Surface Chemistry

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# In Situ Generated Janus Fabrics for the Rapid and Efficient Separation of Oil from Oil-in-Water Emulsions

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**Abstract:** *A cotton fabric was coated with a polymer that contains both poly(dimethyl siloxane) (PDMS) and poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA). When the repeat unit number of PDMS is about three-fold that of PDMAEMA and the fabric is exposed to air, the fabric is superhydrophobic because PDMS in the coating covers the PDMAEMA chains. Upon contact with an oil-in-water emulsion, the water-soluble PDMAEMA rises to the top and the side in contact with the emulsion becomes hydrophilic. The emerged PDMAEMA chains then cause the emulsion droplets to coagulate, and the aggregated oil fills the pores on the superhydrophobic side of the fabric. The oil-impregnated side remains hydrophobic even upon prolonged contact with water. Thus, a Janus fabric is elegantly generated in situ and sustained. This easy-to-prepare Janus fabric rapidly and efficiently separates oil from emulsions and may find practical applications.*

Oil separation from simple oil/water mixtures that contain no surfactants or oil-in-water emulsions that are stabilized by surfactants is important in many industrial processes.[1–5] It also plays a critical role in the cleanup of oil spills on lakes or oceans after accidents, such as the one in 2010 in the Gulf of Mexico. Arguably, the cheapest way to clean a water-surface spill is to collect the oil using barrels with mouths covered by large-pore high-flux filters. Through these filters, oil should selectively permeate but water is blocked. A novel and easy-to-prepare filter that may be suitable for such an application is reported. The filter comprises a polymer-coated fabric that becomes an oil-separating Janus fabric when it comes into contact with an emulsion on one side.

Oil can be easily separated from a simple oil/water mixture using a fabric or metal mesh that is superhydrophobic but oleophilic.[1–4,6–10] In this case, the oil droplets that lack an adsorbed surfactant readily coalesce, and the coalesced oil then fills the oleophilic pores of the filters and selectively permeates them. Water is rejected because of the hydrophobicity of such an oil-impregnated filter. These separations may be rapid because the filter pores may be orders of magnitude larger than the non-aggregated oil droplets. However, the high-flux separation of oil from an oil-in-water emulsion is difficult. Surfactant-stabilized oil droplets typically have diameters of less than ten micrometers[11] and do not readily coalesce. If a superhydrophobic filter with pore sizes reaching hundreds of micrometers is used, the individual stable oil droplets surrounded by water appear as water to the filter and are rejected by it. For separation, polymer membranes with pore sizes smaller than or comparable to the diameter of the droplets must be used.[11–14] To use metal meshes or fabrics as filters, their pore sizes need to be reduced first by nanostructure growth or polymer deposition onto the mesh wires or fabric fibers.[14–18] At small filter pore sizes, the droplets easily deform, fill the pores, and then permeate them. However, decreasing the filter pore size reduces an oil's permeation rate.[1–4]

Our group recently reported an innovative high-flux oil-separating filter that defied this size limitation.[19] In that work, a Janus fabric that featured a hydrophilic polymer, poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMAEMA), on one side and a hydrophobic polymer, poly(dimethyl siloxane) (PDMS), on the other side was prepared. When the PDMAEMA-coated side came into contact with an oil-in-water emulsion stabilized by an ionic surfactant, the partially or fully charged PDMAEMA chains destabilized the emulsion owing to the charge-screening effect. The coagulated oil then selectively permeated the superhydrophobic side. The oil permeation was favored also because of a wicking force that goes unidirectionally from the hydrophilic to the hydrophobic side and is unique to fabrics with a hydrophobicity gradient.[5,20] Our fabrics separated oil from emulsions despite their pores being two orders of magnitude larger than the original oil droplets.

Unfortunately, traditional Janus fabrics are tedious to prepare.[5,21] In our previous example, two polymers, multiple reaction steps, and delicate protocols were required to prepare the Janus fabric.[19] The challenging preparation limits their applications. We then realized that the separation environment of a fabric was asymmetric, with the feed side comprising a polar water-rich emulsion and the permeate side consisting of a non-polar separated oil. Therefore, we hypothesized that this asymmetric environment could be utilized to produce a Janus fabric in situ by using a stimuli-responsive coating from a single polymer. The need to graft only one polymer through a single reaction step would drastically simplify the preparation of the Janus fabric. If successful, we would also demonstrate an application for stimuli-responsive polymers[22–24] and switchable surfaces,[25] which are topics of tremendous current interest.

To verify our hypothesis, we designed and synthesized a family of diblock copolymers P1-*b*-A$_m$ (Scheme 1 a), where P1 denotes P(MMA-*s*-HEMA)-*g*-PDMS with the molar fractions of 91 %, 8.1 %, and 0.9 % for MMA (methyl

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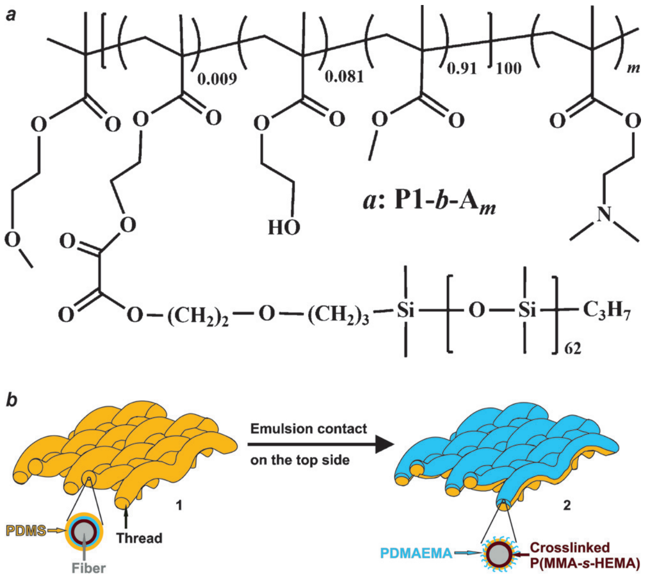

*Scheme 1.* a) Chemical structures of P1-*b*-A$_m$. b) Schematic of a P1-*b*-A$_m$-coated fabric in air and after contact with an emulsion on the top side. The thicknesses of the polymer trilayers and the fiber diameter are not to scale.

methacrylate), HEMA (2-hydroxyethyl methacrylate), PDMS-bearing HEMA units, respectively. A$_m$, *s*, *g*, and *b* signify a PDMAEMA block of *m* repeat units, *statistical*, *graft*, and *block*, respectively. HEMA and MMA were chosen because P(MMA-*s*-HEMA) could form a crosslinked layer around cotton fibers through the attack of the MMA and HEMA ester bonds by the HEMA hydroxyl groups to eliminate methanol and ethylene glycol.[26,27] HEMA was essential also for its ability to react with PDMS-COCl, PDMS bearing a terminal acid chloride group, to graft PDMS.

We imagined that a P1-*b*-A$_m$ coating that was crosslinked by P(MMA-*s*-HEMA) would be covered by the low-surface-tension PDMS chains in air (1, Scheme 1 b), if they were sufficiently long. However, the PDMAEMA chains with their lengths optimized relative to the PDMS chains would rise to the top when the fabric came into contact with an oil-in-water emulsion because of PDMAEMA's preferential solubility in water (1→2, Scheme 1 b). The emerged PDMAEMA chains would then destabilize the emulsion, and the coagulated oil would fill the pores on the fabric side that was not reconstructed. We further imagined that this side might retain its hydrophobicity after oil impregnation because of PDMS's preferential solubility in oil. Thus, the in-situ-generated Janus fabric structure might be maintained, bestowing the fabric with an enduring separation capability.

As discussed in the Supporting Information, five P1-*b*-A$_m$ samples with $m = 4$, 18, 23, 42, and 103 were prepared. As for P1, its backbone consisted of 91 MMA units and 9 HEMA units. On average, each P(MMA-*s*-HEMA) chain was grafted with 0.91 PDMS chain and the repeat unit number was 62 for PDMS. Thus, the weight fraction of PDMS in P1 was 34 %.

The plain-woven cotton fabric used had inter-thread pore sizes reaching 200 μm (Supporting Information, Figure S5). To coat the fabric, swatches were immersed into a P1-*b*-A$_m$ solution in tetrahydrofuran (THF) for 30 min before they were removed and heated under vacuum at 180 °C for 4 h to crosslink the P(MMA-*s*-HEMA) layer around the fibers. Polymer chains not incorporated into the crosslinked layer were removed by extraction with hot THF (Supporting Information). The fabric samples thus coated by P1-*b*-A$_m$ with $m = 0$, 4, 18, 23, and 42 featured water contact angles (WCAs) of $152 \pm 2$, $150 \pm 1$, $151 \pm 1$, $150 \pm 1$, and $150 \pm 2°$, respectively, when they were measured within 10 s after the water droplets had been dispensed. The fact that the high contact angles did not vary much with *m* suggested the surfaces were covered by PDMS in air. However, these angles decreased as the resting time of the water droplets on the coated fabrics increased. Figure 1 a shows the data for fabrics coated by P1-*b*-A$_m$ with $m = 0$, 4, 18, 42, and 103. While the WCAs on P1-*b*-A$_0$- or P1-coated fabrics barely changed with time, water droplets immediately got absorbed by the P1-*b*-A$_{103}$-coated fabrics. As for the samples coated by P1-*b*-A$_m$ with intermediate *m* numbers, the WCA decreased more rapidly with time as *m* increased.

The data of Figure 1 a suggest that the air-impregnated and P1-*b*-A$_m$-coated fabrics with $m > 0$ underwent surface

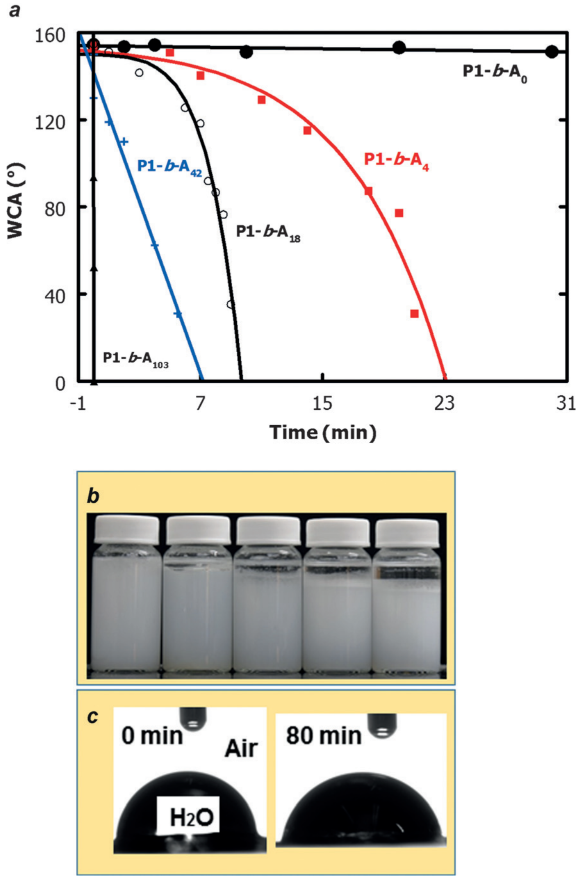

*Figure 1.* a) Variations of water contact angles with time for fabrics that were coated by P1-*b*-A$_m$ with $m = 0$, 4, 18, 43, and 103. b) Photograph of $f_{HD} = 20\%$ emulsions 15 min after the addition of a $1.5 \times 1.5$-cm$^2$ fabric swatch to each vial. From left to right, the fabric was coated using P1-*b*-A$_m$ with $m = 4$, 18, 23, 43, and 103. c) Shapes of water droplets (in air) that had been in contact with a P1-*b*-A$_{18}$-coated HD-impregnated fabric for 0 and 80 min.

reconstruction, as anticipated. Furthermore, the rate of surface reconstruction increased as the length of the PDMAEMA block increased. This trend was reasonable, as the collapsed PDMS layer initially at the top of the coating had a certain thickness. As $m$ decreased, the PDMAEMA chains would be buried more deeply and more time was required for them to break through the PDMS layer. Additionally, short PDMAEMA chains needed to stretch themselves to reach the coating surface, which was not favored entropically.

In another experiment, we placed a series of P1-*b*-$A_m$-coated fabric swatches (1.5 × 1.5 $cm^2$) into vials containing 20 mL of a hexadecane (HD)-in-water emulsion that was stabilized by sodium dodecyl sulfate at a HD volume fraction $f_{HD}$ of 20 %. Figure 1 b shows a photograph of the emulsions 15 min after the addition of the P1-*b*-$A_m$-coated fabric swatches. The extent of HD phase separation increased as $m$ increased. De-emulsification would have been possible only if the PDMAEMA chains reached the coating surface. Thus, these results suggested that the fabrics in contact with the water-rich emulsion could also surface-reconstruct. Another image was taken (Supporting Information, Figure S7) 19 h after fabric addition into the vials shown in Figure 1 b. No clear HD phase was observed in the vial containing a P1-*b*-$A_4$-coated swatch even then. This indicated that this coating had limited de-emulsification ability.

In a real separation, the surface reconstruction on the emulsion-contacting side should be followed by local de-emulsification and the filling of the pores on the unreconstructed side by the coagulated oil, yielding an overall Janus fabric. To determine if this Janus structure could be sustained, we dispensed a water droplet on a HD-impregnated P1-*b*-$A_{18}$- or P1-*b*-$A_{105}$-coated fabric and then waited. Figure 1 c compares photographs of droplets that were taken immediately and 80 min after their dispensing on a P1-*b*-$A_{18}$-coated and HD-impregnated fabric. The droplets were essentially stable, exhibiting a minor contact angle decrease from 88 ± 2° to 82 ± 2°. This was in contrast with the behavior on a P1-*b*-$A_{105}$-coated and HD-impregnated fabric, into which a water droplet was absorbed within 2 s. Thus, the Janus structure could be sustained only by the P1-*b*-$A_{18}$-coated fabric but not by the P1-*b*-$A_{105}$-coated fabric.

For oil separation, the two halves of an H-shaped cell were separated by a coated fabric (Figure 2 a). In one experiment, 20 mL of an $f_{HD}$ = 20 % emulsion was then added to the right half-cell. Under vigorous stirring, the emulsion bombarded the fabric and de-emulsification and separation started. Figure 2 b shows the increase over time of the volume of collected HD in the left half-cell when fabric swatches coated by P1-*b*-$A_m$ with $m$ = 4, 18, 23, and 42 were used. No data are shown for the P1-*b*-$A_0$- and P1-*b*-$A_{105}$-coated fabrics because no permeation occurred with the former and both de-emulsified HD and the emulsion permeated the latter.

Nothing permeated the P1-*b*-$A_0$-coated fabric because the stable emulsion droplets, which had an average diameter of 3.7 ± 0.6 μm (Supporting Information, Figure S8) and were surrounded by water, appeared as water to the fabric. Emulsions also permeated the P1-*b*-$A_{105}$-coated swatches because such a fabric could not sustain a Janus structure. A P1-*b*-$A_4$-coated fabric could not fully separate HD because it had poor de-emulsification ability (Supporting Information, Figure S7). The P1-*b*-$A_{18}$-, P1-*b*-$A_{23}$- and P1-*b*-$A_{42}$-coated swatches allowed the full separation of HD (4.0 mL, theoretically) because they sustained the desired Janus structure.

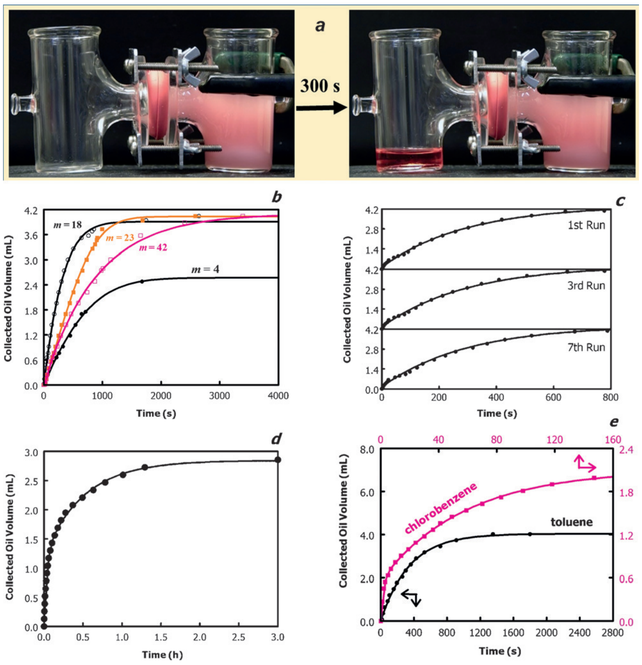

***Figure 2.*** a) Photographs of a separation experiment immediately and 5 min after 20 mL of a dyed $f_{HD} = 20\%$ emulsion was added into the right cell of the H-shaped device. b) Separation data for fabrics coated with P1-*b*-$A_m$ at $m = 4$, 18, 23, and 42. c) Data for three separations in a series of seven consecutive trials using a P1-*b*-$A_{18}$-coated fabric. d) Data for HD separation from 300 mL of an $f_{HD} = 1.00\%$ emulsion. e) Separation data for emulsions containing toluene and chlorobenzene as the oily phase.

Since the separation was fastest with the P1-*b*-$A_{18}$-coated fabric, only this fabric was further investigated. To probe its robustness, we used the same swatch with an effective separation area of only 1.13 $cm^2$ to perform seven consecutive separations. For each separation, the fabric was exposed to the emulsion for about 15 min before the liquids were removed from the feed and permeate sides and another 20 mL emulsion at $f_{HD}$ = 20 % was added to the feed side. Figure 2 c compares data gathered from separations 1, 3, and 7. Even after seven trials, the filter's performance did not degrade. This demonstrated the robustness of the fabric.

To probe the separation limit for HD, we covered one mouth of a three-neck round-bottom flask with a coated swatch and then tilted the flask so that HD could be separated from 300 mL of a $f_{HD}$ = 1.00 % emulsion (Supporting Information, Figure S1). The separated HD volume reached 2.7 mL by 1.5 h and 2.9 mL by 3 h (Figure 2 d). The latter value was close or identical to, within experimental error, the 3.0 mL of HD contained in the feed emulsion. Thus, the residual HD in the final 297 mL emulsion was less than 0.1 mL, and the fabric had an impressive HD separation limit of 0.034 % (which is the same as the measurement error of the instrument).

The fabric also separated other oils. Figure 2e shows the separation data for toluene-in-water and chlorobenzene-in-water emulsions containing 20 vol% of oil. Since a H-shaped cell that accepted 20 mL of emulsion was used for the former separation, the volume of fully separated toluene should be 4.0 mL. In the latter case, a burette with its bottom end covered by a coated fabric was used as the separation device (Supporting Information, Figure S1). A different device was used because the high-density de-emulsified chlorobenzene settled to the bottom and could not reach the fabric in the H-shaped cell. In this case, the fully separated chlorobenzene volume was 2.0 mL. Thus, we note from data shown in Figure 2e that complete separation was achieved in both cases. Strikingly, chlorobenzene was separated far more rapidly than toluene or HD. Our quantitative analysis using the active surface areas of the fabrics and the first three data points of each graph in Figure 2d as well as the data for the P1-*b*-$A_{18}$-coated fabric in Figure 2a yielded the permeation rates of $0.49\times10^3$, $0.87\times10^3$, and $6.7\times10^3\,\mathrm{L\,h^{-1}\,m^{-2}}$ for toluene, HD, and chlorobenzene, respectively. Chlorobenzene was separated more rapidly because of the vertical apparatus used. The hydrostatic pressure exerted on the fabric by the column of the emulsion in the burette accelerated the separation (Supporting Information, Figure S10).

In summary, we have developed a simple method for generating Janus fabrics. When used as filters, such fabrics rapidly and efficiently separate oil from simple oil/water mixtures and oil-in-water emulsions. The filters are also highly robust and can be used for multiple separations. Owing to the simple preparation of the Janus filters, we expect them to find practical applications in oil/water separation.

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