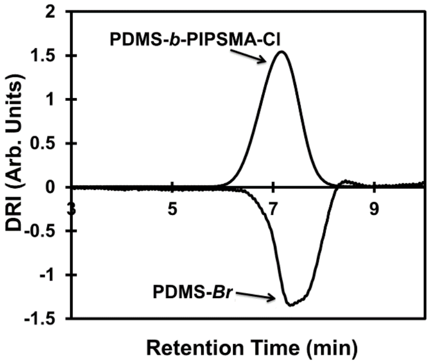


Figure 2. SEC traces of PDMS-Br and PDMS-*b*-PIPSMA. TFT was used as the eluent at a flow rate of 1.0 mL/min at 40 °C.

PDMS-*b*-PIPSMA was synthesized via the ATRP polymerization of the IPSMA monomer using PDMS-Br as the macroinitiator. IPSMA was synthesized from 3-(Trimethoxysilyl)propyl methacrylate (MSMA) by procedure described in the SI. We used IPSMA instead of MSMA to avoid sol-gel chemistry during and after polymerization because of the bulky isopropyl groups at Si. The polymerization was performed at 80 °C until the desired degree of conversion was obtained. The structural properties of PDMS-*b*-PIPSMA were characterized by ^{1}H NMR and SEC analysis. The ^{1}H NMR spectrum of the PDMS-*b*-PIPSMA diblock copolymer is shown in Figure 3 (top).

The signals are assigned for each component of both blocks. The signal integration ratio between signals corresponding to the methyl groups of PDMS block (6 H) at 0.1 ppm and the ester proton of PISPMA block (2 H) at 3.9 ppm, was 20/456 (Figure S5). Based on these calculations, the repeat unit number of the PIPSMA block was found to be 10, while the PDMS block was found to possess 76 repeat units. Therefore, the composition of the diblock copolymer was $PDMS_{76}$-*b*-$PIPSMA_{10}$.

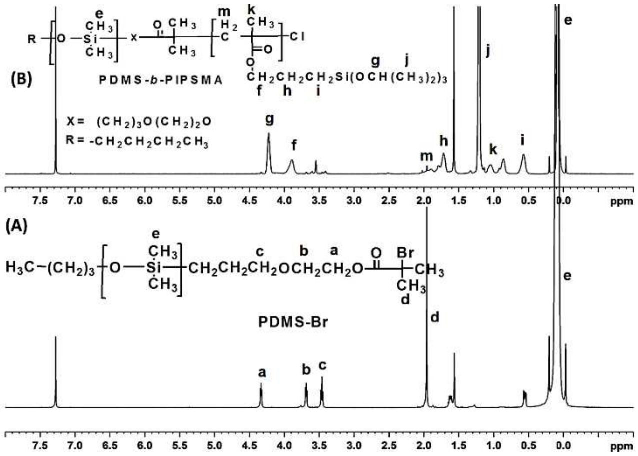


Figure 3. ^1H NMR (recorded in $CDCl_3$ at 400 MHz) spectra of PDMS-Br (A) and PDMS-*b*-PIPSMA (B).

The SEC trace of PDMS-*b*-PIPSMA is also shown in Figure 2. The appearance of this peak at a higher molecular weight region in comparison with its PDMS-Br precursor provides evidence for the successful preparation of PDMS-*b*-PIPSMA. The M_n, M_w and PDI values were found to be 32.2 kg/mol, 34.2 kg/mol and 1.10, respectively. A PDI value of 1.10 indicated that the ATRP polymerization had proceeded in a well-controlled manner.

Table 1. Summary of the properties of PDMS-Br and PDMS-*b*-PIPSMA-Cl

Sample	M_n (kg/mol)[a]	M_w (kg/mol)[a]	M_w/M_n (PDI)[a]	M_n (kg/mol)[b]	m[c]	n[d]
PDMS-*Br*	18.7	20.5	1.09	5.8	76	-
PDMS-*b*-PIPSMA-*Cl*	32.2	34.2	1.1	8.7	76	10

[a] Determined via SEC characterization. [b] Determined via ^1H NMR spectroscopy. [c] Number of repeat units corresponding to the PDMS block. [d] Number of repeat units corresponding to the PIPSMA block.

Preparation of PDMS-*b*-PIPSMA-Coated Cotton Fabrics

Cotton fabrics were coated with PDMS-*b*-PIPSMA via sol-gel chemistry, in which PIPSMA served as the anchoring block. We had previously used sol-gel chemistry to coat cotton fabrics with FHEA-*b*-PIPSMA at pH~2.3, and thus impart these fabrics with water- and oil-repellent properties.[37] In thus study, the PIPSMA block of PDMS-*b*-PIPSMA was first hydrolysed using a 1 M HCl solution, and this hydrolysis reaction was monitored by FT-IR analysis. The FT-IR spectrum of the hydrolyzed PIPSMA block exhibited a new peak near 3500 cm^{-1}, which arose due to the silanol groups, thus indicating that 3-(triisopropyloxysilyl)propyl methacrylate had undergone successful hydrolysis. Cotton fabrics are vulnerable to damage in acidic media, and thus the acidic solution was neutralized with triethylamine prior to the immersion of the cotton fabric. Thermal condensation reactions between the $R\text{-}Si(OH)_3$ moieties of the hydrolysed PIPSMA block and the hydroxyl groups of the cotton fabric was allowed to proceed at 105 °C. This covalent binding caused the PIPSMA block to become securely anchored onto the cotton substrates.

Table 2 shows static, advancing and receding angles for water droplets that were placed on PDMS-*b*-PIPSMA-coated fabrics. When coatings were applied using relatively dilute polymer solution concentrations, the resultant fabrics exhibit contact angles below 140°, and hence these fabrics were only hydrophobic rather than superhydrophobic. However, when a polymer coating solution concentration of 5.0 mg/mL was used to coat the fabrics, the water contact angle on the resultant fabric reached 149±4°. When the concentration of the coating solution was increased above 5.0 mg/mL, the resultant fabrics exhibited no significant increase in the contact angles. This behaviour indicated that 5.0 mg/mL was an optimum coating solution concentration, as it yielded fabrics exhibiting excellent self-cleaning performance without unduly wasting the polymer. The above data confirms the successful preparation of water-repellent fabrics.

Table 2: Static, Advancing and Receding angles for fabrics coatings at various block copolymer concentrations.

Coating Solution Conc.	Static Contact Angles(°)	Advancing Contact Angles(°)	Receding Contact Angles(°)
0.5	137 ± 1	141 ± 3	115 ± 5
1	143 ± 4	146 ± 2	120 ± 5
5	149 ± 4	155 ± 1	136 ± 3
20	150 ± 3	153 ± 3	137 ± 6

Advancing and receding angles were also measured for PDMS-*b*-PIPSMA-coated fabrics that were prepared using various polymer coating solution concentrations. These measurements are shown in Table 2. It is apparent that when the polymer coating solution concentration was very low (such as 0.5 mg/mL), the resultant fabrics exhibited relatively low advancing and receding angles. At 5.0 mg/mL of the coating solution concentration, the advancing angle was reached to 155 ± 1° while receding angle was 136 ± 3°. This indicate that advancing and receding angles for water droplets on coated fabrics are concentration dependent, which reached an optimum value at 5.0 mg/mL.

Atomic force microscopic analysis of the cotton fibers before and after coating were recorded (see Figure S6). AFM for the coated fiber was performed after polymer grafting and extraction with THF at 60 C for 1h. We observed that the Fibers before coatings are smooth, while after coatings are relatively rough compared to the uncoated fibers. The increase in roughness for coated fiber is attributed to the polymer clusters formed as a result of the sol-gel chemistry during the polymer grafting process.

Oil-Water Separation.

PDMS-*b*-PIPSMA-coated fabrics were used as membranes for the separation or oil from water, and this oil-water separation apparatus is shown in Figure 4. For this purpose, chloroform (which was marked with the dye "Red Oil O" for visual clarity) and water (containing 0.050 M $AgNO_3$) were initially mixed via vigorous shaking to prepare the oil-water mixture. This solvent mixture was immediately poured onto the coated cotton filter. The chloroform in this mixture readily passed through the fabric, while the water was blocked by the membrane and remained in the funnel. After separation, 15 mL of water was retained in the funnel without any red oil phase or droplets were seen the water layer, which indicate the successful passage of oil phase through the membrane. Approximately 13 mL of chloroform was collected in the flask on the bottom. The loss of ~2 mL in chloroform are attributed to both absorption by cotton and to the evaporation of chloroform during this process. To further determine that no water traces went through the filter, HCl solution (4.0 M in dioxane) was added into the collected chloroform. After they were well mixed, no white precipitate (AgCl) appeared, which indicates that collected chloroform carries no water.[38]

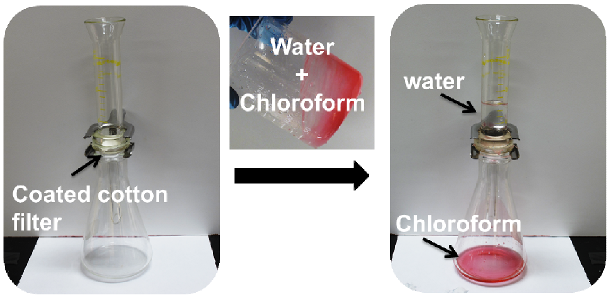


Figure 4. Photographs showing the oil/water separation apparatus, in which the block copolymer-coated cotton fabric served as a membrane. When the chloroform/water mixture was passed through the membrane, the chloroform passed through the membrane, while the water was retained above the membrane. The chloroform was marked with a red dye for visual clarity.

In another test, oil-sorption experiment was performed using coated cotton to selectively absorb hexane (oil) from a heterogonous mixture of water and hexane as shown in Figure 5. Hexane was selectively absorbed by the coated fabric without water absorption. Meanwhile, an uncoated cotton was used to repeat the same test. However, uncoated fabric absorbed water predominantly, while only little hexane was absorbed. This oil water separation test may have potential applications in the remediation of oil spills.

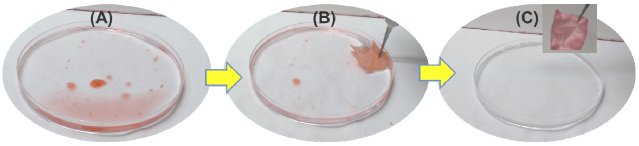


Figure 5. Photographs showing selective oil sorption by coated fabric: (A) oil on surface of water, (B) dragging of coated cotton on oil spill over water, and (C) after completion of oil sorption process.

Preparation of Hydrophilically Patterned Superhydrophobic Fabrics

The batik painting method was used to prepare superhydrophobic fabrics that possessed hydrophilic patterns. First, a circular portion of an uncoated cotton fabric was masked by dispensing melted wax onto both faces of the fabric and solidifying the wax via cooling. This wax-bearing fabric was then immersed into a polymer solution in which DMF served as the solvent. DMF was chosen as the solvent because it did not dissolve the wax, thus allowing it to remain on the fabric. The unmasked regions were consequently coated by the polymer, but the copolymer was unable to coat the wax-bearing regions. After the polymer coating was applied onto the unmasked regions of the cotton substrate, the wax mask was removed by curing the sample at a high temperature. The removal of the wax thus yielded domains consisting of exposed cotton. Cotton is inherently hydrophilic and thus these uncoated domains or patterns readily absorbed the water-based ink, which was repelled by the polymer-coated superhydrophobic domains. Therefore, the ink was selectively absorbed by the uncoated regions and reproduced the pattern left by the original wax mask. Figure 6 shows a photograph of the superhydrophobic cotton fabric bearing a central circular hydrophilic pattern that was stained by ink. The pattern-bearing cotton fabric could be thus applied as a stamp to transfer the ink from the pattern onto another cotton fabric and reproduce the image, as shown in Figure 6. Thus it was demonstrated that the block copolymer solutions could be used in combination with the batik method to create patterned stamps in a convenient and cost-effective manner. These pattern-bearing fabrics could be used repeatedly as stamps to imprint images onto 20 different cotton fabrics, without any loss in the quality of the reproduced images.

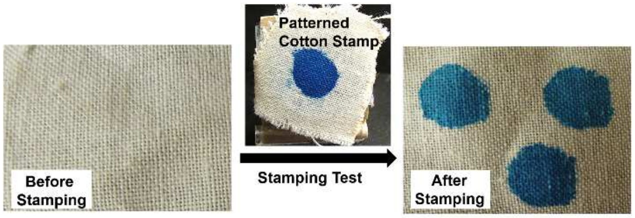


Figure 6. Images recorded during ink-stamping tests performed using the hydrophilically patterned superhydrophobic cotton fabrics. The hydrophilic patterns readily absorbed ink, which was repelled by the surrounding superhydrophobic domains. The ink could be transferred onto other cotton substrates, thus reproducing the original pattern.

Conclusions

A novel diblock copolymer has been synthesized that incorporates a low surface energy PDMS block and a sol-gel-forming PIPSMA block. Superhydrophobic cotton fabrics were prepared by grafting this block copolymer onto cotton fabrics, and their self-cleaning behavior was subsequently evaluated. These superhydrophobic cotton fabrics could be used as membranes to separate water from oil. In particular, an oil-water mixture was passed through the coated fabric, and the organic solvent permeated through the coated fabric membrane while the water was retained by this membrane. Additionally, this coating strategy could be used in combination with the batik method to prepare patterned stamps bearing superhydrophobic and hydrophilic domains. The superhydrophobic domains repelled the ink, while the patterned hydrophilic domains absorbed the ink, which could be subsequently transferred onto new substrates. These patterned fabrics were thus successfully used as stamps for the reproduction of images onto other cotton substrates. The coating strategies described in this report have significant potential for applications such as separations, environmental remediation, and for use in the textile industry.

Notes and references

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Electronic Supplementary Information (ESI) Methods of measuring water contact and shedding angles are provided in the SI. The SI also includes the ^{1}H NMR spectra of IPSMA, PDMS-Br, and PDMS-*b*-PIPSMA along with the signal integrations.

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