Supporting Information

Creating Surface Patterns of Polymer Brushes by Degrafting via Tetrabutyl Ammonium Fluoride

Rohan Patil[1], Douglas Kiserow[1,2], Jan Genzer[1*]

[1] Department of Chemical and Biomolecular Engineering
North Carolina State University
Raleigh North Carolina 27695-7905

[2] US Army Research Office
Research Triangle Park, North Carolina 27709-2211

* Corresponding author: Jan Genzer (jan_genzer@ncsu.edu)

Experimental details

Chemicals

All chemicals were purchased from Sigma Aldrich and used as received unless otherwise specified. Styrene (S) was passed through activated basic alumina to remove 4-tert-butylcatechol which acts as an inhibitor. Methyl methacrylate (MMA) was passed through inhibitor remover column to remove the inhibitor monomethyl ether hydroquinone. Millipore Elix 3 was used to obtain deionized water (DIW) with resistivity >15 MΩ.cm. Anhydrous toluene was prepared by adding molecular sieves (4 Å) activated by heating them using a heating gun for 30 minutes under vacuum. $CuCl_2$ was purified by first dissolving in ethanol and then precipitated in hexanes. (11-(2-bromo-2-methyl) propionyloxyundecyl trichlorosilane (eBMPUS) was purchased from Gelest. ACS grade methanol was obtained from Fisher Scientific. Electronics grade silicon wafers (p-doped, orientation <100>) were purchased from Silicon Valley Microelectronics. Tetrabutyl ammonium fluoride (TBAF) was purchased from Sigma Aldrich as a 1 M solution in THF.

Initiator deposition

In the conventional method a monolayer of the BMPUS initiator was deposited after exposing the silicon substrate to ultraviolet-ozone (UVO) for 15 minutes. A solution of initiator was prepared in anhydrous toluene by adding 1 μl of eBMPUS stock solution (5% w/w in toluene) per 1 ml of anhydrous toluene. The substrates were placed back to back in disposable glass vials so that the polished sides were exposed to the solution. The vials were sealed with parafilm and placed into freezer at -18°C for 18 hours. After that the substrates were thoroughly rinsed with toluene and dried under a stream of nitrogen gas. In case of degrafting and re-deposition of eBMPUS, the substrates were not treated with UVO but directly incubated in eBMPUS solution.

Growing Polystyrene (PS) brushes

Styrene (60.93 ml, 0.59 mol), DMSO (18.50 ml, 0.24 mol), were added to a round bottom flask. The solution was stirred and degassed by bubbling nitrogen gas for 20 minutes. The ligand PMDETA (0.6 ml, 3.4 mmol), catalyst CuBr (184.6 mg, 1.3 mmol) were added and the solution

was further degassed for another 20 minutes. The initiator-containing substrates were placed back to back in a disposable glass vial and the polymerization solution was added. The vial was sealed and stored at room temperature for 24 hours.

Growing Poly (methyl methacrylate) (PMMA) brushes

MMA (32.97 ml, 0.308 mol), Methanol (30.42 ml, 0.751 mol) and deionized water (6.6 ml, 0.367 mol) were added to a round bottom flask, stirred and degassed by bubbling nitrogen gas for 20 minutes. The ligand 2,2'-bipyridyl (1.94 g, 12.4 mmol), catalyst CuCl (0.622 g, 6.29 mmol) and $CuCl_2$ (4.22 mg, 0.031 mmol) were added and the solution was further degassed for 20 minutes. The Cu^{II}:Cu^{I} molar ratio was 0.005 and total solution was 70 ml. The substrates with deposited initiator layers were placed back to back in glass vials. About 20 ml of solution was added to each of the 3 glass vials which were then sealed and stored at room temperature for 24 hours.

Characterization

The dry thickness was determined by fitting data obtained from the variable angle spectroscopic ellipsometry (VASE, J.A. Woollam Co., Inc.) to a 3 layer model (bottom silicon, intermediate silica (SiO_x), and top "Cauchy" polymer layer). Thermo Nicolet 6700 was uses to obtain FTIR spectra in transmission mode (resolution 4 cm^{-1}) with 32 background scans (silicon wafer) and 512 scans of the sample. The static water contact angle was measured using contact angle goniometer (Ramé Hart, model 100-00) using deionized water as a probing liquid. X-ray photoelectron spectroscopy (XPS) experiments were carried using a SPECS FlexMod instrument with Al Kα source (excitation energy 1486.7 eV) with a takeoff angle of 30° measured relative to the normal. Energy calibration was done by using adventitious carbon as a reference (C 1s line with binding energy of 285 eV). Survey scans were measured with steps of 0.5 eV and 0.04 s dwell per point and pass energy (E_{pass}) setting of 24. High resolution scans were collected with a step size of 0.1 eV, with 0.5 s dwell per point and E_{pass} setting of 20.

High resolution XPS spectra
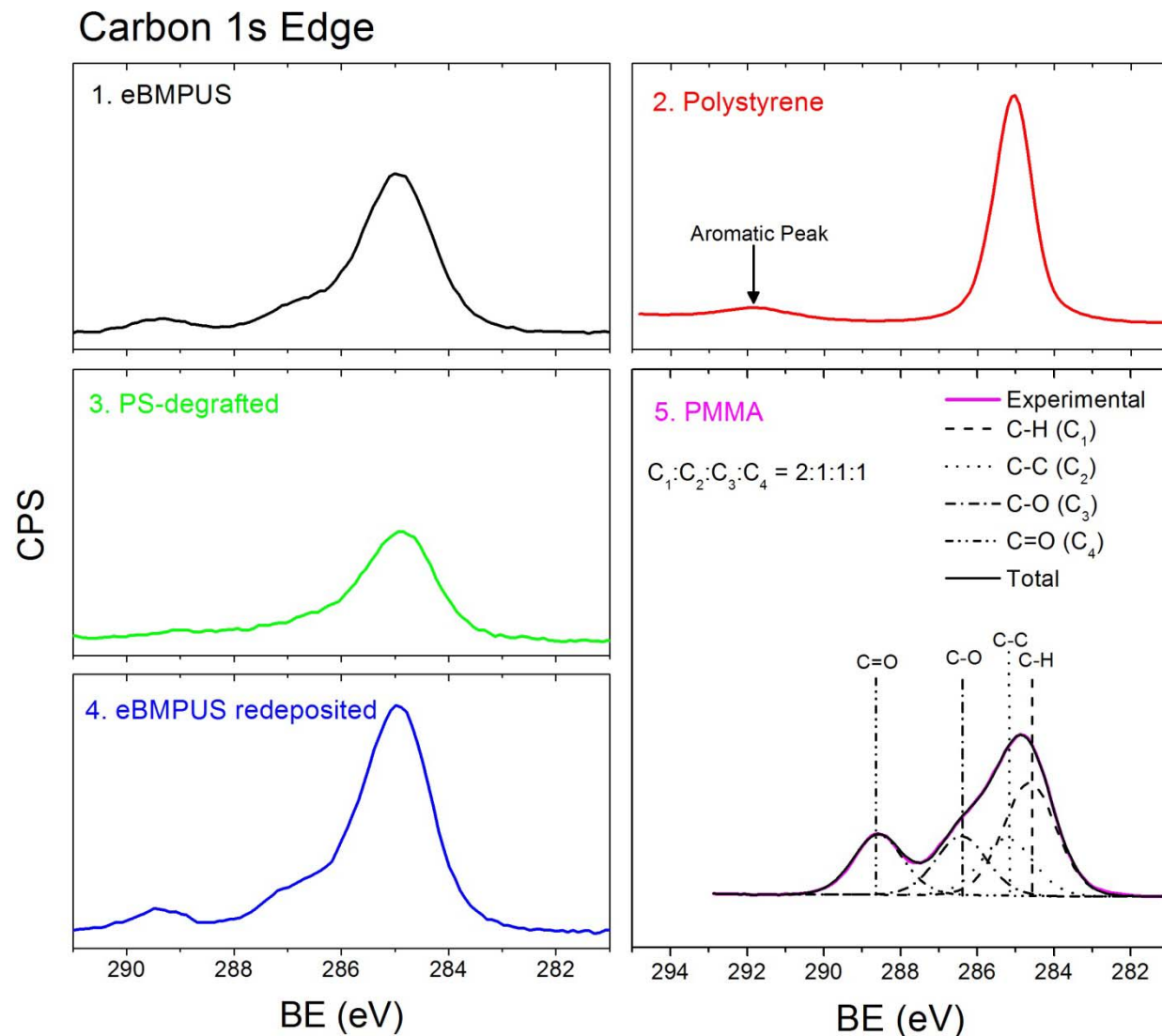
Carbon 1s Edge

Figure S1. High resolution C 1s spectra for substrates corresponding to Figure 1 in the main text. The y axes scales are matched for eBMPUS, PS-degrafted and eBMPUS redeposited while the polystyrene scale is matched with PMMA.

The high resolution spectra for carbon 1s peaks are shown in Figure S1 for the 5 substrates displayed in Figure 1 in the paper. The number of photoelectrons is matched on the y axes for the eBMPUS, the PS-degrafted and the eBMPUS redeposited substrate. There are subtle differences between the shapes of the C 1s peaks for each substrate. For the first eBMPUS and eBMPUS-redeposited substrate a small carbonyl (O–C=O) peak at BE ~289.5 eV is observed.

The overall intensity is smallest for the degrafted substrate which indicates the presence of only a small amount of organic material which could feature undegrafted polystyrene chains, undegrafted and uninitiated initiator or simply adventitious carbon. A strong C-C peak is observed for polystyrene at 285 eV along with a small aromatic peak at ~292 eV. In case of PMMA synthetic components for each type of carbon are fitted to experimental data and the ratio of the areas under the peaks matches with the stoichiometric ratio corresponding to its chemical structure. The ratio of peak areas for C-H (dash), C-C (dot), C-O (dash-dot) and C=O (dash-dot-dot) is 2:1:1:1 which is the ratio of the number of C atoms in the structure for PMMA.
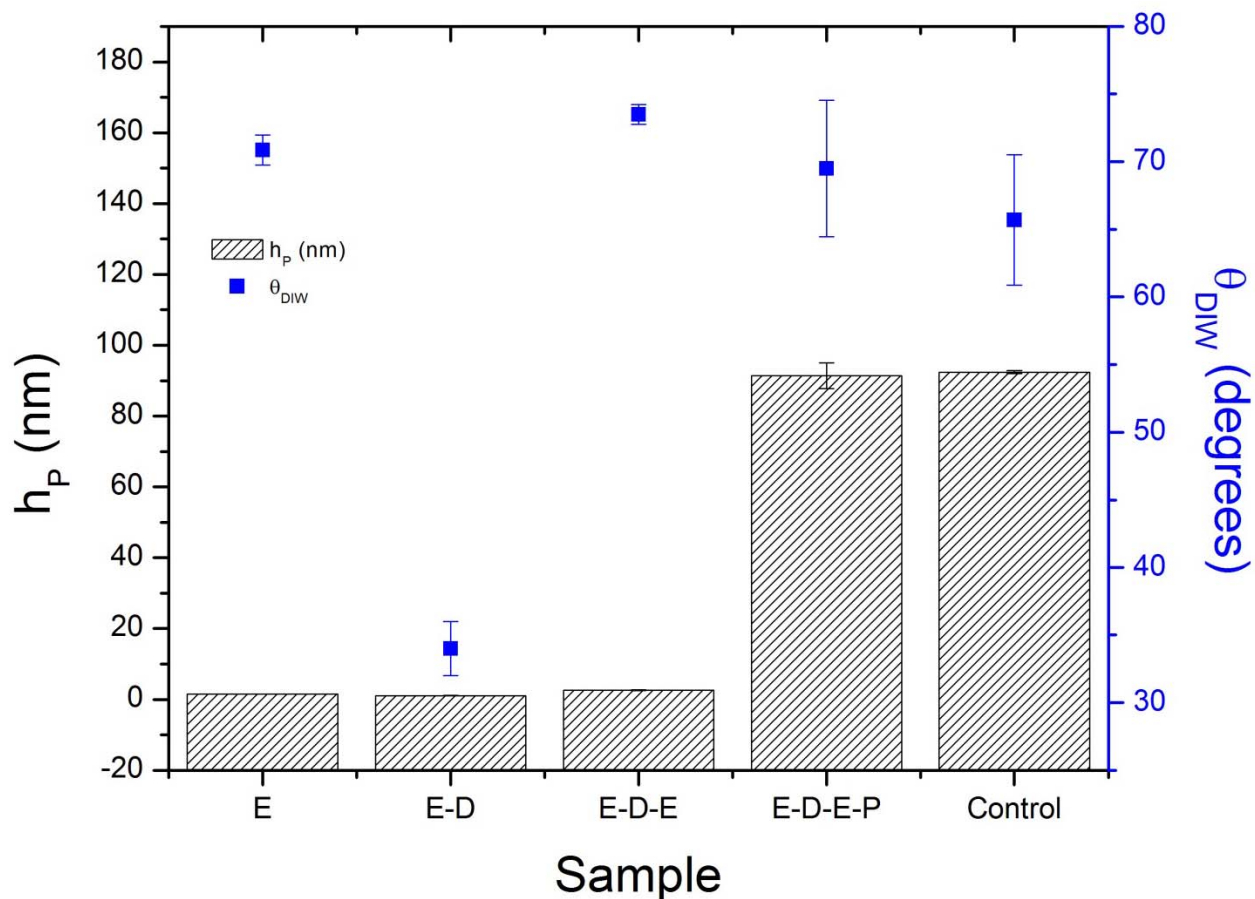
Reusing Substrate after Degrafting Initiator

Figure S2. Dry ellipsometric thickness (h_P) and water contact angle (θ_{DIW}) for eBMPUS (E) initiator degrafting, redeposition and PMMA brush layer (P) grown after degrafting by ATRP.

An alternative experiment to the one described in Figure 2 is shown here in Figure S2 where we first deposit eBMPUS (E) using conventional method, *i.e.*, by using ultraviolet-ozone (UVO) to activate the surface. This initiator layer is degrafted (E-D) by incubating the substrate in 0.1 M TBAF at 50°C for 1 hour. After degrafting the ellipsometric thickness decreases from 1.6 ± 0.2 nm to 1 ± 0.05 nm while the water contact angle (θ_{DIW}) decreases from 71 ± 1 to 34 ± 2 degrees. This substrate is then redeposited by eBMPUS initiator layer (E-D-E) without using UVO treatment which increases its thickness to 2.6 ± 0.15 nm and θ_{DIW} to 74 ± 1 degrees. PMMA is subsequently grown on the initiator layer by ATRP with $Cu^{II}:Cu^{I} = 0.005$ at room temperature for 24 hours. The resulting layer (E-D-E-P) is 91 ± 4 nm thick and has $\theta_{DIW}=66 \pm 5$ degrees, which is comparable to that of the PMMA control sample with conventionally deposited eBMPUS grown in the same polymerization solution.

OTS Pattern to PMMA brush pattern

A complimentary method to that shown in Figure 4 to create surface patterns of polymer brushes involves by first creating a pattern of the initiator by degrafting and then growing brushes. We carried this out by first creating a monolayer of inert *n*-octyltrichlorosilane (OTS) on silicon substrate (*cf.* Figure S3). A pattern was then stamped onto the substrate using TBAF containing hydrogel stamp which removed the OTS layer. This substrate was then incubated in an eBMPUS solution to create an initiator deposited layer which was then amplified by growing PMMA brush using ATRP. The pattern is visible in the optical images shown in Figure S3, (b) due to a dry thickness of >40 nm.
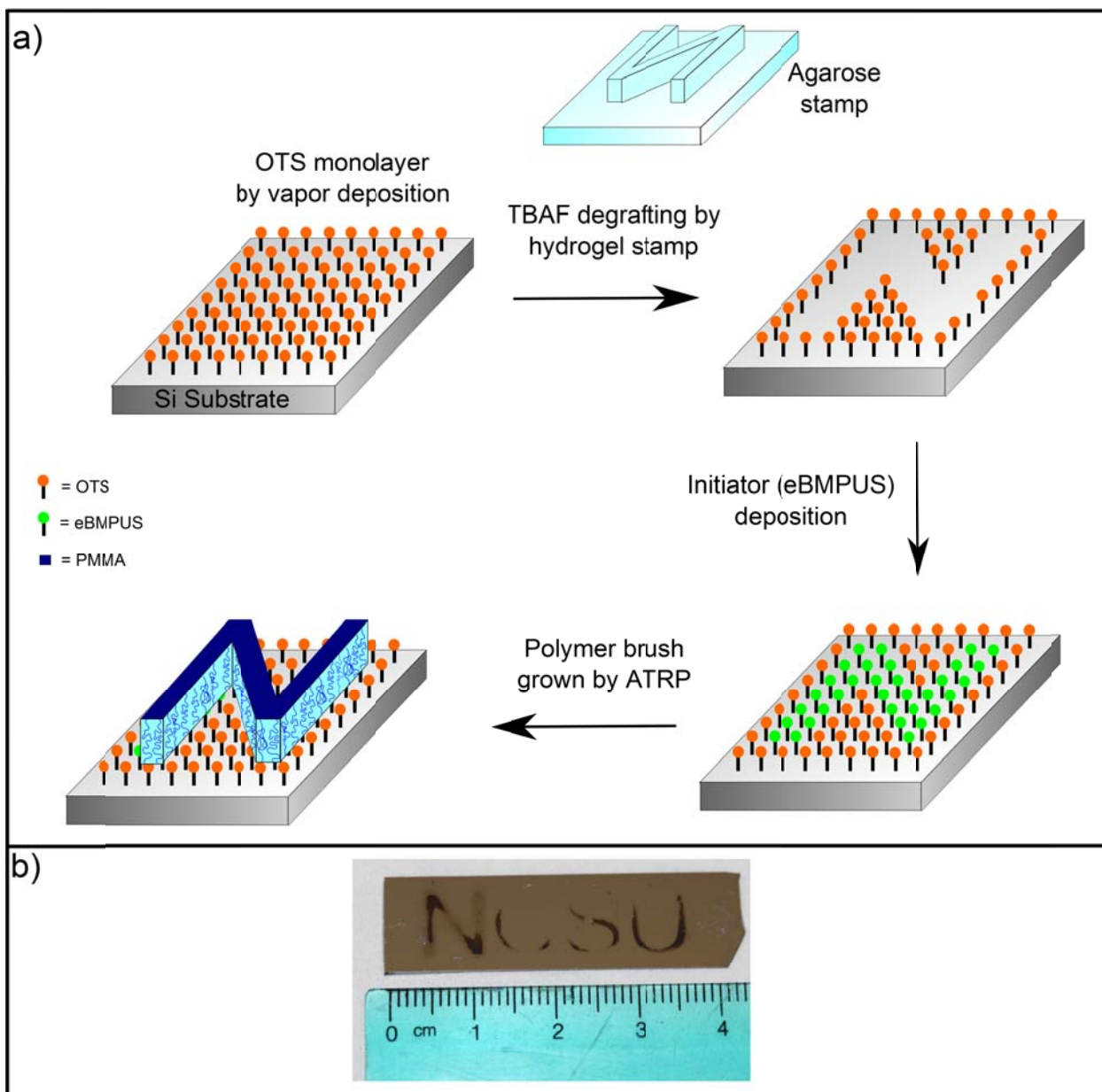
Figure S3: a) Scheme to create polymer patterns by TBAF degrafting of OTS, initiator deposition and PMMA brush growth, (b) Optical images of the PMMA brush pattern on silicon substrate. The size of the entire substrate is approximately 4.3 cm x 1.2 cm.