

Supporting Information

Wafer-scale Synthesis of Defined Polymer Brushes under Ambient Conditions

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Materials

Methyl methacrylate (MMA), 2-(dimethylamino)ethyl methacrylate (DMAEMA), 4-vinylpyridine (4VP), 2-hydroxyethyl methacrylate (HEMA), oligo(ethylene glycol) methyl ether methacrylate (OEGMA₄₇₅) were purchased from Sigma-Aldrich (Weinheim, Germany), purified before use by passing through a basic alumina column to remove the inhibitor. 3-sulfopropyl methacrylate potassium salt (SPMA), *N*-isopropylacrylamide (NIPAAM), (methacryloyloxy)ethyl trimethylammonium chloride (METAC), sodium acrylate (SA), 2-bromoisobutryl bromide (BiBB), 3-aminopropyltriethoxysilane (APTES), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 99%), pyridine (99%), dichloromethane (DCM, dry) dimethyl sulfoxide (DMSO), methanol (all from Sigma-Aldrich) were used as received. Water for reaction solutions, contact angle measurements was bidistilled deionized water.

4-inch silicon wafers with a 300 nm oxide layer were obtained as a generous gift from Wacker AG (Burghausen, Germany).

4-inch copper wafers were from MicroChemicals GmbH, Germany: Prime CZ-Si wafer 4 inch, 1-side polished, p-type (boron) TTV < 10 µm, 1 - 10 Ohm cm; 10 nm Ti adhesion layer; 200 nm Cu (purity > 99.9 %), RMS < 10nm. Copper coated side of the wafer was consecutively washed with portions of ultrapure water, ethanol and DMSO under ultrasonication (5 min). The cleaned Cu plate was immediately used.

Methods

Atomic force microscopy (AFM) was performed on a customized Ntegra Aura/Spectra from NT-MDT (Moscow, Russia) with a SMENA head in semicontact mode. The probes have a

typical curvature radius of 6 nm, a resonant frequency of 47–150 kHz, and a force constant of 0.35–6.10 N/m. Editing, height determination and calculation of the surface roughness was performed with the software Nova Px 3.2.5 from NT-MDT.

Ellipsometry measurements of the optical thickness, d , were performed with a SE800 ellipsometer from (SENTECH Instruments GmbH) equipped with a He–Ne laser source ($\lambda = 632.8$ nm) and a fixed angle of incidence of 60° at ambient conditions. The accumulated spectra were modeled using SpectraRay 3 software. The d -value of macroscopic brush gradients were determined in 3 individual series of measurements along the direction of the gradient using an x-y sample stage. The ellipsometry mapping was performed with M-2000/T-Solar (wavelength range 0.7 – 5 eV) at 65° and 75° angles. Analysis was carried out in CompleteEASE software.

X-ray photoelectron spectroscopy (XPS) was performed on an Omicron Multiprobe spectrometer using monochromatic aluminum $K\alpha$ radiation. The spectra were calibrated by setting the Si 2p signal to 102.0 eV. Spectra were fitted by symmetric Voigt functions with a Shirley background correction.

Static water contact angle measurements were carried out with the Drop Shape Analysis System DSA 10 from Krüss to characterize the wettability of the polymer layers. For each sample, individual measurements at five different spots were performed and averaged. The measurements were performed at RT with bidistilled water. The contact angles (θ) were obtained using the tangent method fitting.

Gel permeation chromatography (GPC) was performed on a PL-GPC-120 (Polymer Laboratories) running under WinGPC software (PSS, Mainz, Germany) with two consecutive Gram columns (2 x 100 Å) with N,N-dimethylacetamide (DMAc) (5 g/L LiBr, 70°C , 1 mL/min) as eluent and calibrated against PMMA standards from PSS, Mainz, Germany.

$^1\text{H-NMR}$ spectroscopy was performed at 500MHz on an Avance DMX500 spectrometer using DMSO- d_6 as the solvent at 25°C and the solvent signal for lock-on.

Self-assembled monolayer (SAM) of APTES-BiBB initiator on Si wafer

An oxygen plasma cleaning system (PDC-002, 200 W) from Harrick (USA) was used to clean the surface of the silicon wafer. The oxygen source of the chamber was supplied by a flow of air of 50 mL/min in 30 min for each wafer.

The clean substrates were functionalized by immersion of the wafers into a 5% (v/v) aminopropyltrimethoxysilane (APTES) solution in dry acetone and ultrasonicated during the SAM formation for 45 min at RT. After SAM formation, the samples were extensively rinsed with dry acetone and dried under argon atmosphere. This procedure results in a highly reproducible and uniform APTES layer. The substrate was then immersed in dry DCM (50 mL) under nitrogen. Pyridine (0.4 mL) was added, followed by dropwise adding of 2-bromoisobutryl bromide (BiBB) (50 mL, 2% in DCM) at 0 °C, and the reaction was allowed to complete within 24 h under stirring at 20 °C. The substrate was removed, washed with portions of DCM, water, ethanol, and acetone, and then dried by a jet of nitrogen. The successful surface modification was confirmed by X-ray photoelectron spectroscopy (XPS) (**Figure S1 and S2**) and water contact angle measurements ($\theta_{\text{static}}(\text{H}_2\text{O}) = 67.3 \pm 1^\circ$). The resulting APTES-BiBB SAM layer thickness $d \sim 2.0$ nm was determined by ellipsometry.

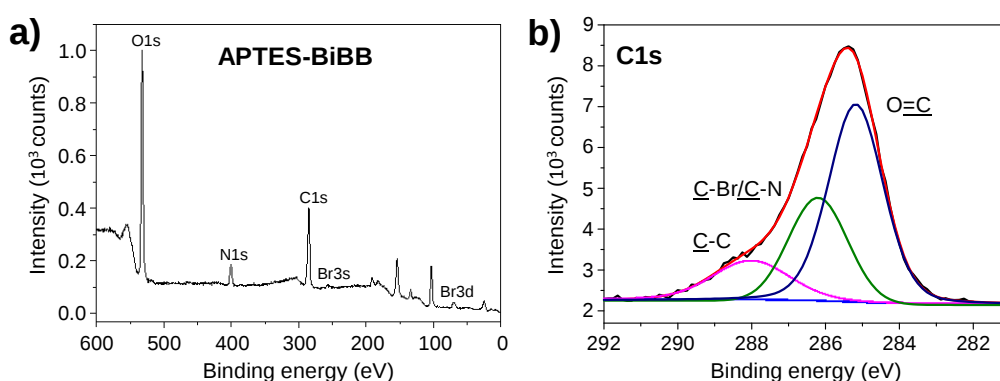


Figure S1. XPS spectra of the BiBB initiator modified silicon surfaces. a) broad spectrum shows Br3d peak at the binding energy of about 68.7 eV indicate that the initiator species for the subsequent polymerization; b) The C1s core-level spectrum comprised three peaks with binding energies of 285.1, 286.2 and 288.0 eV, which are assigned to C-C, C-Br/C-N and O=C, respectively.

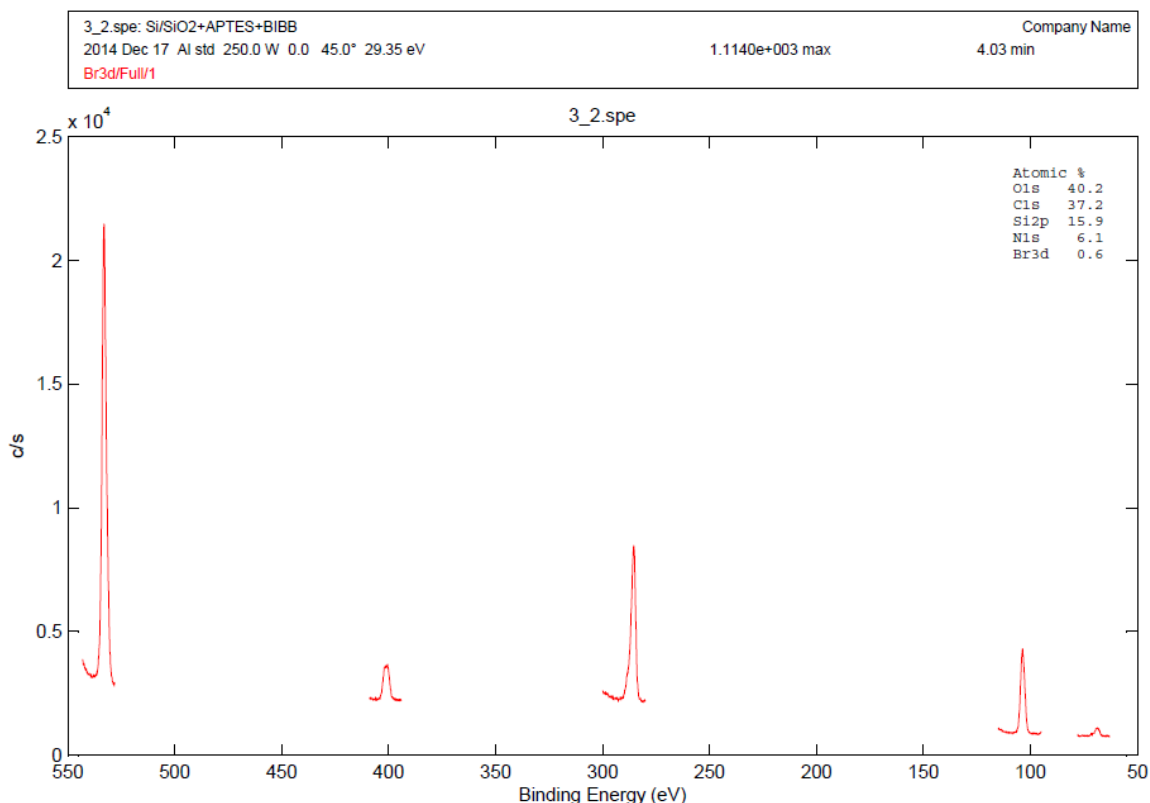


Figure S2. Core-level XPS spectra of O1s, C1s, Si2p, N1s and Br3rd of the BiBB initiator modified silicon surfaces. The C/Br ratio of 37.2/0.6 is quite higher than the theoretical value of 7/1. It is probably due to the elimination of Br by high-energy electrons from X-ray sources. Because in several independent tests of identical samples at different time, the Br concentrations are significantly varied from 0.1 to 1.6%. However, the C/N ratio is consistent with a value of 37.2/6.1 which is close to theoretical value of 7/1.

Surface-initiated Cu(0)-mediated controlled radical polymerization (SI-CuCRP)

A silicon wafer piece modified with APTES-BiBB was sandwiched with a copper plate at a typical distance of $D = 0.5$ mm using two spacers. The assembly was hold horizontally and gap between the two plates was filled with the monomer solution from the side using a pipette. The monomer and ligand concentrations are identical to our previous report.¹ The assembly was left for 1 h at RT. The plates were separated and the substrate immediately washed with fresh a methanol/water mixture. Then, the substrate was submerged in fresh good solvent for the respective polymer and ultrasonicated for 5 min. Finally, the substrates were dried by a jet of dry nitrogen and analyzed. Repetitive experiments (3-5) using the same monomer solution gave no significant differences in terms of the resulting brush layer thickness.

Polymer brushes on the wafer-scale under ambient conditions

In principle, the procedure was identical to the preparation of brushes on smaller substrates. Only,

a slightly larger amount of reaction mixture was first dropped onto the wafer until the liquid covered the entire wafer. Then, four spacers were placed onto the wafer, the copper plate was placed on top and weighed down by a jar filled with water. The stock solution was prepared from: 3 mL METAC (or 1.5 g NIPAAM), 55.2 μ L PMDETA and 4.5 mL methanol/water (v/v, 1/2). The total reaction volume between the two plates is only 4 mL ($V = G \times D = \pi(d/2)^2 \times D = \pi(10.16 \text{ cm}/2)^2 \times 0.05 \text{ cm} = 4.05 \text{ mL}$).

Copper plate proximity printing (CP³)

A new 2 Euro cent coin (Deutsche Bank, Dresden branch) was cleaned by ultrasonication in portions of deionized water, ethanol and DMSO for 5 min each. A APTES-BiBB modified wafer piece was covered by a reaction solution with METAC and the coin placed directly onto the substrate. After 1 h, the coin was removed and the substrate was excessively rinsed with water and dried by a jet of nitrogen.

Polymer brush gradient

The PMETAC brush gradient was prepared as reported previously but under ambient conditions.¹ The optical thickness was obtained by ellipsometry with an error calculated from 3 individual measurement series. The error is within the data dot size shown in **Figure 5g**.

Block copolymer brushes

The first POEGMA₄₇₅ was prepared as described above but with a SI-CuCRP time of 30 min. The substrate was cleaned by the same procedure, analyzed by ellipsometry, AFM and water contact angle measurements. Then the wafer was subjected to a second SI-CuCRP reaction using HEMA for 30 min and cleaned again. The same process was repeated for the third block with OEGMA₄₇₅ and the fourth with HEMA to give a tetrablock copolymer brush.

Degrafting of polymer brushes

The polymer modified wafer was cut into small pieces and submerged in a concentrated aqueous KOH solution (30wt.%) and left for 2 h.² The detached polymer formed a film which was collected from each piece and dried in vacuum for 24 h at RT. Polymer films were dissolved in minimal amounts of DMAc and analyzed.

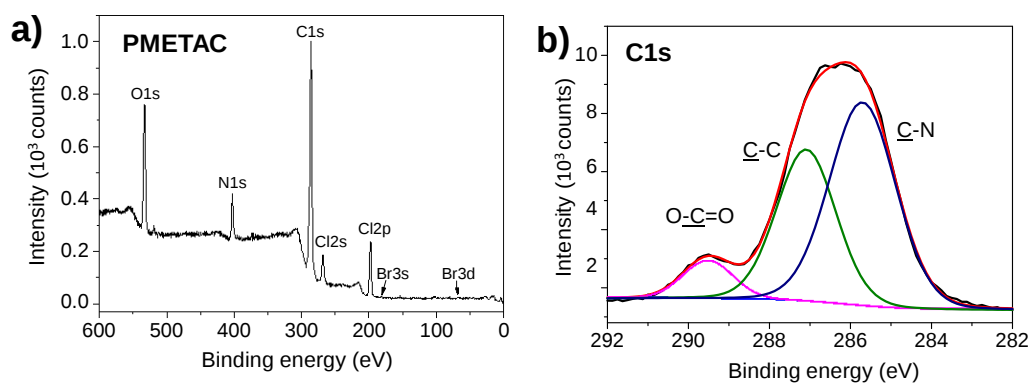


Figure S3. XPS spectra of the PMETAC brushes grafted from silicon surfaces. a) broad spectrum shows significant Cl peaks from PMETAC as well as Br peaks from initiator; b) C1s core-level spectrum of the polymer brushes which could be fitted with the expected contributions of different carbon atoms. The time of the surface-grown polymerization is 1 h.

Table S1. The optical thickness of PNIPAAm brush along radial lines as indicated in **Figure S4a** and the average brush thickness. Two non-representative data were omitted.

Measurement point	line 1	line 2	line 3	line 4
1	220.16			
2	270.55	269.49	288.16	352.61
3	272.37	275.64	274.63	336.37
4	277.35	277.73	293.48	277.91
5	279.96	283.12	309.09	263.73
6	284.69	275.55	301.13	266.79
7	282.75	284.7	291.98	279.61
8	271.14	279.44	286	290.75
9	275.7	265.61	283.32	282.2
10	269.91	279.83	279.63	283.78
11	277.64	286.05	250.14	274.44
12	287.93	272.33	235.78	270.64
		254.45	232.47	260.72
Average thickness = 278 ± 21 nm				

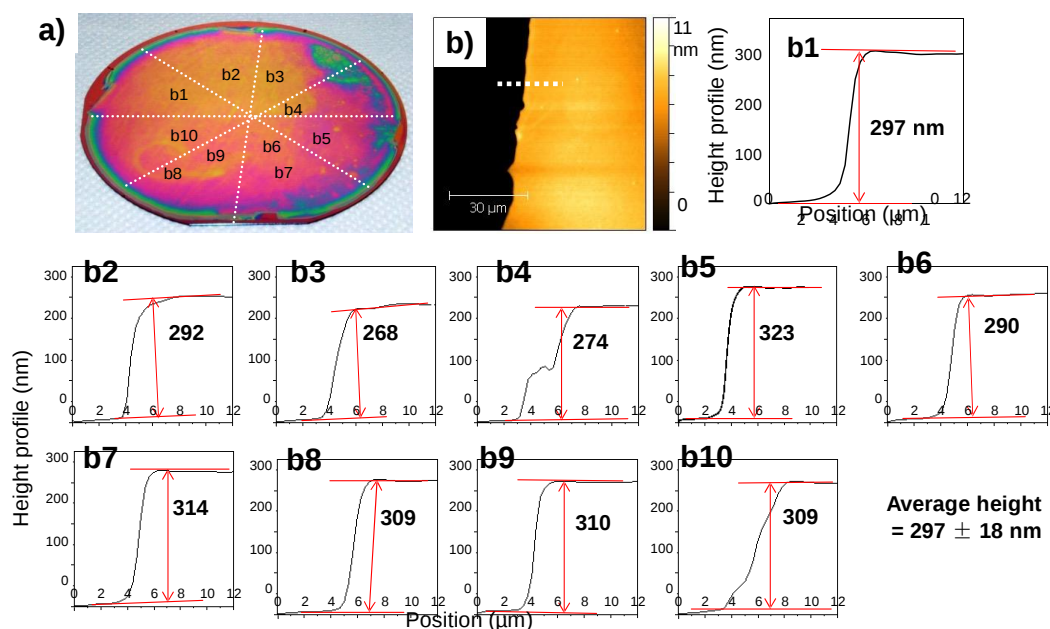


Figure S4. a) Photograph of the 4-inch wafer covered by a PNIPAAm brush with radial lines along which the ellipsometry mapping was performed given Table S2. A typical topographic AFM scan at an inflicted scratch in the brush layer to obtain the height of the dry brush. Corresponding cross-section analysis (b1) at an implied scratch on the sample of a); b2) - b10) Cross-section analysis at different regions indicated in a) resulting in PNIPAAm brush heights between 268 and 323 nm.

Calculation of the grafting density

The height (h) of the PNIPAAm brush surfaces after SI-CuCRP was obtained by ellipsometry (SENTECH Instruments GmbH) as well as contact mode AFM (NT-MDT, Russia) measurements (see **Table S1** and **Figure S4**). By using gel permeation chromatography (GPC) (PSS, Germany), we next estimated M_n and $\bar{D}$ of the grafting polymer by characterizing polymer chains cleaved from the polymer brushes on the substrate in KOH bath (30%).² GPC results display that the M_n of those polymer brushes is $M_n = 240$ kg/mol with a narrow molar mass distributions of $\bar{D} = 1.10$. Afterwards, grafting density σ was determined by $\sigma = h\rho N_A/M_n = 764.21 h/M_n$, where M_n (= 240 kg/mol) is the molecular weight of PNIPAAm polymer brush measured by GPC, N_A is the Avogadro's number, and ρ (= 1.269 g/cm³) is the density of PNIPAAm dry films. Due to systematic errors in the film thickness determinations of both ellipsometry and AFM methods, we suppose the value of grafting density of PNIPAAm polymer brush in our case is between that of value obtained from ellipsometry (0.89 chain nm⁻²) and AFM (0.94 chain nm⁻²) measurements.

The optical thickness of the PNIPAAm brush was obtained by ellipsometry and the dry brush heights by AFM (**Table S1** and **Figure S3**). With GPC we determined the number average molar mass $M_n = 240$ kg/mol and dispersity $\bar{D} = 1.10$ for the degrafted polymer. The grafting density σ was determined by $\sigma = h\rho N_A/M_n = 764.21 h/M_n$,³ where N_A is the Avogadro's number, and ρ (= 1.269 g/cm³) is the density of dry PNIPAAm. As the polymer brush layer thickness determined by ellipsometry and AFM is different, we give the both calculated σ based on both datasets (**Table S2**). The radius of gyration, R_g , is and is calculated by $R_g = a(P_n/6)^{1/2} = 5.64$ nm with $a = 0.3$ nm being the statistical segment length for the PNIPAAm monomer unit⁴ and P_n the degree of polymerization.⁵ The contour length of polymer chain, L is calculated by $L = aP_n = 636$ nm.

Table S2. Grafting density and polymer dimensions of the PNIPAAm brush.

	d or h (nm)	σ (chains/nm ²)	$h R_g$	h/L
Ellipsometry	278 ± 21^a	0.89	49.29	0.44
AFM	297 ± 18^b	0.94	52.66	0.47

^a)The value was averaged from measurements at 46 different spots. ^b)The value was averaged from measurements at 10 different spots.

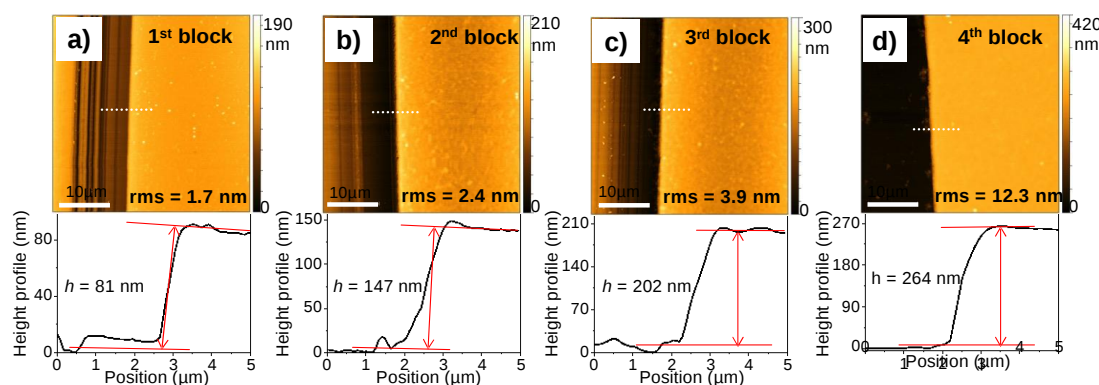


Figure S5. Characterization of wafer-scale tetrablock copolymer brushes. AFM topographic image as well as corresponding height profile of a) homopolymer brush (POEGMA), b) diblock (P(OEGMA-*b*-HEMA)), c) triblock (P(OEGMA-*b*-HEMA-*b*-OEGMA)) and d) tetrablock polymer brush (P(OEGMA-*b*-HEMA-*b*-OEGMA-*b*-HEMA) prepared by consecutive SI-CuCRP for 30 min for each step. The rms value of was calculated from a $10 \times 10 \mu\text{m}^2$ area selected from the surface of polymer film without prominent particles or holes.

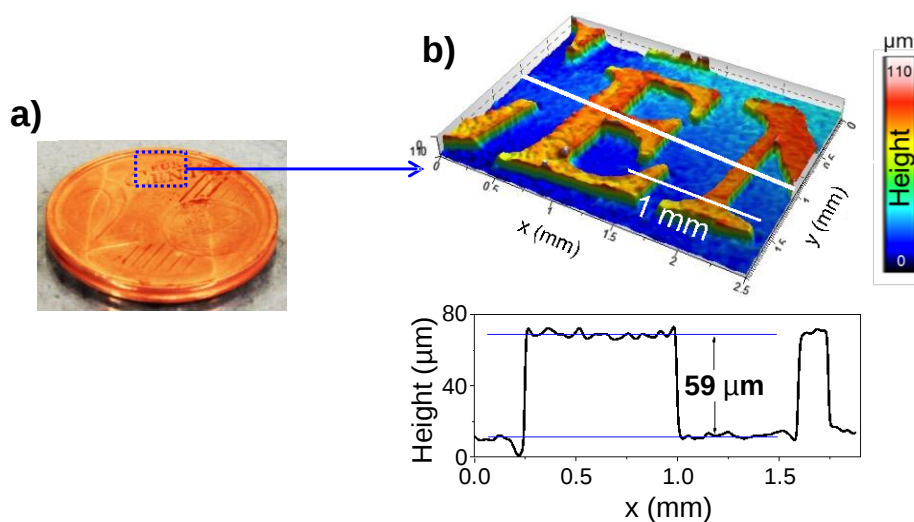


Figure S6. a) A 2 euro cent coin was used as the template for copper plate proximity printing (CP³). b) An exemplary white light interferometry scan of a detail of the coin profile with the corresponding height section analysis.

References

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