Supporting Information


Reproducing Superhydrophobic Leaves as Coatings by Micromolding Surface-Initiated Polymerization

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Experimental Methods

Materials.  4-Mercapto-1-butanol (97%), Grubbs catalyst 2nd generation (1,3-Bis-(2,4,6-trimethylphenyl)-2-(imidazolidinylidene) (dichlorophenylmethylene) (tricyclohexylphosphine) ruthenium), trans-3,6-endomethylene-1,2,3,6-tetrahydrophthaloyl chloride (NBDAC) (97%), Copper(I) chloride (CuCl) (99.995+%), Copper(II) bromide (CuBr₂) (99.999%), 2,2'-bipyridine (bpy, 99+%), N,N-dimethylformamide (DMF, 99.9%), 2-hydroxyethyl methacrylate (HEMA, >99%), 1H,1H,2H-perfluoro-1-decene (99%), hydroquinone, and Bis[2-(2bromoisobutyryloxy)undecyl] disulfide ((BrC(CH₃)₂COO(CH₂)₁₁S)₂) (97%) were acquired from Sigma-Aldrich. Tridecafluoro-1, 1, 2, 2-tetrahydrooctyl-1-trichlorosilane (TFOCS) was purchased from UCT Specialties. Anhydrous methylene chloride (DCM) (99%) was obtained from Acros Organics. Methylene chloride (DCM) (99%) was purchased from Fisher. Gold shot (99.99%) was obtained from J&J Materials, and silicon (100) wafers were purchased from WRS Materials. Chrome-plated tungsten rods were obtained from R.D. Mathis. Deionized water (16.7 MΩ) was purified with a Modu-Pure filtration (Contiental Water Systems Corporation) system and used for rinsing. Ethanol (200 proof) was obtained from AAEPER and used as received. Nitrogen gas was obtained from AL compressed gases. The synthesis of 5-(perfluoroctyl)norbornene (NBF₈) is described elsewhere. [(7–8% vinylmethylsiloxane)-(dimethylsiloxane)] copolymer, 1, 3, 5, 7-tetramethylocyclotetrasiloxane, platinum divinyltetramethyldisiloxane, and [(25–35% methylhydrosiloxane)-(dimethylsiloxane)] were purchased from Gelest, Inc. Tetraethoxysilane (99.9%) was purchased from Alfa Aesar. Dow Corning Sylgard® 184 Silicon Elastomer Kit was obtained from Ellsworth Adhesives. Leaves from Aristolochia esperanzae plants were provided by the Vanderbilt University
Greenhouse. Leaves from *Trifolium repens* were obtained from plants growing locally in the wild. Scotch double-sided adhesive tape was purchased from a hardware store.

**Preparation of Gold Substrates.** Silicon wafers were cleaned with ethanol and water and dried in a nitrogen stream. Subsequently, the wafers were placed inside a CVC-PSM66 evaporator in order to sequentially evaporate 100 Å of chromium and 1250 Å of gold onto the wafers using an evaporation rate of 1 – 2 Å s\(^{-1}\) and a base pressure of \(< 4 \times 10^{-6}\) Torr. After the evaporation process, wafers were cut to samples of 1.2 cm × 3.5 cm in size.

**Preparation of Leaves for Scanning Electron Microscopy (Fixing).** Leaves underwent a primary fixation step by exposing them to 1% paraformaldehyde and 1.25% gluteraldehyde in 0.1 M sodium cacodylate buffer (pH 7.1) at room temperature for 2 – 4 h. Afterward, the leaves were rinsed three times with a 0.1 M sodium cacodylate buffer pH (7.1) at room temperature. Subsequently, the leaves underwent a secondary fix by exposing them to 1% osmium tetroxide in 0.1 M sodium cacodylate buffer (pH 7.1) at room temperature for 15 min. Warning: osmium tetroxide is a dangerous chemical; wear the appropriate protective personal equipment and use a fume hood when working with it. Afterward, the leaves were washed three times with 0.1 M sodium cacodylate buffer (pH 7.1) at room temperature. The leaves were dehydrated in an aqueous solution containing increasing concentrations of ethanol as follows: 25% – 1 h, 50% – 1 h, 75% – 0.5 to 0.75 h, 95% – 1 h, 100% – 1 h, 100% – 1 h, 100% – 1 h. Finally, the samples were dried using a Polaron critical point dryer.

**Molding.** The molds bearing the inverse pattern of the master leaves, *Trifolium repens* and *Aristolochia esperanzae*, were produced by means of soft lithography. Only freshly cut, fully developed leaves were used. Samples of 10 mm × 10 mm, cut from the center of the leaf lamina, were affixed to the bottom of a plastic petri dish (5 cm in diameter) by double-sided adhesive tape to ensure a fully extended, flat surface. Once secured, a drop of tetraethoxysilane was added onto the leaf masters to create a thin layer on the surface of the masters that prevented the resulting mold from adhering to it. The molding process, which yielded a polymeric composite comprising hard-PDMS (h-PDMS) and Sylgard 184 PDMS, proceeded as follows: 3.4 g of [(7–8% vinylmethylsiloxane)-(dimethylsiloxane)] copolymer, two drops of 1, 3, 5, 7-tetramethylecyclotetrasiloxane, and 1 drop of platinum divinyltetramethyldisiloxane were thoroughly mixed for at least 8 min with a glass rod in a
weighing boat. During mixing, air bubbles were trapped within the mixture; to remove these, the weighing boat was placed in a desiccator connected to a vacuum line and evacuated until bubbles were no longer visible. As pressure decreases, bubbles begin to expand and rise. Therefore, to prevent any spilling while degassing, vacuum was broken and restored several times. Subsequently, 1 g of [(25–30% methylhydrosiloxane)–(dimethylsiloxane)] was added to the degassed mixture and rapidly stirred with the glass rod for 3 min. The mixture was poured onto the petri dishes containing the masters and placed once again in a desiccator connected to a vacuum line to remove the entrapped bubbles resulting from the rapid mixing. Similarly, vacuum was broken and restored several times. To cure the h-PDMS, the petri dishes containing the leaf masters were placed in an oven at 60 °C for 10 min. During the curing process, a mixture of Sylgard polymer base (4.0 g) and curing agent (0.4 g) was added to a weighing boat and thoroughly mixed using a glass rod for at least 8 min. Once the h-PDMS was cured, the petri dishes were removed from the oven, and the freshly prepared Sylgard 184 PDMS/curing agent mixture was poured onto them. As in the previous step, the petri dishes were placed in a desiccator for degassing. Once free of bubbles, these were placed in an oven set at 60 °C and allowed to cure for 6 h. The resulting molds, exhibiting two layers, namely h-PDMS (~1 mm thick) and Sylgard 184 PDMS (~2 mm thick), were removed by gently breaking the entire wall surrounding the petri dish with pliers and carefully peeling them off the masters. The composite elastomeric molds were also exposed to the vapor of TFOCS for 20 min in order to facilitate the separation of the substrate from the mold after polymerization.

**Polymerization.** SI-ROMP was initiated from an initiator-activated self-assembled monolayer (SAM). Briefly, the gold-coated silicon samples were exposed to a 1 mM ethanolic solution of 4-mercapto-1-butanol for at least 1 h to create a hydroxyl-terminated SAM on the gold surface. Afterwards, samples were rinsed in ethanol and dried in a stream of nitrogen. Subsequent exposure of the SAM-decorated substrates to a 5 mM solution of NBDAC in DCM for 30 min resulted in the coupling of norbornenyl groups to the underlying hydroxyl monolayer via ester linkages. Next, samples were rinsed with DCM and ethanol and dried in a stream of nitrogen. To immobilize the initiator and render the surface active for SI-ROMP, the norbornenyl decorated surfaces were exposed to a 5 mM solution of Grubbs second-generation catalyst in DCM for 10 min. Subsequently, samples were rinsed in DCM and immediately pressed against (load ~194 ± 18 mN) a monomer-
loaded h-PDMS mold. Prior to placing the initiator-activated surface against the mold, the mold had been coated with initiator species, by depositing 200 µL of a 3 mM solution of Grubbs catalyst in diethyl ether and letting the solvent evaporate, and then filled with pure NBF8 monomer (5 µL of NBF8 were added to the mold 1 – 2 seconds before pressing the substrate against the mold). Pressing the activated surface against the monomer-filled mold resulted in the growth of partially fluorinated polymer films from the gold surface. After polymerization, the coatings were rinsed with DCM, ethanol, and water, and dried in a stream of nitrogen.

**Characterization Methods.** Advancing and receding water contact angle measurements were made using a Rame-Hart contact angle goniometer equipped with a microliter syringe. The tip of the syringe was kept inside the liquid drop as the measurements were taken on both sides of ~5 μL drops. Reported values represent the average and standard deviations of at least three different measurements.

**Scanning Electron Microscopy (SEM).** Scanning electron micrographs of the polymer-coated substrates were taken with a Quanta 250 scanning electron microscope using an accelerating voltage of 10 kV. The polymer coatings and the fixed leaves were sputtered with gold (~2 nm in thickness) before taking the images. The MetaMorph Offline version 7.7.0.0 image analysis software was used to analyze the images (Molecular Devices, Downington, PA).

**Profilometry.** The thickness of the polymer coatings was measured with a Veeco Dektak 150 Stylus Profilometer. The samples were manually scratched[2] and measurements were performed over a distance of 1500 μm using a Stylus with a 12.5 μm radius, applying 5 mg of force, and employing the hills and valleys detection mode. The scan results were plane-fitted using the software of the instrument.

References
