Supplementary Materials:

"Stimuli Responsive surfaces through Recognition Mediated Polymer Modification"

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1. Experimental Section:

All chemicals were reagent grade, and were used without further purification.

1) Synthesis of silane coupling agents and preparation of monolayers.

The synthesis of Thymine-undecytriethoxysilane and N-Methyl-Thymine-undecytriethoxysilane were completed using previously reported methods (J. Am. Chem. Soc. 2002, 124, 13366). Prior to use, the silicon wafer was cut into pieces (10 mm × 10 mm) and cleaned in an oxidizer bath (250 ml concentrated sulfuric acid and 9g Nochromix) overnight, rinsed with deionized water and distilled chloroform respectively, and then placed directly in 1.5 mM chloroform solutions of thymine functionalized triethoxysilane overnight. Physisorbed materials were removed by rinsing with fresh chloroform and ethanol, followed by sonication in chloroform for 60 seconds and dried with Argon.

2) Synthesis of Tri-DAP polystyrene *10*. (See Figure S1 for the synthetic route)

Compounds **2**, **3**, and **4** were synthesized in analogous fashion to published protocols (P. R. Ashton, et. al. *J. Chem. Soc. Chem. Commun.* **1993**, 1274; P. R. Ashton, et. al. *J. Am. Chem. Soc.* **1996**, *118*, 4931.)

Tris(4-methylphenyl) methanol (*2*): In a 500 ml flame-dried 3-neck round-bottom-flask fitted with separatory funnel and a reflux condenser was placed 2.4 g (0.1 mol) magnesium and then a few amount of a solution of 11.5 g (0.067 mol) p-bromotoluene in 100 ml dry ether was introduced. A crystal of iodine was added and heated gently until the reaction began. Then the rest of the ether solution of p-bromotoluene was added at such a rate that the ether boiled gently. Under dry argon, the reaction mixture was stirred and kept refluxing 4 hrs. After most of the magnesium was consumed, a solution of 3.75g (0.025 mol) methyl 4-methylbenzoate in 150 ml dry ether was added slowly over a period of several hours. The mixture was left refluxing overnight and acidified by 1 M HCl. The ether layer was separated and the water solutions were extracted with a little ether. Then, all the ether solutions were combined together and ether was removed under vacuum. Column chromatography (EtOAc : Hexanes = 1 : 10) and followed recrystallization from hexanes provided **2** as colorless crystalline solid: 4.0 g (yield 59%). m.p. 91-92 °C; ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 9 H, ArCH_3), δ 2.68 (s, 1 H, C O*H*), δ 7.07-7.18 (m, 12 H, Ar*H*).

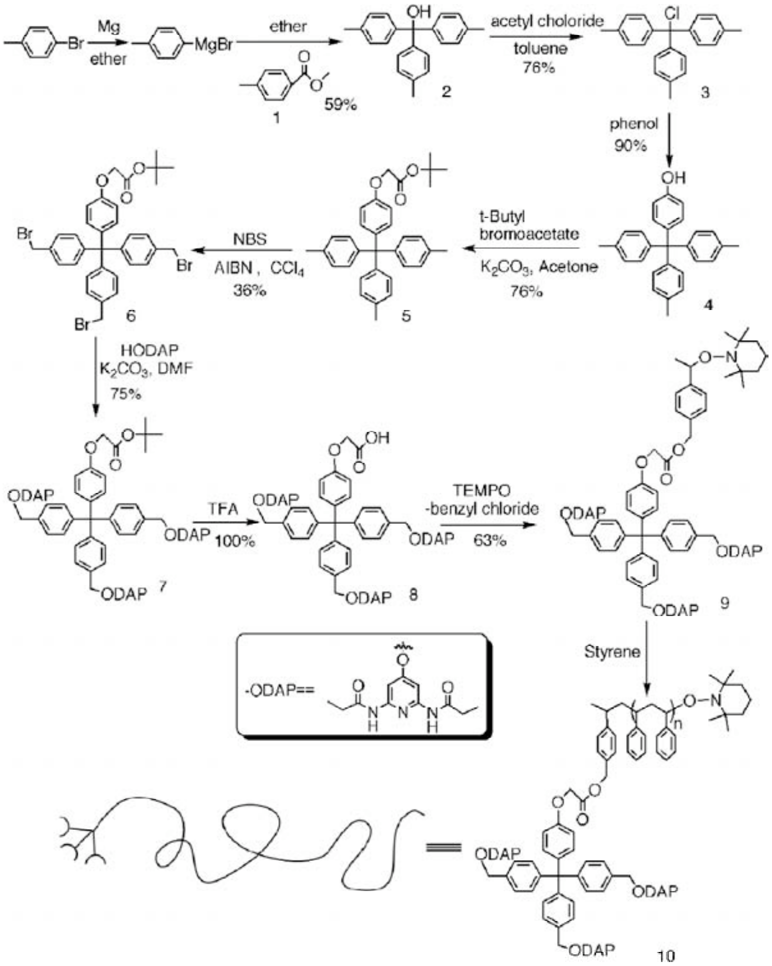


Figure S1, Synthesis of the tri-DAP end-functionalized polystyrene 10.

Tris(4-methylphenyl) methyl chloride (*3*): Acetyl chloride (6 ml) was added to 3 g of tertiary alcohol **2** in 3 ml of toluene. The solution was refluxed under Ar for 10-15 mins, monitored be TLC. Two volumes of hexanes were added, and the solution was cooled under 0 °C to precipitate the chloride **3** as white solid: 3.18 g (yield 76%). m.p. 167-169 °C; ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 9 H, ArCH_3), δ 7.07-7.16 (m, 12 H, Ar*H*).

4-tris(4-methylphenyl)-methyl phenol (*4*): Tertiary chloride **3** (1.9 g, 4.68 mmol) was added portionwise to molten phenol (4.24 g, 45.1 mmol), and the relation mixtures were heated at 110 °C for 3-4 hrs, monitored by TLC. Excess amount of 40% aqueous KOH was added. The resulting white solids were washed thoroughly with water and dried under high vacuum to avoid **4**: 2.19 g (yield 90%). m.p. 105-107 °C; ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 9 H, ArCH_3), δ 6.67-6.73 (d, 2 H, O Ar*H*), δ 6.98-7.14 (m, 14 H, C Ar*H*).

t-butyl 4-tris(4-methylphenyl)-methyl phenoxyacetate (*5*): The substituted trityl phenols (2.14 g, 5.66 mmol), potassium carbonate (5.37 g, 33.98 mmol), and t-butyl-1-bromo acetate were mixed into acetone. The reaction mixtures were heated under reflux for 6 hrs. After acetone was removed under vacuum, water was added and the mixtures were extracted with dichloromethane for 3 times. After evaporation most of the solvent, hexanes were added to precipitate the phenoxyacetate **5** as white solid: 2.12 g (yield: 76%). m.p. 143-145 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 1.47 (s, 9 H, t-butyl). δ 2.30 (s, 9 H, $ArCH_3$), δ 4.48 (s, 2 H, OCH_2CO), δ 6.73-6.76 (d, 2 H, O Ar*H*), δ 7.01-7.11 (m, 14H, C Ar*H*).

t-butyl 4-tris(4-bromo-methylphenyl)-methyl phenoxyacetate (6): A mixture of phenoxyacetate **5** (2 g, 4.07 mmol), NBS (2.28 g, 12.81 mmol) and AIBN (catalytic amount) was dissolved in dry carbon tetrachloride and heated up to reflux for 4-6 h, monitored by TLC. The reaction mixture was filtered and washed with hot carbon tetrachloride. Solvent was removed under vacuum. Chromatography (EtOAc : Hexanes = 1 : 9) gave the fair pure tribromo-phenoxyacetate **6** as white powder: 1.04g (yield: 36%). ^{1}H NMR ($CDCl_3$) δ 1.47 (s, 9 H, t-butyl). δ 4.47 (s, 8 H, OCH_2CO & $ArCH_2Br$), δ 6.76-6.79 (d, 2 H, O Ar*H*), δ 7.05-7.08 (d, 2 H, C Ar*H*), δ 7.14-7.20 (m, 12 H, $BrCH_2ArH$).

t-butyl 4-tris(4-DAP-methylphenyl)-methyl phenoxyacetate (7): Tribromo-phenoxyacetate **6** (391mg, 0.54 mmol) was dissolved in a small amount of DMF, then hydroxyl-diamidopyridine (HODAP) (382 mg, 1.61 mmol) and potassium carbonate (424.23 mg, 2.69 mmol) were added. The reaction mixtures were heated at 80 °C overnight. Water was added to precipitate and followed chromatography (MeOH : EtOAc = 1 : 25) to give triDAP-phenoxyacetate **7** as white solid, 482 mg (yield, 75%). ^{1}H NMR ($CDCl_3$) δ 1.21-1.26 (t, 18 H, CH_2CH_3), δ 1.47 (s, 9 H, t-butyl), δ 2.36-2.42 (q, 12 H, CO CH_2CH_3), δ 4.49 (s, 2 H, OCH_2CO), δ 5.11 (s, 6 H, $ArCH_2O$), δ 6.76-6.79 (d, 2 H, O Ar*H*), δ 7.11-7.14 (d, 2 H, C Ar*H*), δ 7.21-7.31 (m, 12 H, $DAPOCH_2ArH$), δ 7.50 (s, 6 H, Pyridine C*H*), δ 7.63 (s, 6 H, N*H*). See the attached NMR spectrum (**Figure S2**).

4-tris(4-DAP-methylphenyl)-methyl phenoxy-acetic acid (8): TriDAP-phenoxyacetate **7** (125mg), TFA (2.5 ml), DCM (12.5 ml) were mixed and stirred at room temperature overnight. Solvent and excess TFA were removed under vacuum. The resulting solid was washed with hexanes to give triDAP-phenoxyacetic acid **8** as white powder: 118mg (yield: 100%). m.p. 110-112 ^{o}C; ^{1}H NMR (DMSO) δ 1.04-1.07 (t, 18 H, CH_2CH_3), δ 2.38-2.44 (q, 12 H, CO CH_2CH_3), δ 4.63 (s, 2 H, OCH_2COOH), δ 5.12 (s, 6 H, $ArCH_2O$), δ 6.85-6.87 ((d, 2 H, O Ar*H*), δ 7.07-7.09 (d, 2 H, C Ar*H*), δ 7.20-7.22 (d, 6 H, C Ar*H*), δ 7.28 (s, 6 H, Pyridine C*H*), δ 7.40-7.42 (d, 6 H, $DAPOCH_2ArH$), δ 10.36 (s, 6 H, N*H*). Mass spectrum (ESI) found: m/z = 571.8 / 1142.4; calcd: M = 1141, (M+1)/1 = 1142, (M+2)/2 = 571.5. See the attached spectra of NMR and MS (**Figure S3**).

The initiator (9): Phenoxyacetic acid **8** (83mg, 0.073mmol) and TEMPO-benzyl chloride (23 mg, 0.076 mmol) were mixed and dissolved in DMF, potassium carbonate (50 mg, 0.36 mmol) was added and the reaction mixture was heated at 70 °C overnight. Water was added to precipitate and followed chromatography (MeOH: EtOAc = 1 : 19) gave the initiator **9**, 65 mg (yield, 63%). ^{1}H NMR ($CDCl_3$) δ 0.66, 1.01, 1.15, 1.27 (each br s, 12H, C CH_3), δ 1.21-1.55 (m, hard to distinguish), δ 2.36-2.42 (q, 12 H, CO CH_2CH_3), δ 4.64 (s, 2H, $ArOCH_2CO$), δ 4.68-4.79 (m, 1H, C*H*), δ 5.11 (s, 6 H, OCH_2Ar), δ 5.22 (s, 2H, $COOCH_2Ar$), δ 6.79-6.81 (d, 2H, O Ar*H*), δ 7.12-7.14 (d, 2 H, C Ar*H*), δ 7.21-7.31 (m, 16 H, aromatic H), δ 7.51 (s, 6 H, Pyridine C*H*), δ 7.63 (s, 6 H, N*H*). Mass spectrum (ESI) found: m/z = 708.7 / 472.9; calcd: M = 1415.7, (M+2)/2 = 708.9, (M+3)/3 = 472.9. See the attached spectra of NMR and MS (**Figure S4**).

The TriDAP-PS (10): Polymer **10** was obtained through "living" free radical polymerization as previously described (C. J. Hawker, et. al. *Macromolecules* **1996**, *29*, 5245-5253). Mn = 53806, PD = 1.39. See the attached spectra of NMR and GPC (**Figure S5**).

3) X-ray Photoelectron Spectroscopy.

XPS spectra were obtained on a Physical Electronics Quantum 2000 XPS spectrophotometer using a monochromatic A1 Kα source. Survey spectra were acquired at 15º takeoff angles with pass energy of 117.40 eV and multiplex regions were also recorded with pass energy of 46.95 eV to obtain the relative intensity integration of the different elements on the surfaces.

4) Atomic Force Microscopy.

Light tapping mode atomic force microscopy (AFM) was performed at ambient conditions with a Dimension 3100, Nanoscope III from Digital Instruments Corp. Imaging was done at a scan rate of 1 Hz. The set-point amplitude ratio $r_{sp} = 0.9 \pm 0.05$ was used to reveal the topmost surface characteristics of the sample. (See **Figure S7-S12** following SAM (**S7**), toluene treatment of brush (**S8**), ethanol treatment (**S9**), desorption of brushes (**S10**), readsorption (**S11**), and redesorption (**S12**). The root-mean-square (RMS) roughness, standard deviation of feature height values within a given area, was evaluated from the AFM height images recorded using commercial software.

2, NMR, MS, and GPC spectra:

Figure S2, NMR spectra of t-butyl phenoxyacetate 7

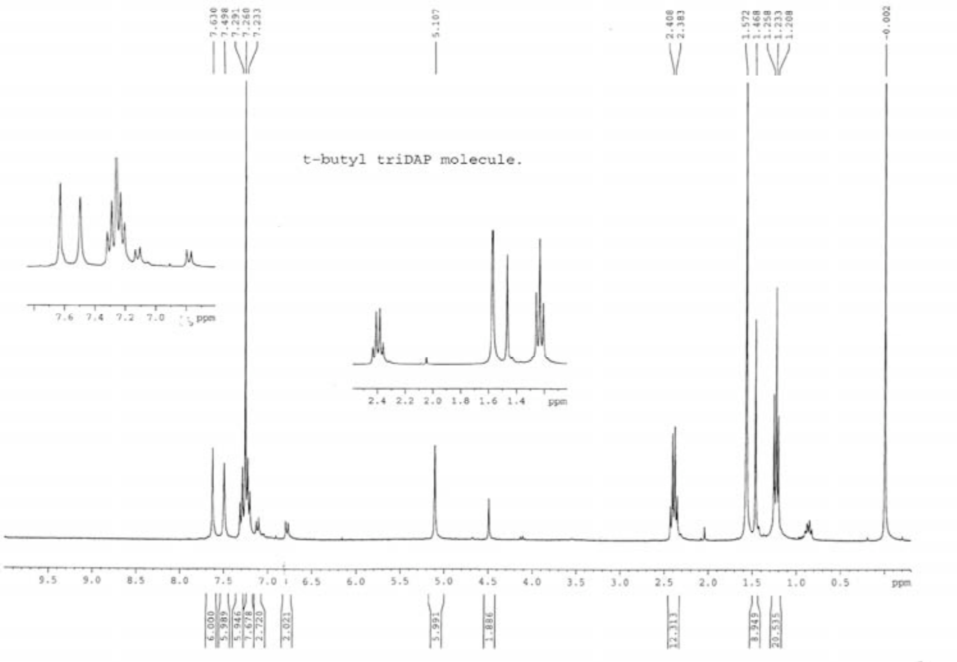


Figure S3, NMR and MS spectra of phenoxyacetic acid 8

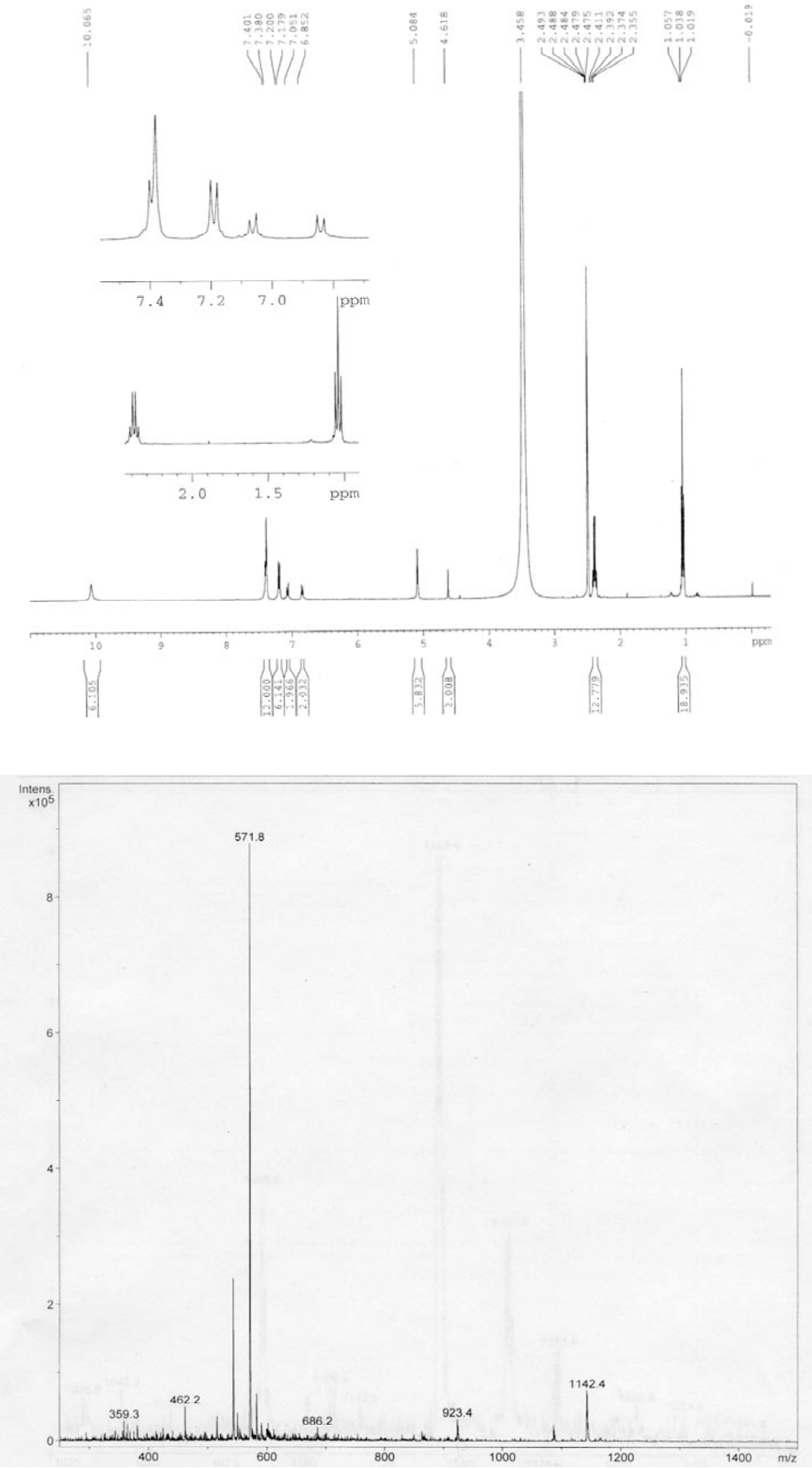
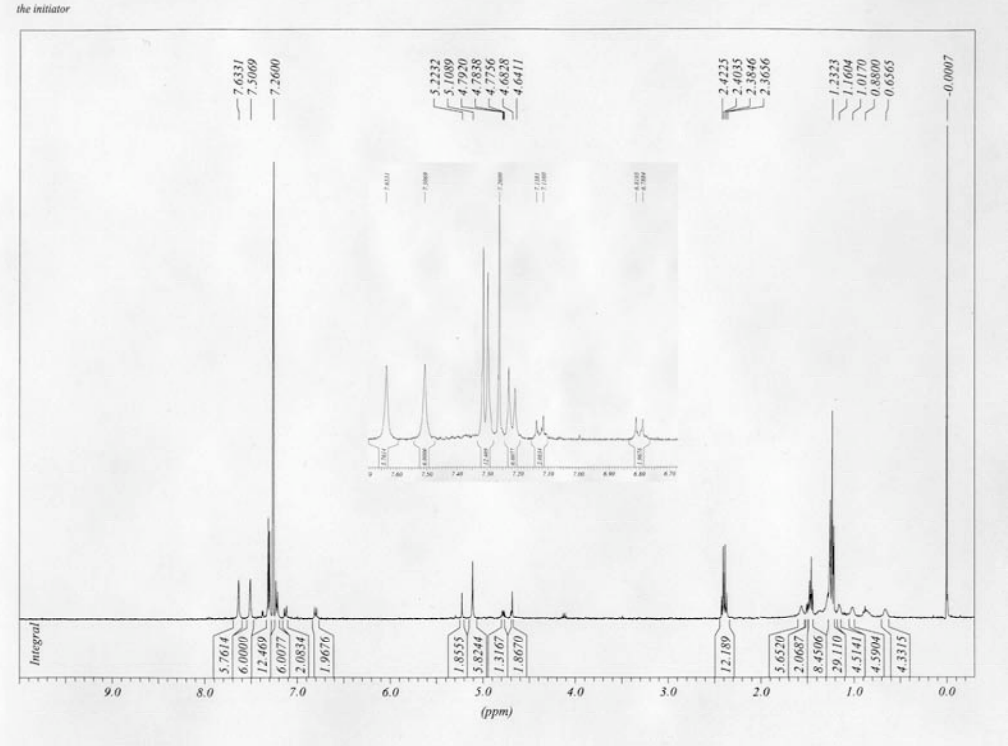


Figure S4 NMR and MS of the initiator 9:



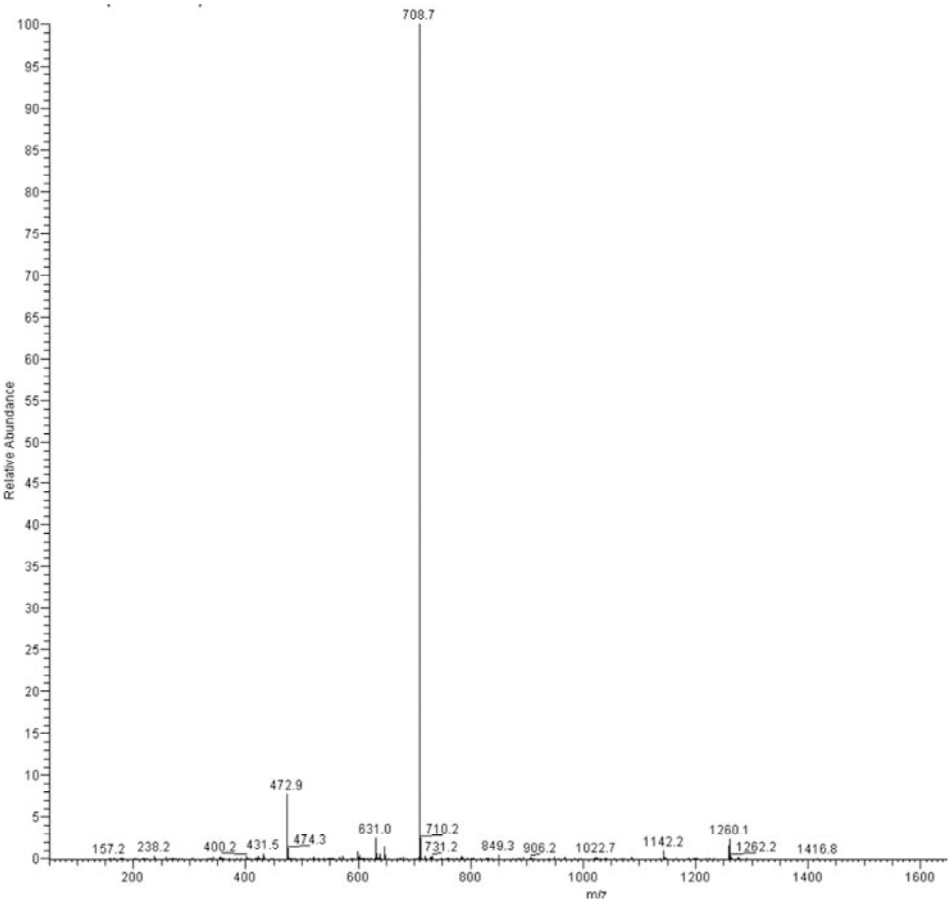
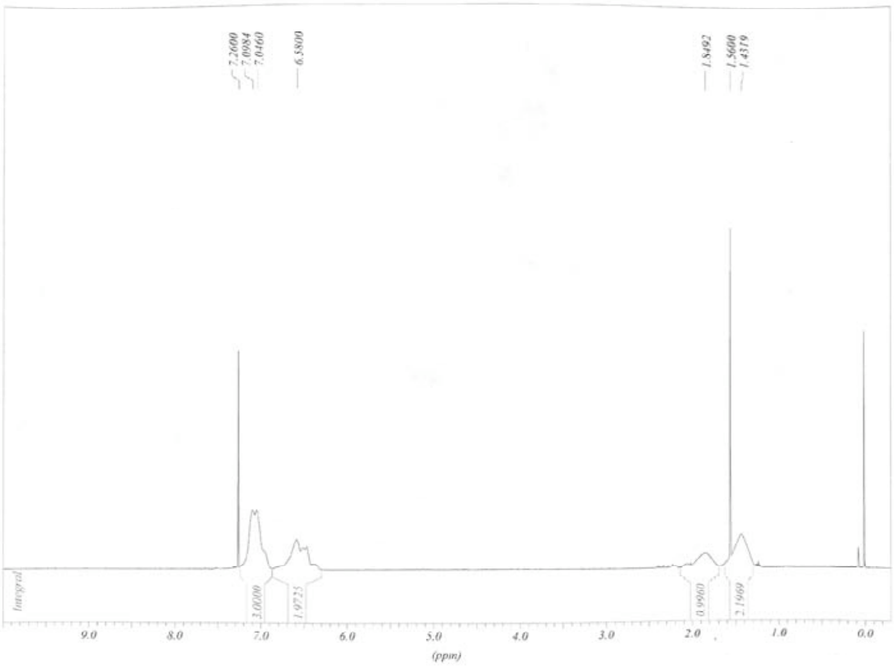
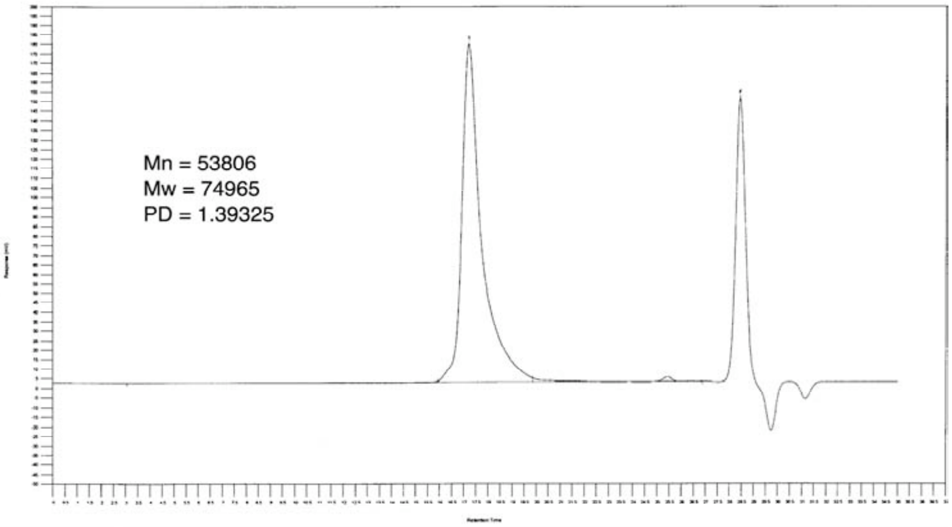


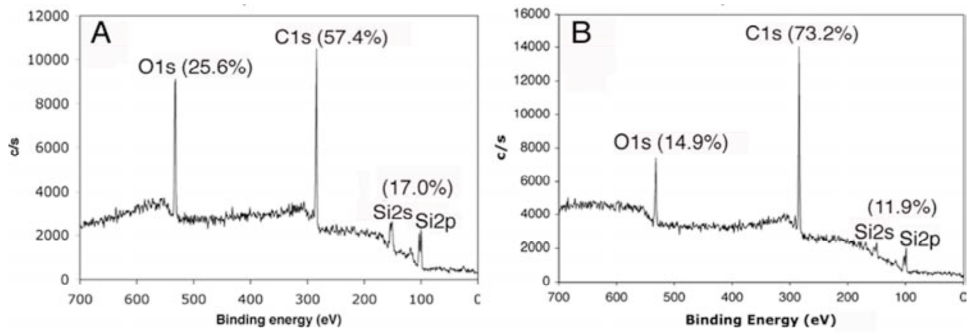
Figure S5, NMR and GPC of Polymer 10:





3, XPS

Figure S6, Comparison of XPS survey of Ethanol (A) treated surface and Toluene (B) treated surface.



4. AFM images:

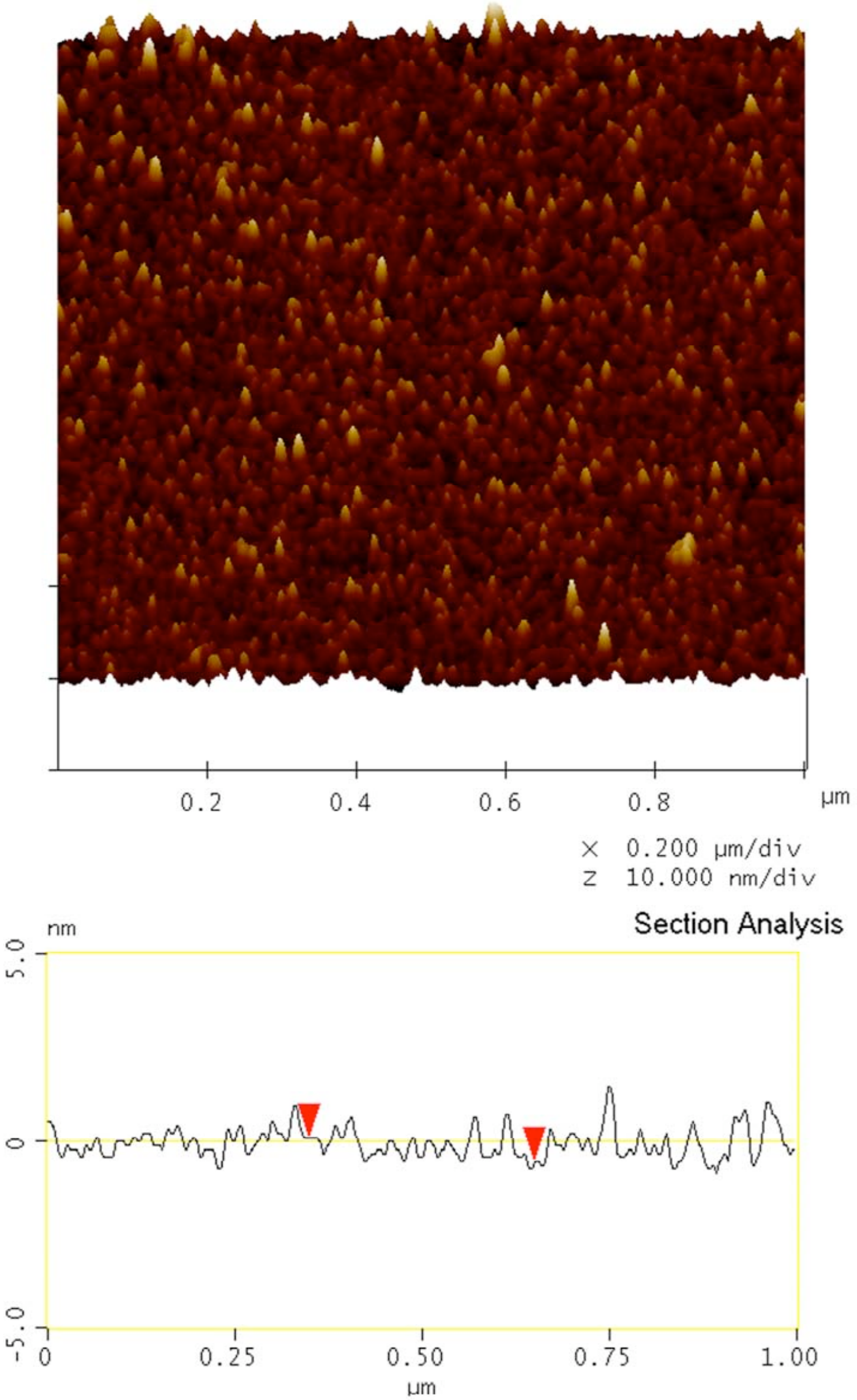


Figure S7, SAMs

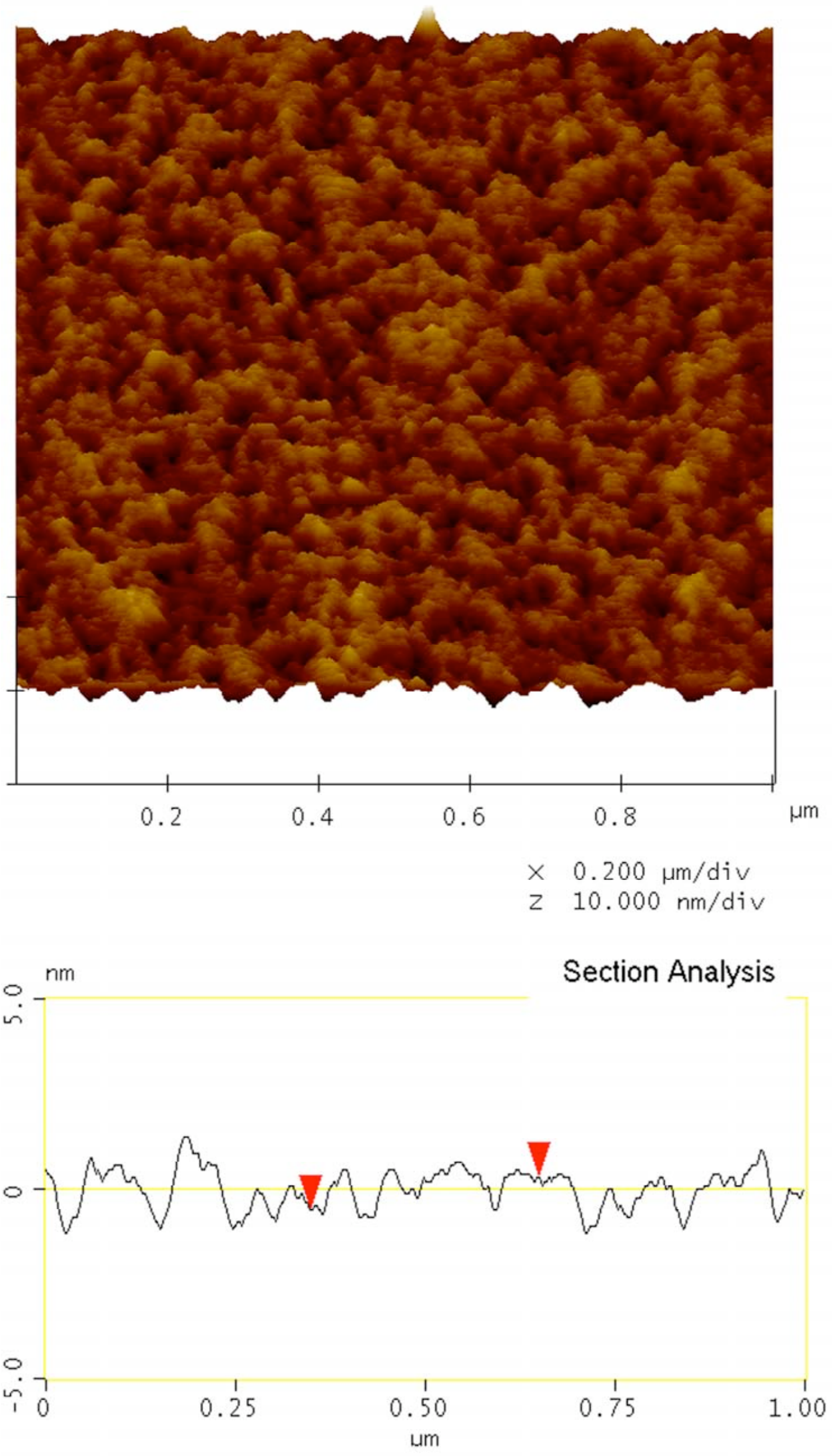


Figure S8, Polymer on surface, after toluene treatment.

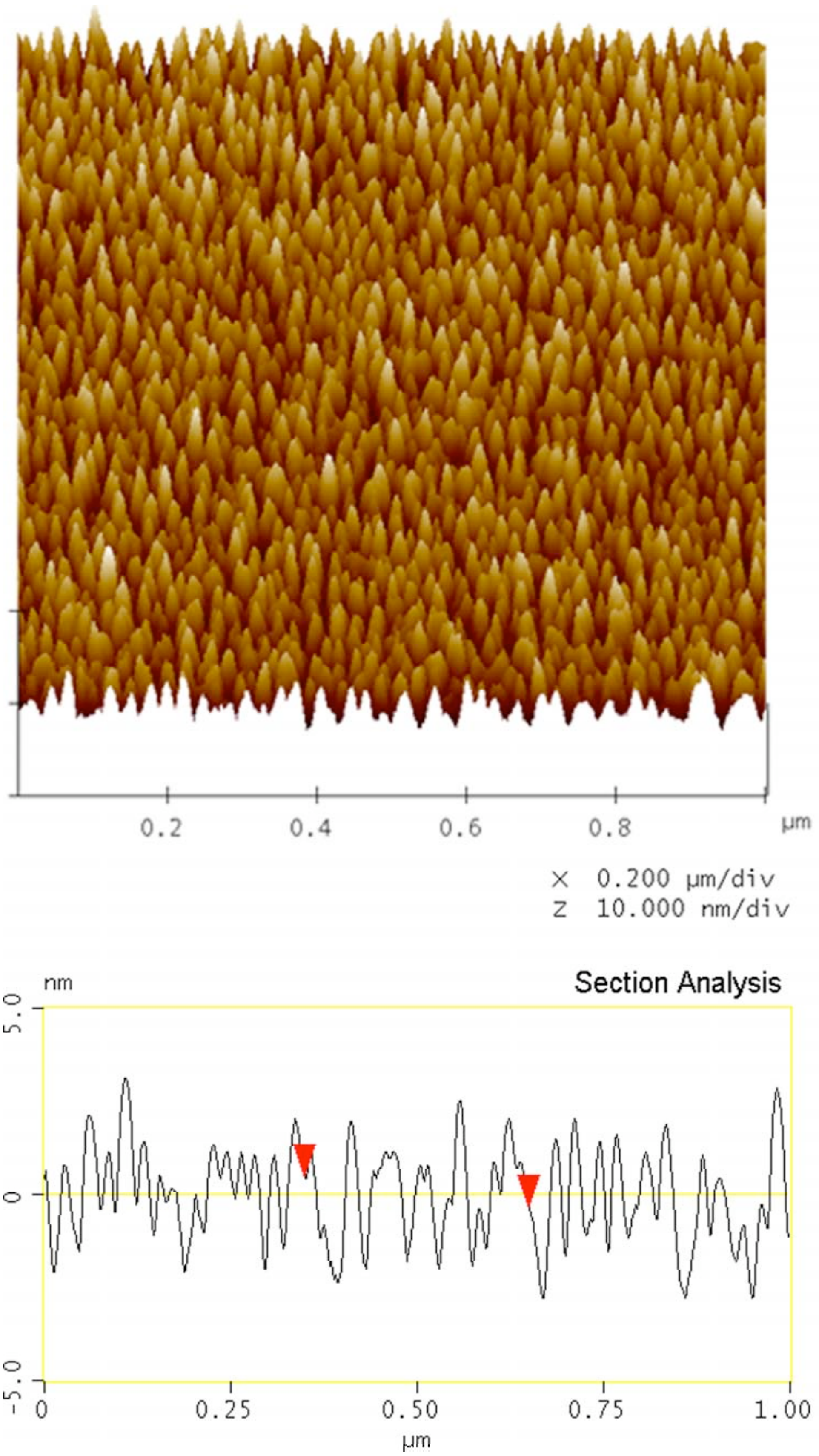


Figure S9, Polymer on surface, after ethanol treatment.

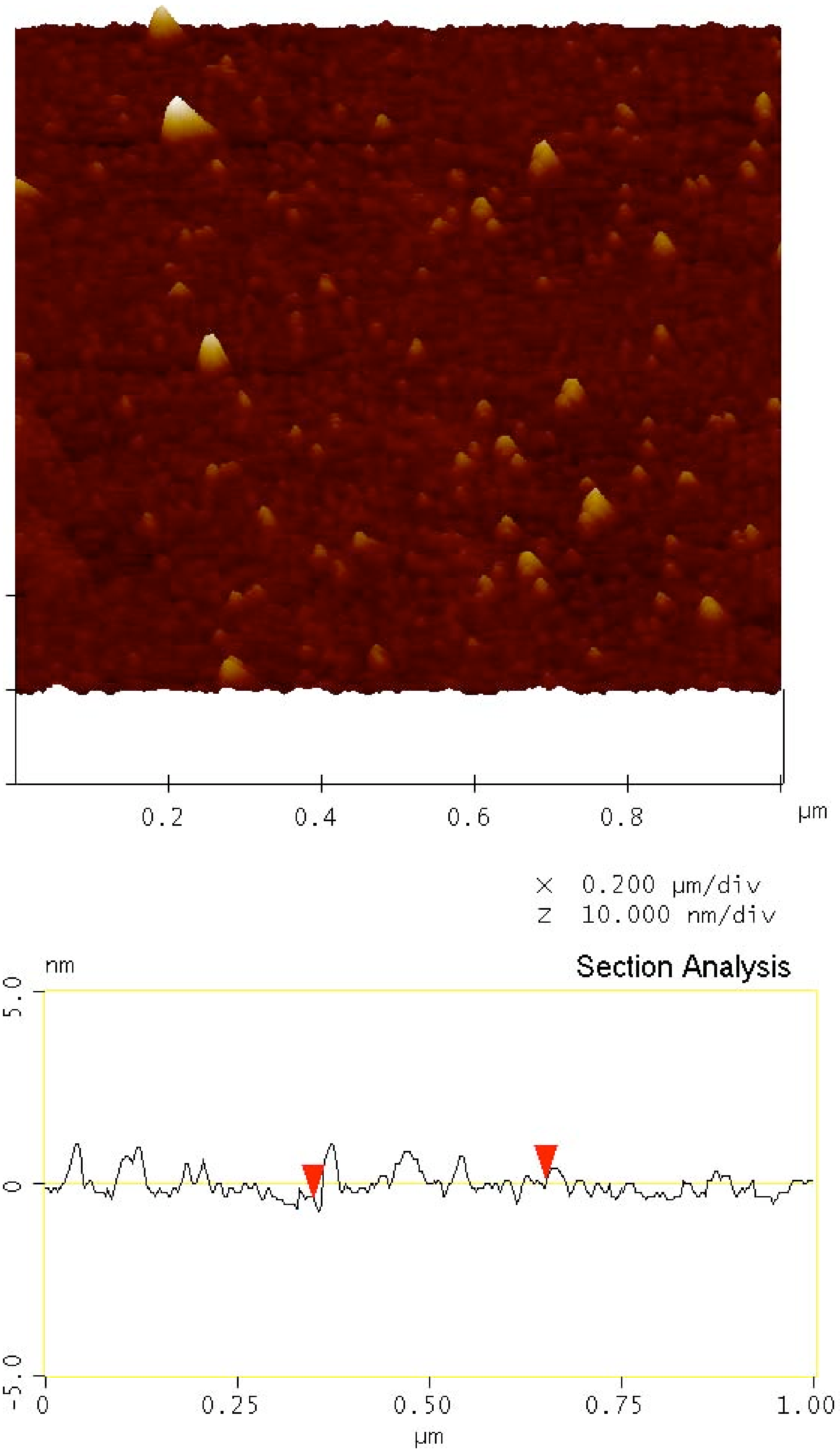


Figure S10, Surface after desorption of the polymer.

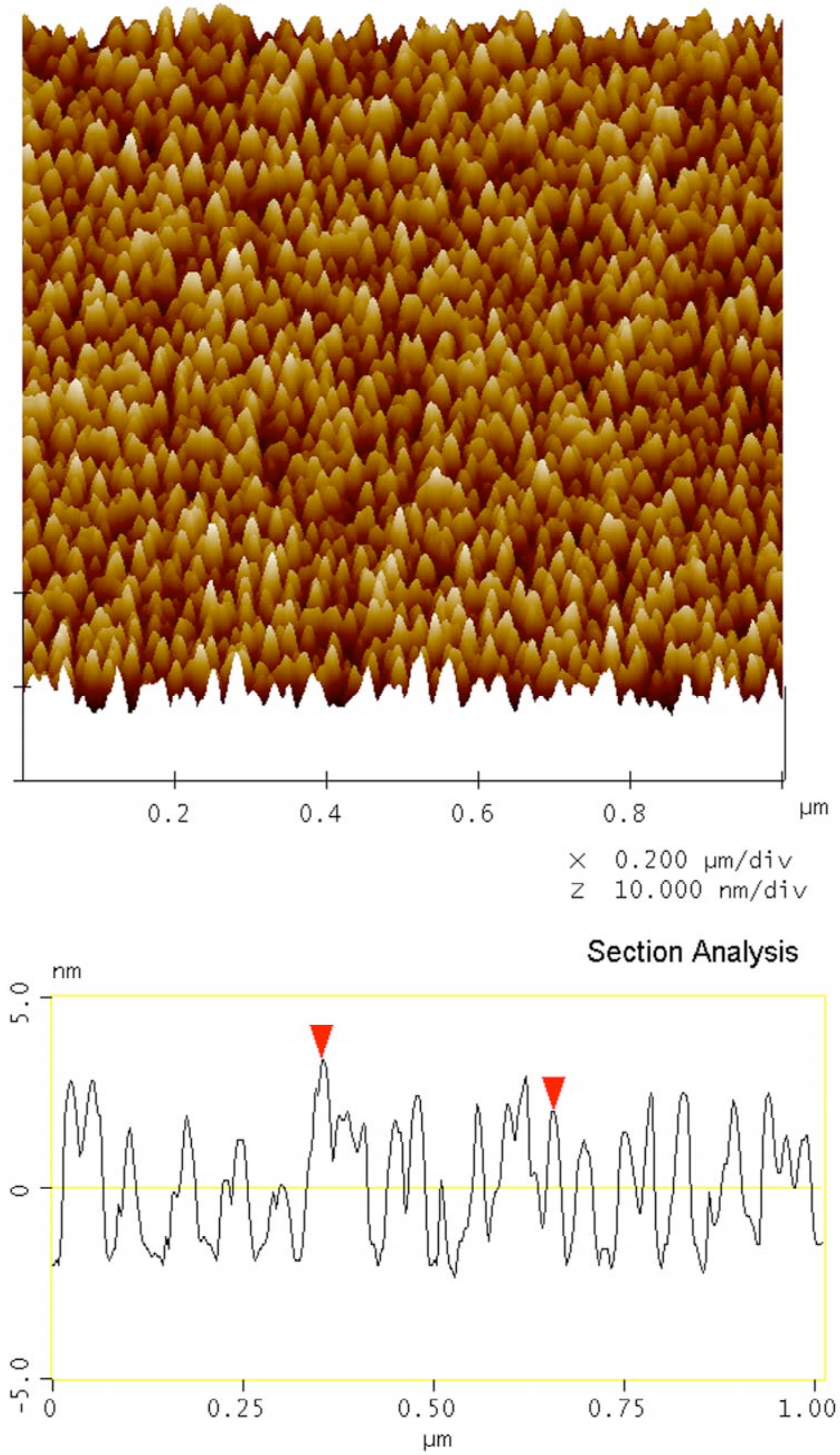


Figure S11, Surface after second adsorption of the polymer.

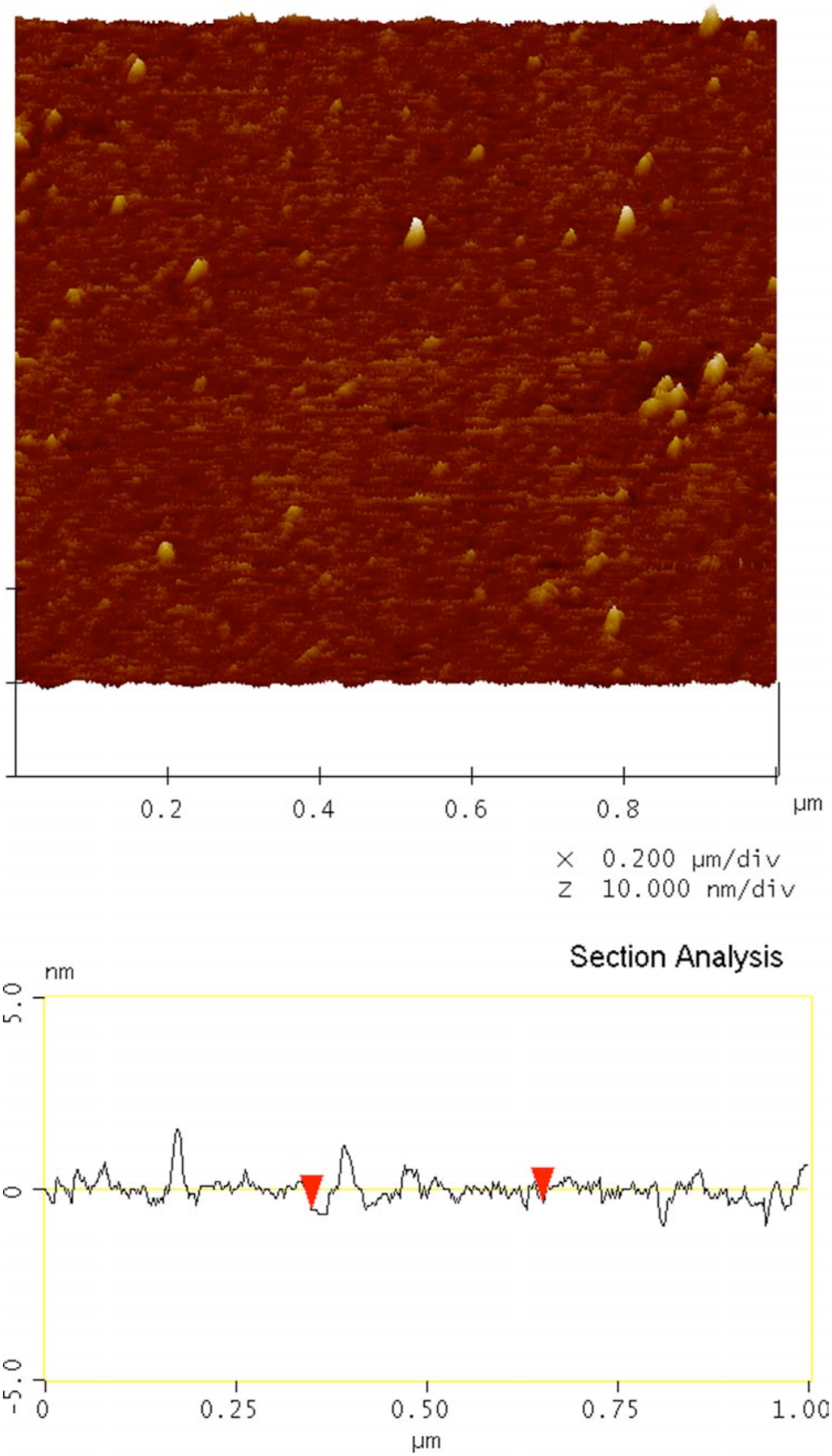


Figure S12, Surface after second desorption of the polymer.