

Supporting information for

Tailoring the Surface Chemistry and Morphology of Glass Fiber Membranes for Robust Oil/Water Separation using Poly(dimethylsiloxanes) as Hydrophobic Molecular Binder

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1. Supplementary Experimental Section

Synthesis of PDMAEMA-PDMS-PDMAEMA Block Copolymers. N,N-dimethylamino ethyl methacrylate (Sigma-Aldrich, 98%) was passed through a short column with basic alumina oxide to remove the inhibitors. CuBr (Sigma-Aldrich, 98%) was stirred overnight in acetic acid and then washed with methanol, followed by drying under vacuum.

Synthesis of PDMAEMA-PDMS-PDMAEMA triblock copolymer. The triblock copolymers were synthesized by atom transfer radical polymerization (ATRP). Functional Br-PDMS-Br macroinitiators were prepared from aminopropyl-terminated poly(dimethylsiloxanes) by using BiBB and TEA (molar ratio 1:10:10) in anhydrous DCM with a final polymer concentration of 15 wt% in solution. The TEA/PDMS solution was cooled using an ice bath under nitrogen circumstance for 15 min, followed by dropwise addition of BiBB. This reaction solution was stirred at RT for 24 h. Subsequently, the polymer solution was filtered to remove precipitates and then washed with methanol to yield a colorless viscosity liquid. The absence of primary amine protons ($\delta = 2.66$ ppm) and the presence of secondary amine protons ($\delta = 6.77$ ppm) indicate the complete elimination of the amine end groups (Figure S2). NH₂-PDMS-NH₂ **1**): ¹H NMR (400 MHz, CDCl₃, δ): 3.49 (quint, J=8.5 Hz, 2H, -CH₂-NH₂), 2.66 (t, J=6.6 Hz, 2H, -NH₂), 1.66–1.38 (m, 2H, -CH₂-), 0.53 (tt, 2H, -Si(CH₃)₂-CH₂-), 0.07 (br, 6H, -Si(CH₃)₂-). Br-PDMS-Br **2**): ¹H NMR (400 MHz, CDCl₃, δ): 6.77 (s, 1H, -NH-CO-), 3.49 (m, 2H, -CH₂-NH-), 2.0–1.9 (m, 6H, -C(CH₃)₂-Br), 1.60–1.50 (m, 2H, -CH₂-), 0.53 (tt, 2H, -Si(CH₃)₂-CH₂-), 0.07 (br, 6H, -Si(CH₃)₂-).

In a typical ATRP experiment, the Br-PDMS_{25k}-Br macroinitiator (0.55 g), PMDETA ligand (9 μ L, 0.04 mmol) were firstly added to a 50 mL Schlenk tube. After three vacuum-nitrogen

purging cycles, the monomer (DMAEMA) (3 mL, 17.8 mmol) and toluene (5 mL) were added under nitrogen flow. The solution was further bubbled with nitrogen for 20 min, and then CuBr powder (6 mg, 0.04 mmol) was added quickly under nitrogen flow. Subsequently, the Schlenk tube sealed with rubber plug was placed in an oil bath (90 ± 0.1 °C) and stirred (600 rpm) for 18 h. The reaction was quenched by cooling and exposing to air, followed by diluting with THF. The copper catalyst was removed by passing through a neutral alumina column. Finally, the polymer solution was precipitated in cold methanol, the resultant white solid was dried under vacuum at 45 °C for 24 h. PDMAEMA-PDMS-PDMAEMA: ^1H NMR (400 MHz, CDCl_3 , δ): 4.04 (s, 2H, $-\text{CH}_2-\text{COO}-$), 2.55 (s, 2H, $-\text{CH}_2-\text{N}$), 2.26 (s, 6H, $-\text{N}(\text{CH}_3)_2$).

Membrane Filtration Experiments. The benchtop apparatus shown in Figure S1a was used to evaluate the separation efficiency and long-term performance of superhydrophobic/superoleophilic GF membranes. Free hexadecane/water mixture in the two-neck round bottom flask was stirred (600 rpm) and the permeate was collected in the Erlenmeyer flask. To maintain a continuous separation, the collected hexadecane would be poured back into the round bottom flask once there was no oil flow. The hexadecane purity was evaluated at different time points.

Surfactant-stabilized oil in water emulsion (1:9 v/v) was prepared by mixing 0.01 M HCl aqueous solution and hexadecane at 800 rpm for 30 min. Sodium dodecyl sulfate (SDS) was used as the surfactant with a concentration of 0.5 mg/mL. The small dead-end microfiltration assembly shown in Figure 6a was used to batch-wise (70 mL) separate hexadecane-in-water emulsions via the pH-responsive /underwater superoleophobic GF membranes. The purity of the permeate (water) was measured after a certain number of batch separation.

Measurements. Measurement of membrane flux was performed by using the apparatus with an effective filtration area of 4.9 cm² at a constant liquid height (Figure S1b). The membrane flux per unit applied pressure was determined by measuring the volume of liquid permeated within 2 min via $J=Q/Atp$ where Q is the volume of permeate (L); A is effective filtration area (m²); t is filtration time (h); p is the hydrostatic pressure. The water content in hexadecane (C₁₆H₃₄, boiling point: 286.8 °C) was measured using thermal gravimetric analysis (TGA) at nitrogen condition, purge flow of balance and sample are 40, 15 mL/min respectively. Approximately 30 μL of the sample was heated from 25 to 105 °C at a rate of 10 °C /min and then equilibrated at 105 °C for 30 min. The TGA curves of the samples were compared with that of the anhydrous hexadecane to estimate its purity. Oil content in water-rich permeate was determined using a Total Organic Carbon (TOC) analyzer (ASI-L Shimadzu).

Characterizations. ¹H nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker 400 MHz Ultrashield NMR instrument at room temperature using CDCl₃ containing 0.03% (v/v) TMS (tetramethylsilane) as a solvent. Thermal gravimetric analysis (TGA) was performed on a TA Q500 TGA instrument from 100 to 600 °C at a heating rate of 10 °C/min under N₂ atmosphere.

2. Supplementary Figures and Discussion

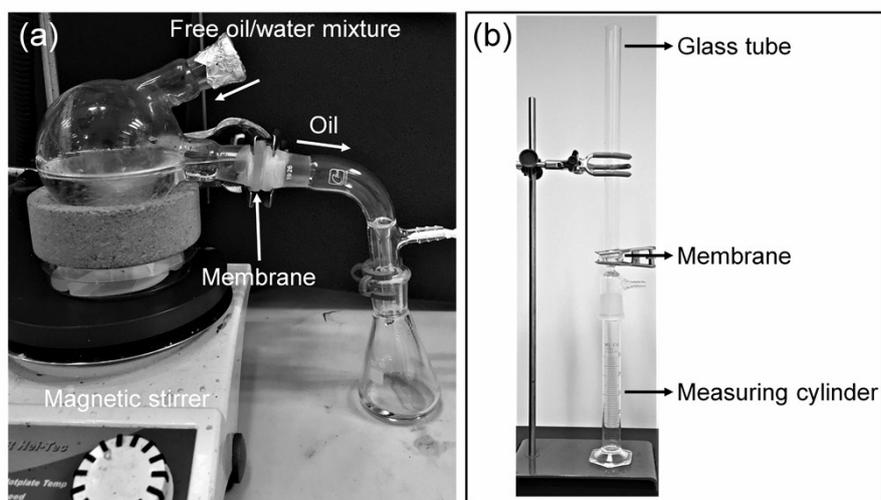


Figure S1. Batch systems for (a) separation of free hexadecane/water mixture and (b) measurement of membrane flux.

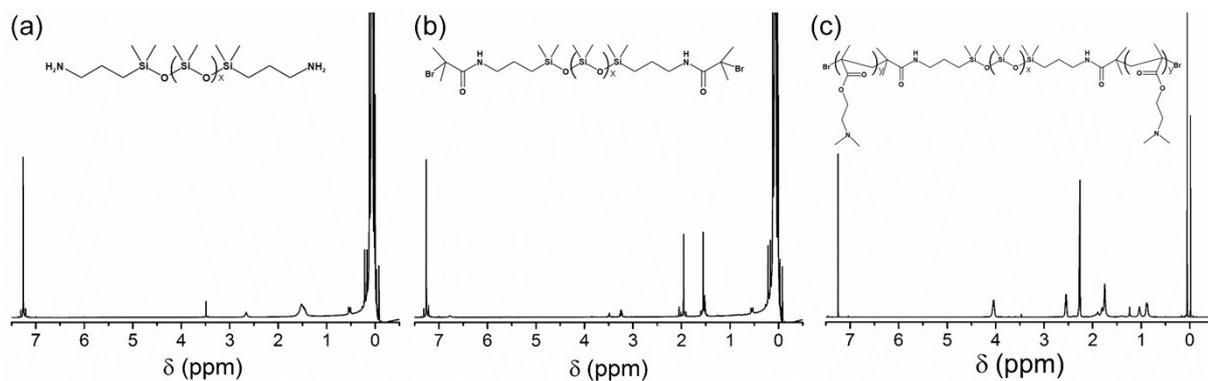


Figure S2. Typical ¹H NMR (400 MHz) spectra of polymers in CDCl₃. (a) NH₂-PDMS-NH₂, (b) Br-PDMS-Br, (c) PDMAEMA-PDMS-PDMAEMA.

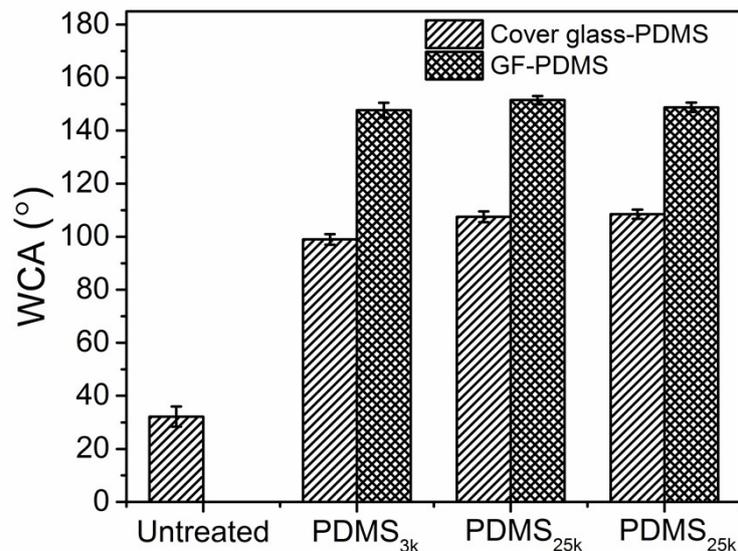


Figure S3. Apparent water contact angles of GF filters and coverglasses before and after PDMS modification. The water drop rapidly infiltrates the GF filters due to its hydrophilic nature (WCA of smooth coverglass was $32.2 \pm 3.8^\circ$), leading to a WCA of 0° . After PDMS modification, the WCA increases dramatically to $147.4 \pm 2.8^\circ$, $151.5 \pm 1.6^\circ$, $148.8 \pm 1.8^\circ$ for GF-PDMS_{3k}, GF-PDMS_{25k}, and GF-PDMS_{50k} respectively. The WCA of PDMS_{3k}, PDMS_{25k}, PDMS_{50k} modified coverglasses are $99 \pm 2^\circ$, $107.5 \pm 2^\circ$ and $108.5 \pm 1.7^\circ$ respectively which are in good agreement with typical PDMS surfaces with WCA between 98 and 112° .¹

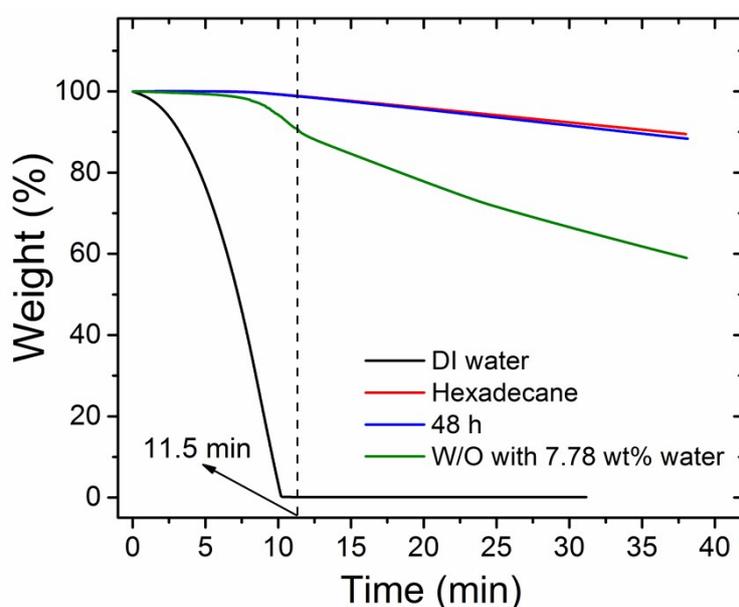


Figure S4. TGA trace for the permeate obtained from the batch separation of hexadecane/water

by using superhydrophobic/superoleophilic GF-PDMS_{3k}/Silica_{0.5} membrane, only the data of 48 h is shown for the sake of simplicity. The TGA traces of DI water and as-received hexadecane are also shown to facilitate comparisons. Since water will lose all its weight after 10 min, the weight percentages at 11.5 min were used for calculating the water content in oil via $W_{\text{water}} = W_{\text{hexadecane}} - W_{\text{permeate}}$ equation, where W is the remaining weight (%) at 11.5 min. To check its validity, a hexadecane/water mixture with a known water content (7.78%) was tested and calculated by the above method. The estimated water content is 8.1% which provides a good approximation to the actual value.

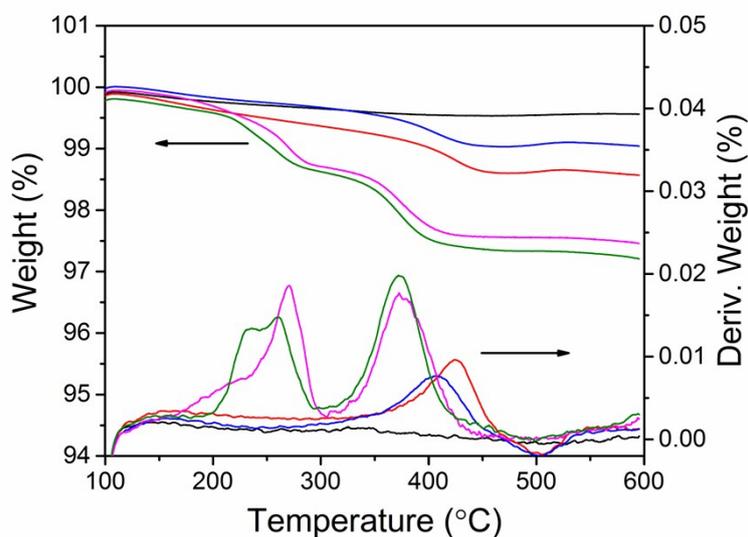


Figure S5. TGA traces and corresponding derivative weight loss curves of pristine and polymer coated GF-filters: (black) GF filters, (blue) GF-PDMS_{3k} (red) GF-PDMS_{25k}, (magenta) GF-A₃₅₃B₆₉A₃₅₃, and (olive) GF-A₃₂₅B₃₂₂A₃₂₅. The TGA curve of GF filters shows little weight loss up to 600 °C due to its good thermal stability. GF-PDMS_{3k} and GF-PDMS_{25k} show one weight loss stage from 340 to 450 °C which is attributed to the degradation of PDMS. In the case of PDMAEMA-PDMS-PDMAEMA coated samples, two weight loss stages were observed which follows the same pattern of PDMAEMA polymer. These results suggest the

successful coating of the block copolymers.



Figure S6. Photograph of SDS-stabilized hexadecane/water emulsion after 5 min addition of a 1.5 x 1.5 cm² swatch to each vial. From left to right, the swatches were GF-A₃₅₃B₆₉A₃₅₃, GF-A₃₂₅B₃₂₂A₃₂₅, and pristine GF filters. The last vial was CTAB- stabilized emulsion with GF-A₃₂₅B₃₂₂A₃₂₅. When placed the GF-A₃₂₅B₃₂₂A₃₂₅ membrane into a SDS-stabilized emulsion, phase separation appeared after 5 min immersion. In contrast, no phase separation was observed for CTAB-stabilized (cationic surfactant) emulsion.

3. References

1. J. S. Smith, O. Borodin, G. D. Smith and E. M. Kober, *J. Polym. Sci., Part B: Polym. Phys.*, 2007, **45**, 1599-1615.