Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

Recodable Surfaces Based on Switchable Hydrogen Bonds

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Characterization methods and equipment

^{1}H NMR spectroscopy was performed using a Bruker Ascend 400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz). All samples were dissolved in chloroform-d^1. The δ-scale is referenced to the internal standard tetramethylsilane (TMS, $\delta = 0.00$ ppm).

ToF-SIMS *(Time-of-Flight Secondary Ion Mass Spectrometry)* was performed on a TOF.SIMS5 instrument (ION-TOF GmbH, Münster, Germany), equipped with a Bi cluster liquid metal primary ion source and a non-linear time-of-flight analyzer. The Bi source was operated in the "high current bunched" mode providing 0.9 ns Bi_3^+ ion pulses at 25 keV energy and a lateral resolution of approx. 4 µm. The short pulse length allowed for high mass resolution to analyze the complex mass spectra of the immobilized organic layers. Images larger than the maximum deflection range of the primary ion gun of 500×500 µm^2 were obtained using the manipulator stage scan mode with a pixel distance of 10 µm. Spectra were calibrated on the C^+, CH^+, CH_2^+, CH_3^+; or on C^-, CH^-, CH_2^- and C_2^-, respectively. Primary ion doses were kept below 10^{11} ions/cm^2 (static SIMS limit).

MS *(Mass Spectrometry)* was performed on a LXQ mass spectrometer (ThermoFisher Scientific) equipped with an atmospheric pressure ionization source operating in the nebulizer-assisted electrospray mode. A constant spray voltage of 4.5 kV and a dimensionless sweep gas flow rate of 2 and a dimensionless sheath gas flow rate of 12 were applied. The capillary voltage and the tube lens offset voltage were set to 60 and 110 V, respectively. The capillary temperatures were 320 °C. Spectra were measured in positive mode.

SEC (*Size-Exclusion Chromatography*) experiments in THF were carried out on a Shimadzu system equipped with 3 columns (HR2, HR1 and HR0.5 from waters) with a flow rate of 1 mL min^{-1}. Samples were analyzed using a conventional calibration with PS standards.

AFM (*Atmonic-force Microscopy*) was performed on a MultiMode AFM (Bruker) with a scan area of 5 µm, a scan speed of 0.25 Hz, a resolution of 512 lines and points, a scan angle of 0° and a MikroMasch HQ:NSC18/Al BS cantilever with a resonance frequency of 75 kHz and a force constant of 2.8 N/m. The measurements were performed in the tapping mode.

Experimental Data

Materials

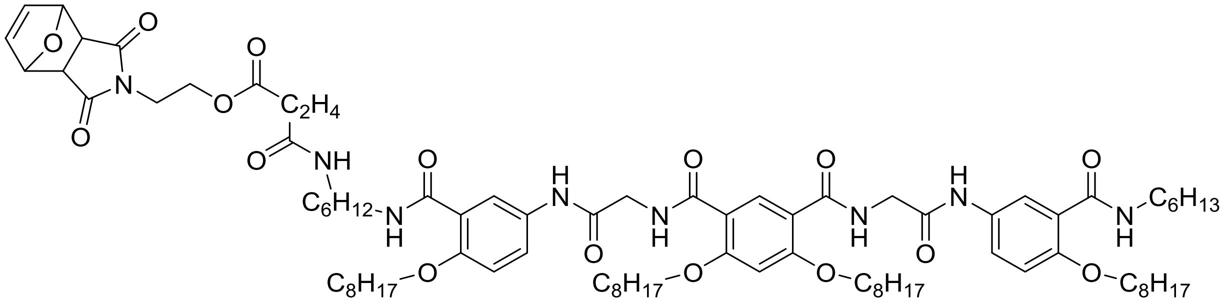
Anhydrous dichloromethane (DCM, 99.8 %, AcroSeal®, Acros), anhydrous toluene (AcroSeal®, Acros), chloroform-d$_1$ (99.8 %, EURISO-TOP), dichloromethane (99.5%, VWR), 4-dimethylaminopyridine (DMAP, Fisher), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC•HCl, >99%, Roth), triethylamine (NEt_3, 99 %, Acros), trifluoroacetic acid (>98%, Roth,) were used as received. Methyl Methacrylate (MMA, Aldrich) was purified through an alumina plug before polymerization. For the surface control experiment we used a commercial PMMA standard for GPC calibration from Polymer Standard Service, which consists of narrowly distributed polymers of M_n = 1370000, 372000, 38100 and 5880 g mol^{-1}.

For the treatment of the surfaces, if not stated otherwise, dichloromethane (p.a., Fisher), methanol (p.a., Acros), toluene (p.a., Alfa) and chloroform (VWR, distilled once) were used.

Synthesis

Species **3**:

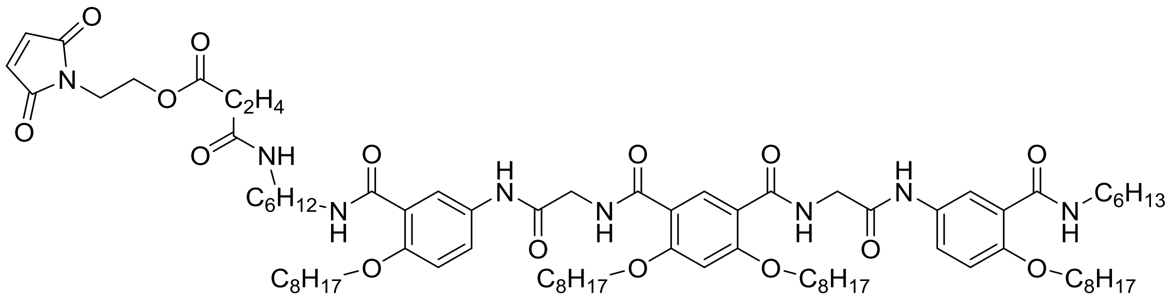
26 mg (0.02 mmol) **1** were stirred in TFA and the reaction was monitored *via* TLC according to literature.[1] The resulting ammonium salt was stirred for 1 day with 36 mg (0.2 mmol) EDC•HCl, 2.1 mg (0.02 mmol) DMAP, 27 mg (0.09 mmol) **2**, which was prepared according to literature,[2] and 7.2 mg (0.07 mmol) NEt_3 in 3 mL dry DCM at ambient temperature. The solvent was removed under reduced pressure and the crude product was purified *via* column chromatography (5% MeOH in DCM) resulting in 12 mg (0.008 mmol) **3**. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm) = 9.92-9.60 (2 H, -**H**N-CO), 8.90 (1 H, s, $\mathbf{H}_{\mathbf{Ar}}$), 8.56-8.44 (2), 8.25-7.95 (6 H, $\mathbf{H}_{\mathbf{Ar}}$, -N**H**-CO-), 6.93-6.80 (2 H, m, $\mathbf{H}_{\mathbf{Ar}}$), 6.45-6.30 (3 H, m, -C**H**=C**H**-, $\mathbf{H}_{\mathbf{Ar}}$), 5.17 (2 H, s, -C**H**-), 4.43 (4 H, s, CO-NH-C$\mathbf{H_2}$-NH-CO), 4.20-3.95 (10 H ,m, O-C$\mathbf{H_2}$-, CO-O-C$\mathbf{H_2}$-), 3.67 (2 H, t, J = 5.4 Hz , CO-NH-C$\mathbf{H_2}$-), 3.50-3.35 (2 H, m, CO-NH-C$\mathbf{H_2}$-), 3.20-3.10(2 H, m, O-CO-NH-C$\mathbf{H_2}$-), 2.81 (2 H, s, -CH-), 2.56 (2 H, t, J = 7.0 Hz, -O-CO-C$\mathbf{H_2}$-), 2.40 (2 H, t, J = 7.0 Hz, -O-CO-C$\mathbf{H_2}$-), 2.03-1.73 (8 H, m, O-CH_2-C$\mathbf{H_2}$-CH_2-), 1.70-1.10 (-C$\mathbf{H_2}$-), 0.85-0.73 (15 H, m, -C$\mathbf{H_3}$). m/z $([M+Na]^+)_{exp}$ =1525.7, $([M+Na]^+)_{theo}$ = 1525.9



(**3**)

Species **4**:

12 mg AOA-Mal-PG (**3**) was heated for 6 h at 100 °C in a Schlenk tube to give a yellow solid that was used without further purification. ^{1}H NMR (CDCl$_3$, 400 MHz), δ (ppm) = 9.74-9.40 (2 H, -**H**N-CO), 8.90 (1 H, s, **H**$_{Ar}$), 8.55-8.40 (2), 8.25-7.95 (6 H, **H**$_{Ar}$, -N**H**-CO-), 6.93-6.80 (2 H, m, **H**$_{Ar}$), 6.65 (2H, s, -C**H**=C**H**-), 6.42 (1 H, s, **H**$_{Ar}$), 4.45 (4 H, s, CO-NH-C**H**$_2$-NH-CO), 4.20-3.95 (10 H ,m, O-C**H**$_2$-, CO-O-C**H**$_2$-), 3.72 (2 H, t, J = 5.3 Hz , CO-NH-C**H**$_2$-), 3.50-3.35 (2 H, m, CO-NH-C**H**$_2$-), 3.20-3.10(2 H, m, O-CO-NH-C**H**$_2$-), 2.56 (2 H, t, J = 7.1 Hz, -O-CO-C**H**$_2$-), 2.40 (2 H, t, J = 7.1 Hz, -O-CO-C**H**$_2$-), 2.03-1.73 (8 H, m, O-CH$_2$-C**H**$_2$-CH$_2$-), 1.70-1.10 (-C**H**$_2$-), 0.87-0.70 (15 H, m, -C**H**$_3$). m/z ([M+Na]$^+$)$_{exp}$ =1458.0, ([M+Na]$^+$)$_{theo}$ = 1457.9



(**4**)

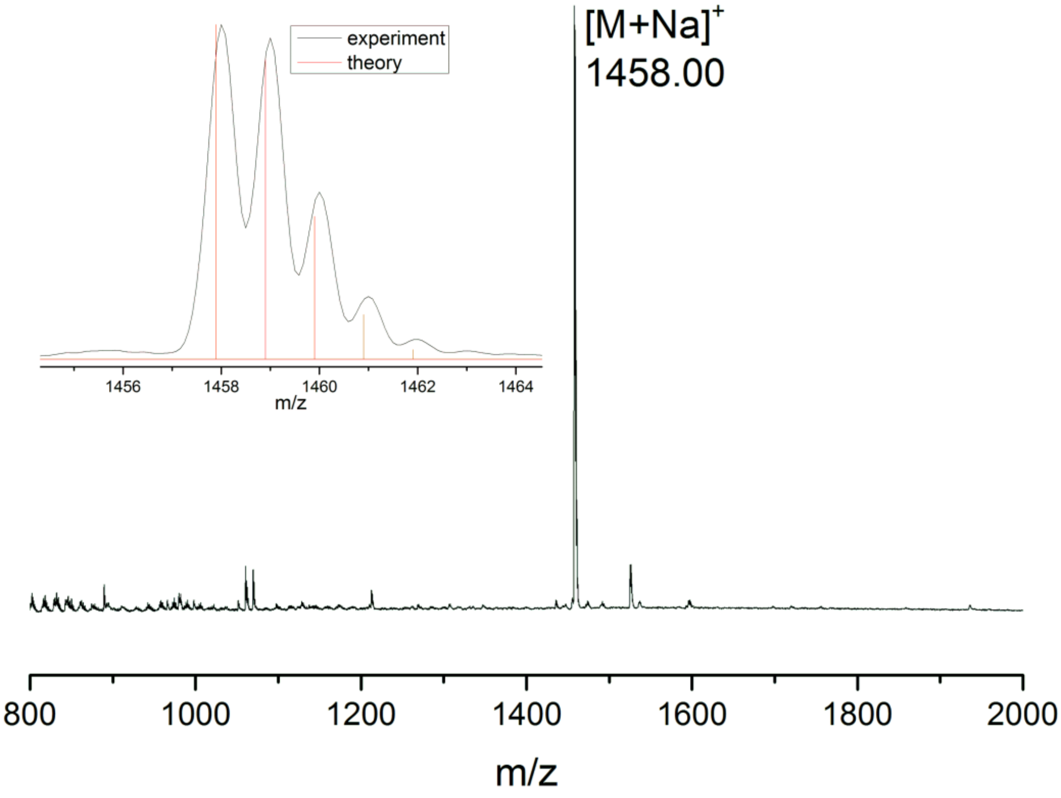


Figure S1: ESI-MS spectrum of **4** (black) compared with a theoretical spectrum (red).

SOA-PMMA (**P1**):

For RAFT polymerization towards SOA-PMMA (**P1**) 3.1g of MMA was added in a Schlenk flask and the RAFT agent (50 mg) and AIBN (0.33 mg) were added as dilute solutions in toluene. Further addition of toluene kept the overall toluene/monomer ratio about 30 wt%. Three freeze-pump-thaw cycles were conducted before starting the polymerization in an oil bath preheated at 80°C. The polymerization was monitored with SEC, and quenched after 22 h of reaction. The PMMA-SOA (**P1**) polymer was reprecipitated twice in cold MeOH and dried. A further fractionation step was carried out by slowly adding 75:25 MeOH/CHCl3 mixture in concentrated polymer/CHCl3 solution. The first fraction that precipitated (about 5wt% of total polymer weight) was discarded as it contained a small amount of unfunctionalized chains.

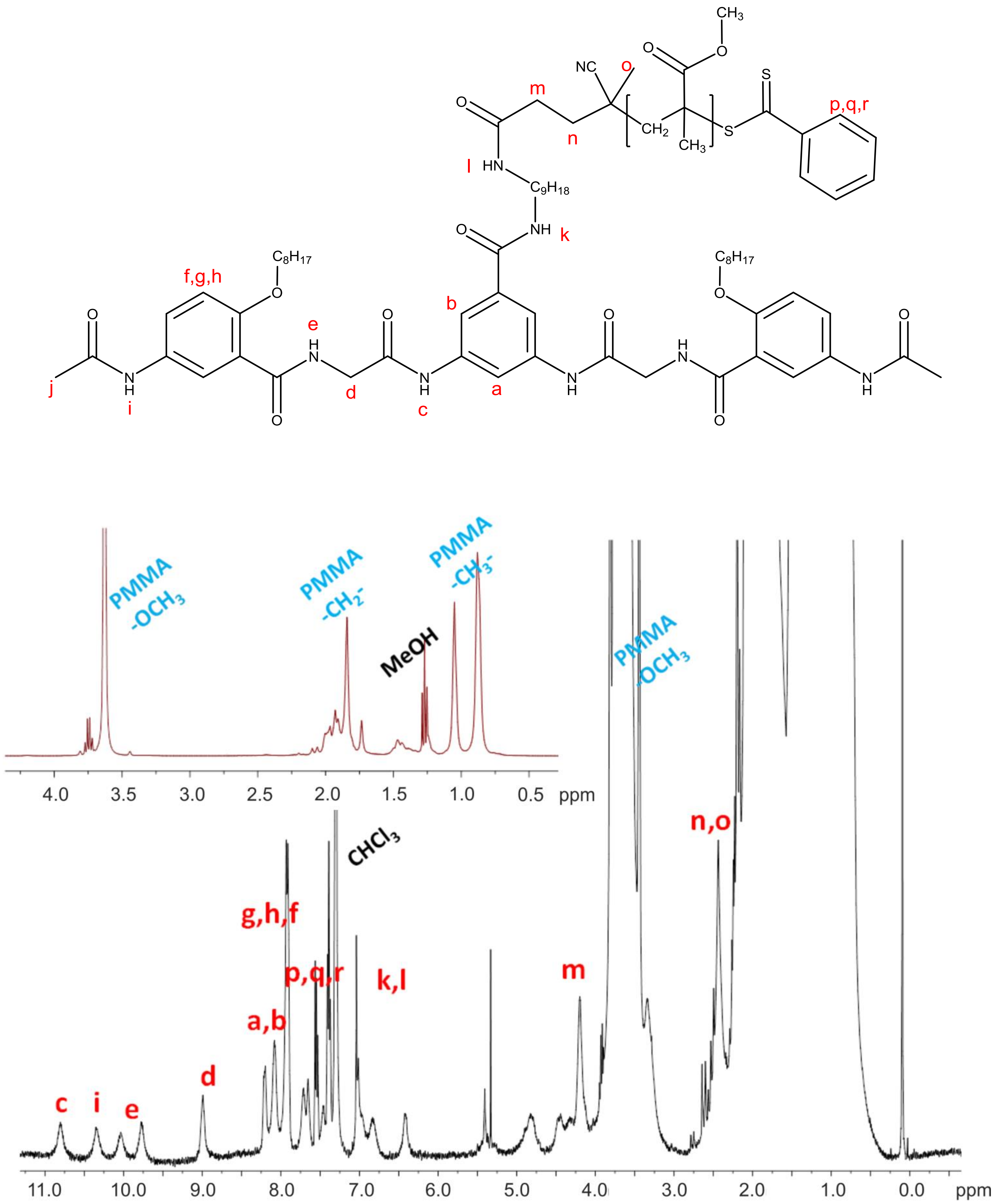


Figure S2: ^{1}H-NMR of **P1** with proton assignments.

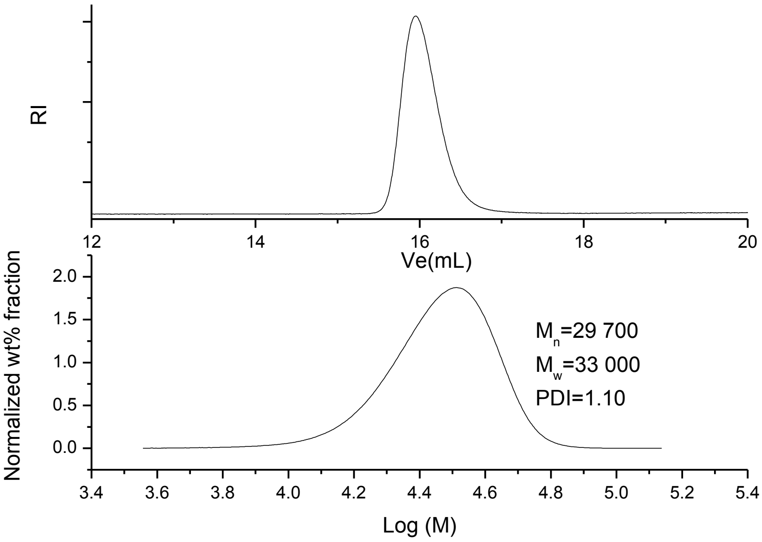


Figure S3: SEC data of **P1**.

Surface Functionalization:

Surface S2:

Surface **S1**, which was prepared according a literature procedure,[3] was mounted in a sample holder with a shadow mask and immersed in a solution of **4** in dry DCM (*c* = 0.6 g•mL^{-1}). The solution was degassed for 15 min in an ice bath and the surface was irradiated for 24 h with an Arimed B6 lamp. The surface was removed from the solution and the sample holder and extensively washed with DCM and dried in a N_2 stream. The emission spectrum of the Arimed B6 lamp and the design of the sample holder can be found in reference 3.

General procedure for immobilization of P1:

The washed surface **S2** was immersed in a filtered solution of **P1**, which was prepared according to a literature procedure,[1] in dry toluene (*c* = 0.6 g•mL^{-1}) for 10 min. The surface **S3** was washed extensively with toluene to remove any physisorbed **P1** and subsequently dried in a N_2 stream.

General procedure to wash off P1 from S3:

The surface **S3** was washed with 10 mL of 10% MeOH in $CHCl_3$ and dried in an N_2 stream.

Control experiment with neat PMMA in comparison to P1:

The washed surface **S2**, which was used for all other immobilization and washing cycles before, was immersed in a filtered solution of PMMA in dry toluene ($c = 0.6$ g•mL^{-1}) for 10 min. The surface was washed extensively with toluene to remove any physisorbed polymer and subsequently dried in a N_2 stream. A comparative ToF-SIMS image is given below (Fig. SI2).

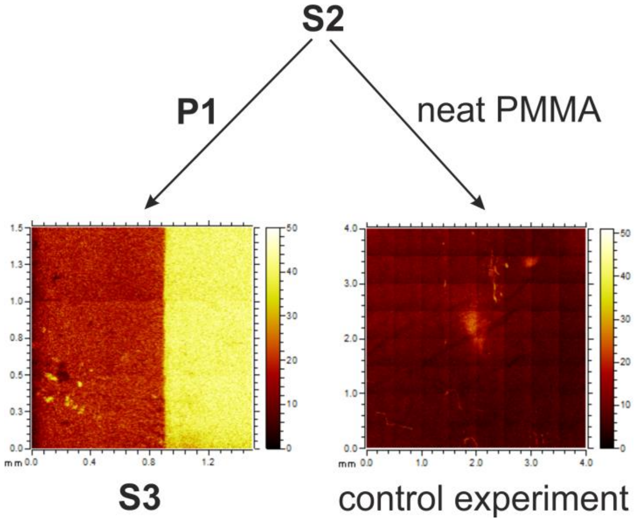


Figure S4: Comparative ToF-SIMS image between S3 and a control experiment employing neat PMMA instead of SOA-PMMA (**P1**). The imaged fragment is $C_4H_5O_2^-$.

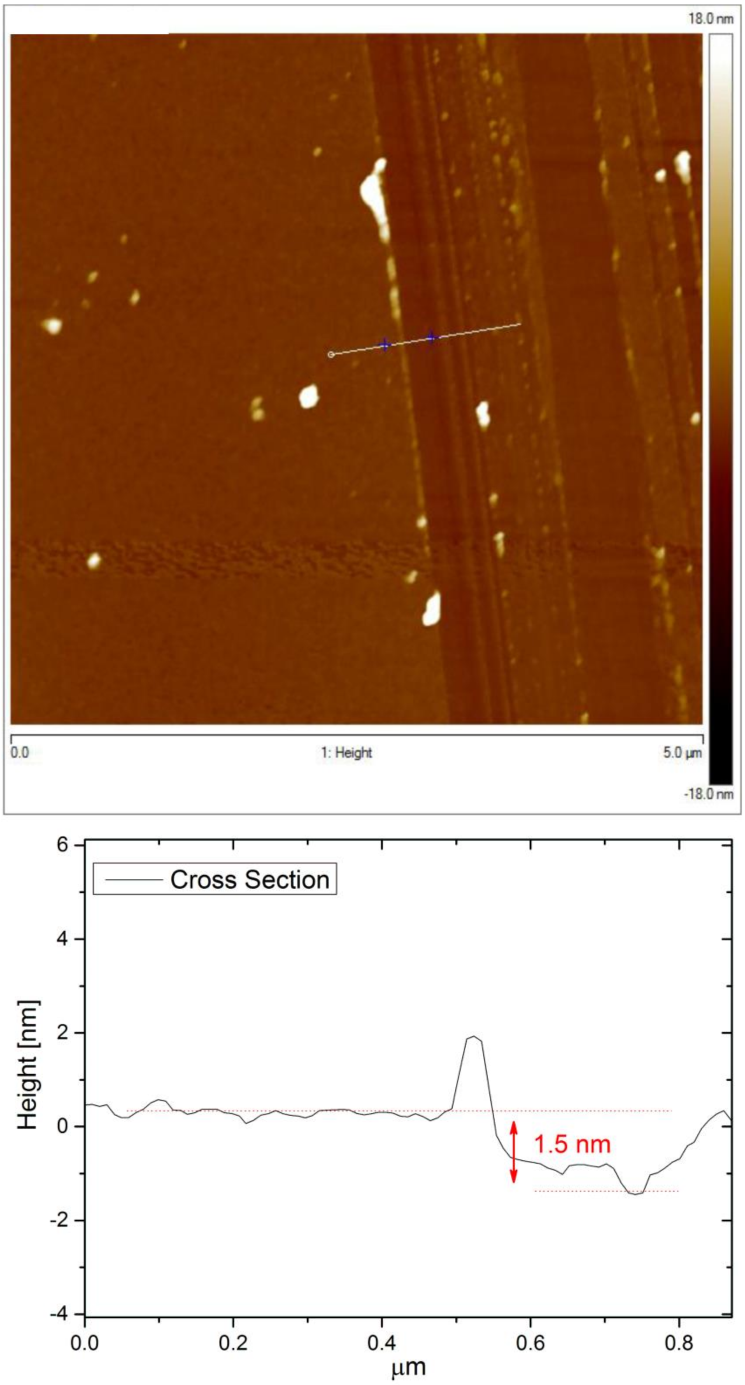


Figure S5: AFM image of a scratch test on a loaded surface. The scratching of polymer (P1) off the surface down to the neat silicon wafer suggests a film thickness for the coating of 1.5 nm with very flat lying polymer strands.

References

(1) Montarnal, D.; Delbosc, N.; Chamignon, C.; Virolleaud, M.-A.; Luo, Y.; Hawker, C. J.; Drockenmuller, E.; Bernard, J. *Angew. Chem. Int. Ed.* 2015, *54*, 11117.

(2) Willenbacher, J.; Wuest, K. N. R.; Mueller, J. O.; Kaupp, M.; Wagenknecht, H.-A.; Barner-Kowollik, C. *ACS Macro Letters* 2014, *3*, 574.

(3) Sugawara, Y.; Jasinski, N.; Kaupp, M.; Welle, A.; Zydziak, N.; Blasco, E.; Barner-Kowollik, C. *Chem. Commun.* 2015, *51*, 13000.