Supporting Information

A Non-biofouling Polymer Brush with Latent Aldehyde Functionality as a Template for Protein Micropatterning

Yuquan Zou[1], Po-Ying J. Yeh[3], Nicholas A. A. Rossi[1], Donald E. Brooks[1, 2,] and Jayachandran N. Kizhakkedathu[1]**

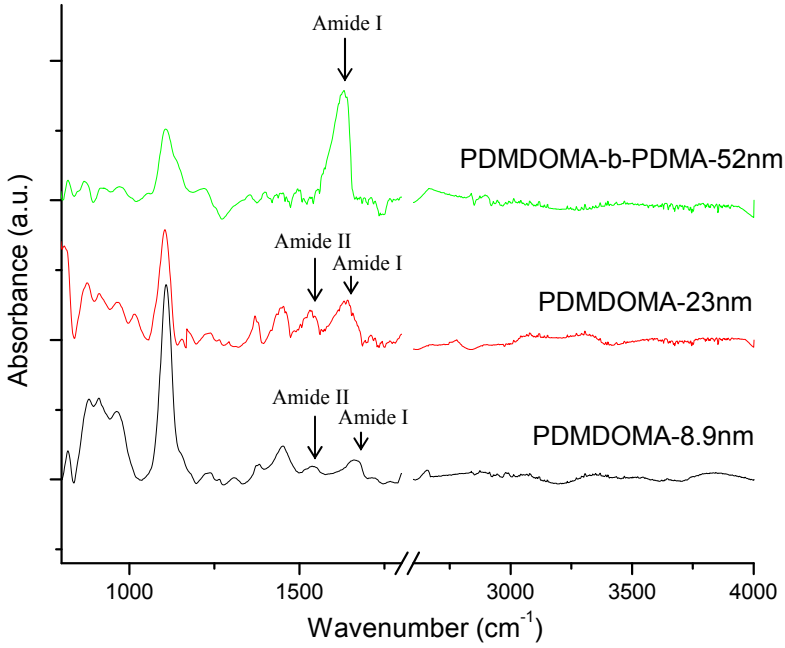


Figure 1S ATR-FTIR spectra of PDMDOMA brushes. A PDMDOMA brush with 8.9 nm thickness was grafted from silicon wafer via 1st SI-ATRP. With a subsequent feed of DMDOMA monomer, thickness of the PDMDOMA brush was increased to 23 nm (2nd SI-ATRP). Block copolymerization of another monomer, DMA, from PDMDOMA-8.9 nm, increased the thickness to 52 nm. This observation verified the controlled nature of SI-ATRP of DMDOMA in DMF.

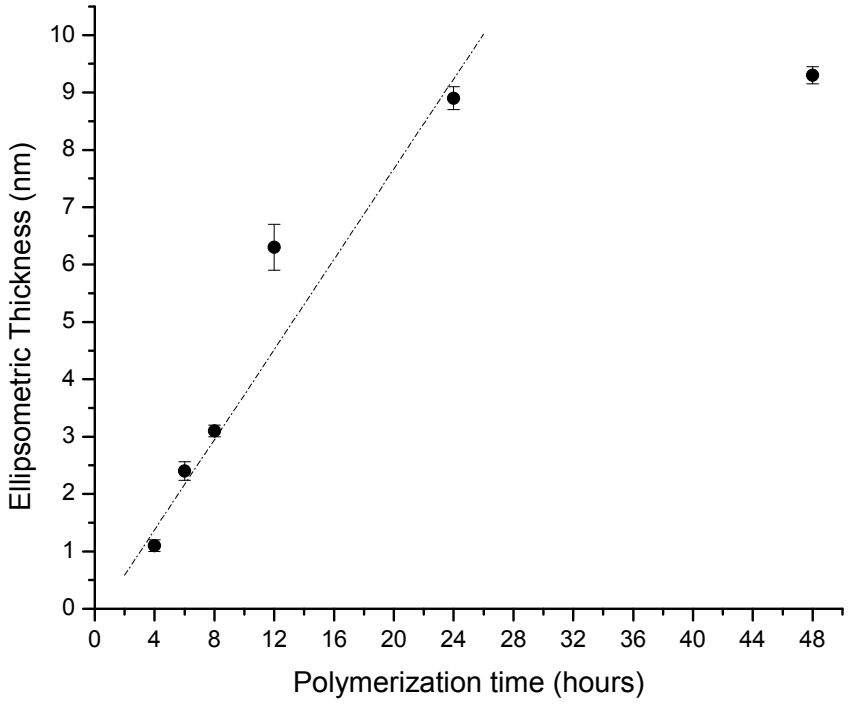
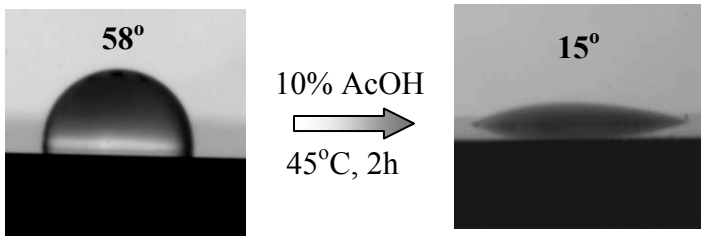


Figure 2S Dependence of the grafted PDMDOMA brushes on polymerization time. Polymerization conditions: Solvent: DMF; [DMDOMA]=2.5M; molar ratio of [CuCl]: [$CuCl_2$]: [HMTETA] = 1: 0.1: 2



PDMDOMA
(S7)

PDHPA
(S7-diol)

Figure 3S Images of water droplet on PDMDOMA (S7, left) and PDHPA brush (right). A moderately high contact angle was observed for the PDMDOMA brush at ambient temperature, in which PDMDOMA brush was in a collapsed state. After complete hydrolysis, the PDMDOMA brush was converted to the highly hydrophilic PDHPA brush, which shows much lower contact angle.

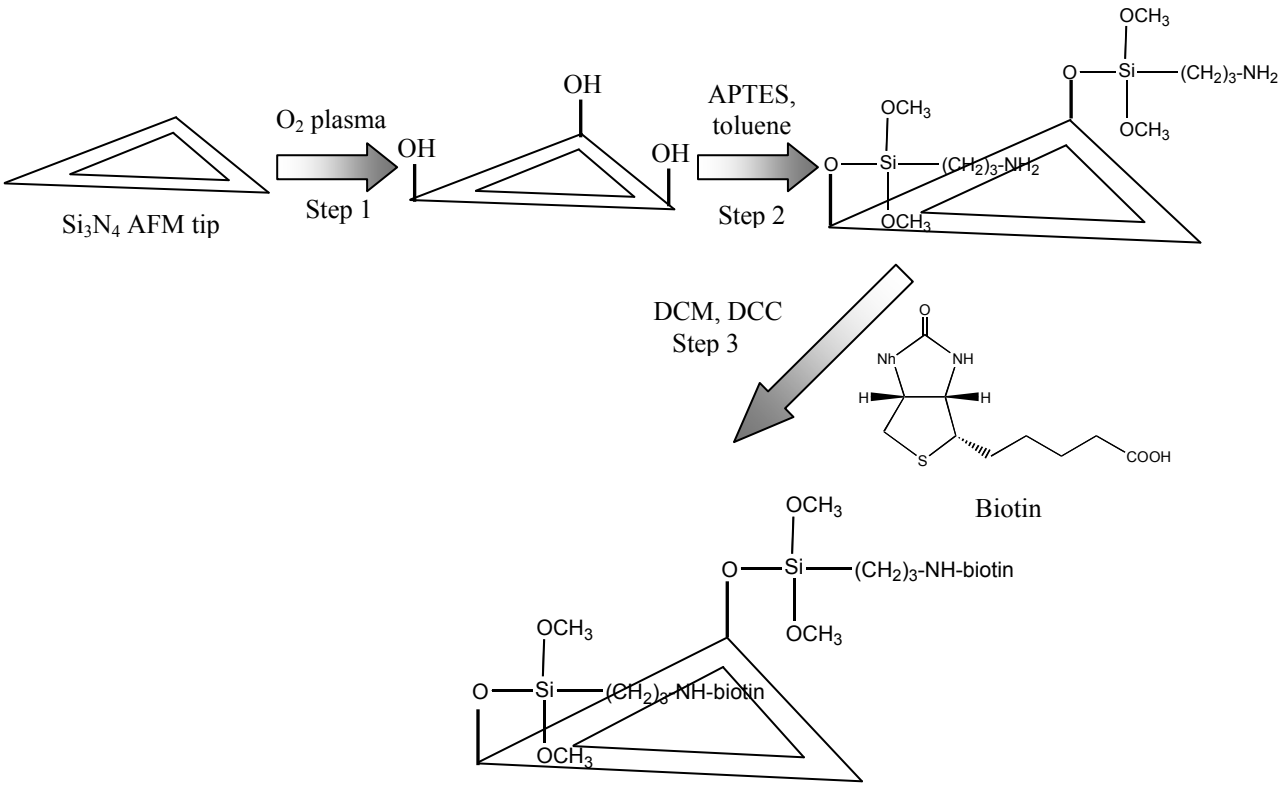


Figure 4S Modification of an AFM tip (Si_3N_4) with biotin. Step 1: Generation of hydroxyl groups via gas plasma generator (M4L^{TM}, PVA TePla America, Inc.). Treatment condition: time: 30 s, power: 25 W, chamber pressure (oxygen): 230 psi. Step 2: Amination. Reaction condition: APTES (aminopropyltriethoxysilane): 100 µl, Toluene: 5 ml, temperature: 60 ^{o}C, time: 2 h. Step 3: Coupling of biotin. Reaction conditions: DCM: 5 ml; DIC: 0.1 g; biotin: 50 mg; time: 30 min.

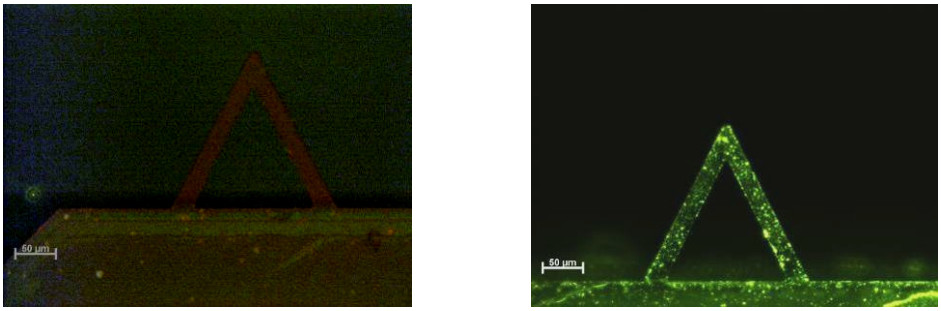
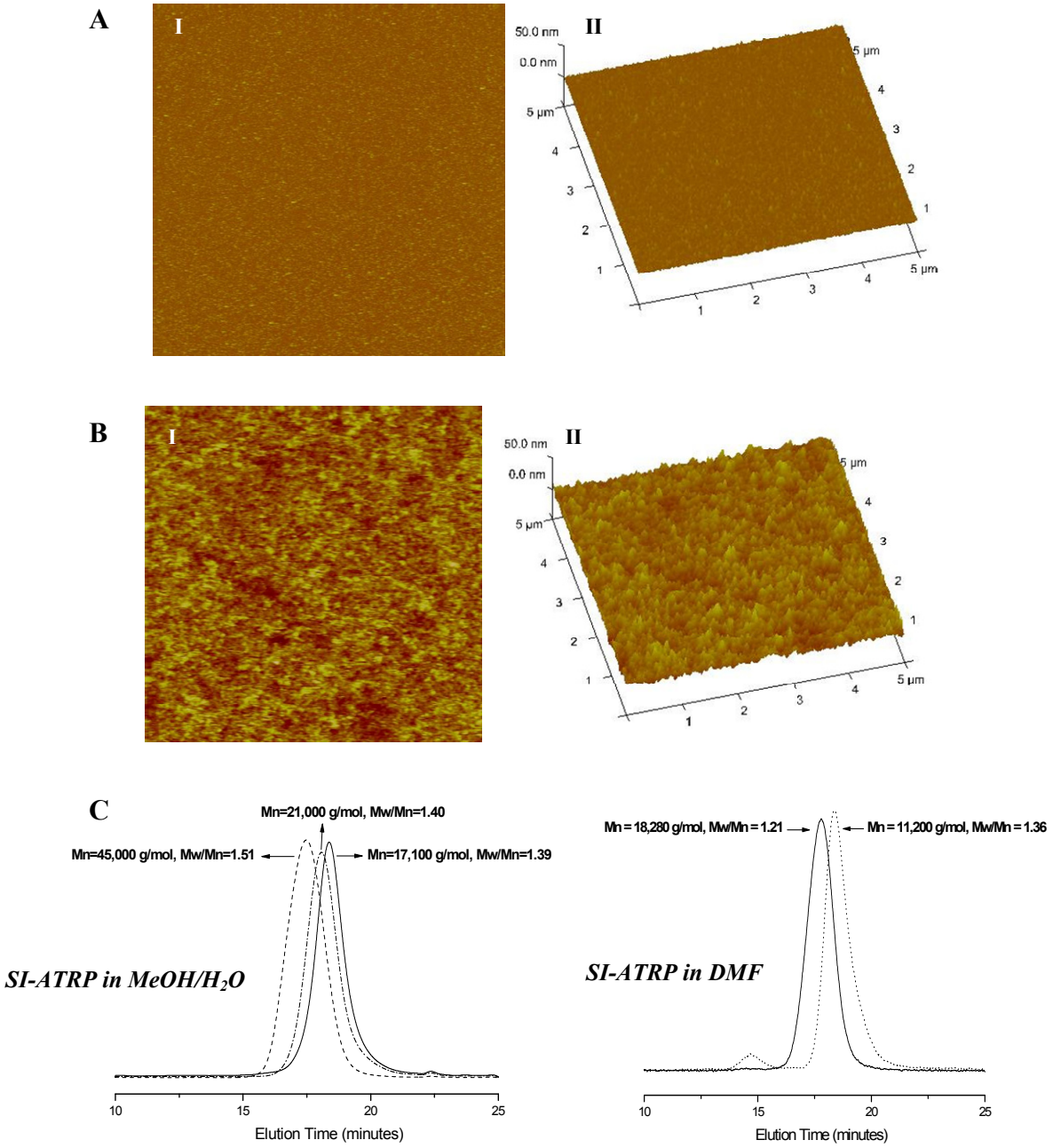


Figure 5S Fluorescence images of AFM tip a) before biotin coupling; b) after biotin coupling. Biotin(5-fluorescein) (Fluka, 53608) was used for this experiment. Coupling conditions: DCM: 2 ml; DIC: 0.5 g; biotin (5-fluorescein): 1 mg; time: 30 min. Clear contrast of fluorescence intensity before and after modification verified the successful modification of AFM tip by biotin.



Figures 6S A) AFM topography (I) and 3-D image (II) of ATRP initiator modified surface (thickness of the initiator layer = 2.1 nm). The xy scale of I was 5 um×5um; Z scale was 50 nm; **B**) AFM topography (I) and 3-D image (II) of PDMDOMA brush grafted wafer surface (thickness of the grafted PDMDOMA brush = 23 nm). The xy scale of I was 5 um×5um; Z scale was 50 nm; **C**) Representative GPC-MALLS profiles

of PDHPA polymers, which were obtained by complete hydrolysis of "free" PDMDOMA polymers formed during SI-ATRP. Left: PDMDOMA obtained as "free" polymer from SI-ATRP in a H_2O/MeOH (1:1) system (the detailed information for these samples was listed in Table 1S, supporting information); Right: PDMDOMA obtained as "free" polymer from SI-ATRP in a DMF system.

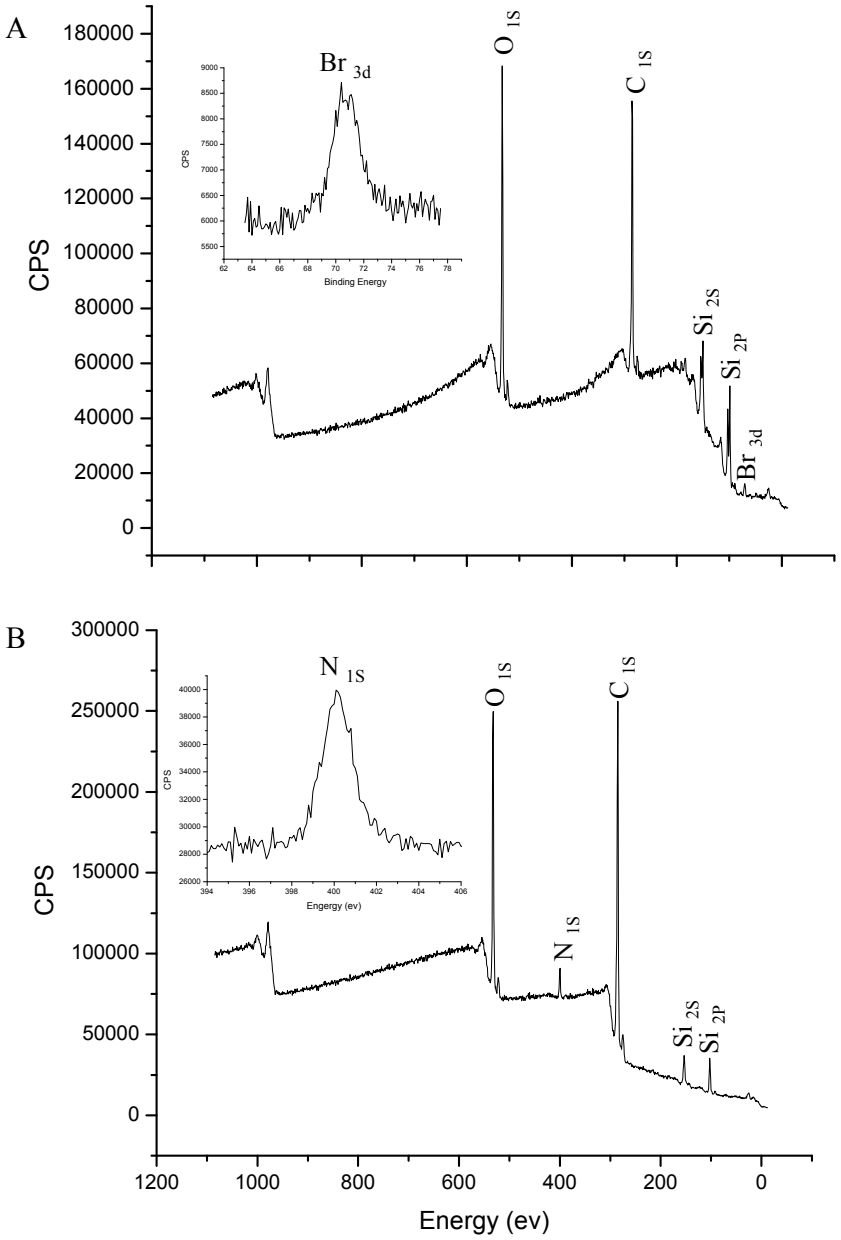


Figure 7S A) XPS spectrum of silicon wafer surface modified with bromine-containing ATRP initiator; B) XPS spectrum of PDMDOMA (S3) grafted silicon wafer surface.

Table 1S Characteristics of PDMDOMA brushes prepared in MeOH/H_2O (1:1) solvent system [a]

Samples	Reaction time	Initiator	Ligand	Solvent	Dry Thickness (nm)	$M_{n,SEC}$ and Mw/Mn of "free" polymer[b]	Graft density [c] (chains/nm^2)
S8	4	Cl	Me_6TREN	MeOH/H_2O (1:1)	6.7 ± 0.3	17,100, 1.39	0.28
S9	6	Cl	Me_6TREN	MeOH/H_2O (1:1)	9.6 ± 0.5	21,000, 1.40	0.33
S10	12	Cl	Me_6TREN	MeOH/H_2O (1:1)	24.9 ± 0.8	45,000, 1.51	0.40

Note: a) Molar ratio of [CuCl]: [$CuCl_2$]: [Ligand] = 1: 0.1: 2; monomer concentration [DMDOMA] = 2.5 M

b) "Free" solution polymer was obtained by addition of sacrificial initiator into the polymerization system. Methyl 2-chloropropionate was used as the free initiator.

c) Graft density of PDMDOMA brushes was calculated following the equation: $\sigma = h\rho N_A/M_n$, where ρ is the density of PDMDOMA (1.20g/cm^3), N_A is Avogardro's number, and M_n is the number average molecular weight.