Supporting Information for:

Surface-Initiated Cu(0) Mediated Controlled Radical Polymerization (SI-CuCRP) Using a Copper Plate

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Materials

Styrene (S), methyl methacrylate (MMA), 2-(dimethylamino)ethyl methacrylate (DMAEMA), 4-vinylpyridine (4VP), tert-butyl methacrylate (tBMA), 2-hydroxyethyl methacrylate (HEMA), oligo(ethylene glycol) methyl ether methacrylate(OEGMA475) and 2-isopropenyl-2-oxazoline (IPOX) were purchased from Sigma-Aldrich (Weinheim, Germany), purified before use by passing through a basic alumina column to remove the inhibitor and distilled under nitrogen to remove oxygen. 3-sulfopropyl methacrylate potassium salt (SPMA), N-isopropylacrylamide (NIPAAM), (methacryloyloxy)ethyl trimethylammonium chloride (METAC), 2-bromoisobutryl bromide(BIBB), copper(I) bromide (CuBr, 99.99%), 3-aminopropyltriethoxysilane (APTES), 1,1,4,7,7- pentamethyldiethylenetriamine (PMDETA, 99%), dimethyl sulfoxide (DMSO) and methanol (all from Sigma-Aldrich) were used as received. For reactions and contact angle measurements bidestilled deionized water was used.

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

For the studies of the influence of the Cu plate oxidation upon its catalytic activity, an oxygen plasma cleaning system (PDC-002, 200 W) from Harrick (N.Y., USA) was used to oxidize the surface of the Cu plate. The oxygen source of the chamber was supplied by a flow of air of 50 mL/min.

PDMS mask: The PDMS mask was prepared using a 10:1 (v/v) mixture of Sylgard 184 and curing agent. The PDMS slurry was thoroughly stirred and poured into a plastic container. The container was evacuated under vacuum for 1 h to remove the air bubbles. Afterwards, the PDMS slurry was injected into a confined space between two glass slides, in which the distance was adjusted by a spacer as used in SI-SET-LRP polymerization. A PDMS film with

~ 0.5 mm thickness was peeled off after curing at 70 °C for 3 h. The gaps in the PDMS film with identical width and length were prepared manually by a graver.

Characterization

Atomic force microscopy (AFM) was performed on a customized Ntegra Aura/Spectra from NT-MDT (Moscow, Russia) with a SMENA head in semicontact (tapping) mode. The used 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 done with the software Nova Px 3.2.5 from NT-MDT. Microscope images were taken with a high resolution microscopy installed in a NT-MDT confocal spectrometer (Moscow, Russia).

X-ray photoelectron spectroscopy (XPS) was performed on an Omicron Multiprobe spectrometer using monochromatic aluminum Kα 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. UV-vis spectroscopy was performed on a Shimadzu UV-1601 spectrometer.

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. WCA measurements were performed at room temperature with bidestilled water. The contact angles were obtained using the tangent method fitting.

Ellipsometry measurements were performed with a SE800 ellipsometer from SENTECH Instruments GmbH, equipped with a He−Ne laser source (λ = 632.8 nm) and a fixed angle of incidence of 60° at ambient conditions. The accumulated spectra were modeled using SpectraRay 3 software. For each sample, measurements on three randomly selected different spots were determined and averaged. Due to a systematic discrepancy between the fits and the data of PSPMA in ellipsometry measurement, probably caused by the high thickness and charge, all PSPMA samples were measured by AFM. The optical thicknesses of macroscopic brush gradients were determined in 3 individual series of measurements along the direction of the gradient using an x-y sample stage.

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-dimethylacetaminde (DMAc) (5 g/L LiBr, 70°C, 1 mL/min) as eluent and calibrated against PMMA standards from PSS, Mainz, Germany.

Preparation and Synthetic procedures

Self-assembled monolayer (SAM) of APTES-BiBB initiator: Silicon wafer pieces with a 300 nm oxide layer were obtained as a generous gift from Wacker AG (Burghausen, Germany). Silicon substrates were cleaned with piranha solution (H_2O_2 : H_2SO_4, 1:3 v/v, 90 °C, 45 min; WARNING: Piranha solution reacts violently with organic matter!), washed extensively with bidistilled water, and dried by a jet of dry argon.

The clean substrates were amine-functionalized by immersion into a 5% (v/v) aminopropyltrimethoxysilane (APTES) solution in dry acetone and ultrasonicated during the SAM formation for 45 min. After SAM formation, the samples were extensively rinsed with dry acetone and dried under argon atmosphere. This procedure results in highly reproducible APTES monolayers. The substrate was then immersed in dry DCM (20 mL) under nitrogen. Triethylamine (0.4 mL) was added, followed by dropwise addition of 2-bromoisobutyryl bromide (BiBB) (20 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 with a dry nitrogen stream. The quality of this surface-bonded initiator preparation method was confirmed by X-ray photoelectron spectroscopy (XPS) and water contact angle measurements (θ^s = 67.3±1.1°). The resulting APTES-BiBB initiator-SAM layer thickness was ~2.0 nm as determined by ellipsometry.

Patterned APTES-BiBB Initiator-SAM: Patterned initiator was achieved on a selectively etching of as-prepared uniform initiator on SiO_2 by UV illumination (200 W Hg (Xe) lamps, LOT-oriel, Germany) through a photomask. The samples were clamped with Cu TEM grids with various hole size (Plano, Germany) and irradiated for 45 min at a distance of ~10 cm.

SI-SET-LRP catalyzed by a copper plate: Methyl methacrylate (MMA), 4-vinylpyridine (4VP), *tert*-butyl methacrylate (tBuMA), styrene (S): 1 mL monomer, 0.5 ml DMSO, 18.4 µL PMDETA. 2-(dimethylamino)ethyl methacrylate (DMAEMA), 2-hydroxyethyl methacrylate (HEMA), oligo(ethylene glycol) methyl ether methacrylate (OEGMA475), (methacryloyloxy)ethyl trimethylammonium chloride (METAC): 1 mL monomer, 1 mL bidestilled H_2O and 0.5 mL MeOH, 18.4 µL PMDETA. 3-sulfopropyl methacrylate potassium salt (SPMA): 1 g monomer, 1 mL H_2O and 0.5 mL MeOH, 18.4 µL PMDETA. N-isopropylacrylamide (NIPAAM): 0.5 g monomer, 1 mL H_2O and 0.5 mL MeOH, 18.4 µL PMDETA.

A silicon wafer piece modified with an APTES-BiBB-SAM was sandwiched with a copper plate at a typical distance of D = 0.5 mm adjusted by two spacers. The assembly was

submerged into a reaction mixture containing the monomer, the ligand PMDETA and a suitable solvent. The assembly was left for typically 1 h at room temperature while the solution was stirred. Alternatively, in a glove box (dry argon), the assembly was hold horizontally and gap between the two plates was filled with the reaction solution from the side using a pipette. Repetitive series of experiments gave no significant differences in terms of the resulting brush layer thickness.

After reaction, the plates were separated and the substrate immediately washed with either fresh DMSO or MeOH/water mixture. Then, the substrate was submerged in fresh good solvent for the respective polymer and ultrasonicated for 5 min. Finally, the substrates were blow-dried by a jet of dry nitrogen and analyzed.

Polymer brush gradients: A silicon wafer piece modified with an APTES-BiBB-SAM was sandwiched with a copper plate with one side in direct contact and the other spaced at a distance D = 1 mm using a 1 mm thick wafer stripe of a silicon wafer (12 mm in length). The assembly was fixed with clamps and submerged into the respective reaction solution.

Thickness values were obtained by ellipsometry except for PSPMA (AFM). SI-SET-LRP was performed as described before for 1 h at room temperature in 0.5 mL DMSO (for MMA) or MeOH/water (all other monomers) with 18.4 μL PMDETA and 1 mL monomer. The brush thickness scales linear with the distance between the initiator-SAM bearing substrate and the tilted copper plate. The dependence was found to be individual to the respective monomers and solvent used and is steeper for monomers in accelerating aqueous solvent and faster grafting monomers (e.g. SPMA). Maximum brush thickness for PMMA in DMSO is 68 nm at $D = 0.52$ mm; in MeOH:water 157 nm at $D = 0.70$ mm (PDMAEMA), 266 nm at $D = 0.71$ mm and 457 nm at $D = 0.33$ mm for PSPMA. Brush thicknesses were measured by ellipsometry except for PSPMA (AFM as ellipsometry data could not be fitted). The error calculated from 3 individual measurements are mostly within the dot size.

Block copolymer brushes: The first block was prepared from either OEGMA or SPMA as described above in 30 min, the substrate cleaned by the same procedure, analyzed by AFM and then subjected to a second SI-SET-LRP reaction using HEMA as the second monomer with 30 min reaction time.

Polymer brush arrays: An initiator modified substrate was firmly attached by a PDMS mask (thickness: ~0.5 mm) with several separate gaps. Then small volume (~20 μL) of various monomer solutions were filled into the each groove, independently, and followed by covering the PDMS/substrate assembly with a Cu plate. The final cleaning processes were as mentioned above.

SI-SET-LRP using a copper wire: All the parameters were same as above except a fresh Cu wire (21.5 cm of gauge 30 wire, wrapped around a Teflon-coated stir bar) was used as catalyst.[1,2]

SI-ATRP: The SI-ATRP was performed using the same APTES-BiBB initiator-SAM modified substrates, solvent and ligand under identical reaction conditions (1 h, room temperature, same reaction volume) only that CuBr was additionally added at a ratio of 1:3 of CuBr : PMDETA.[3] Polymerization proceeded with stirring, the work-up was identical to the procedure of SI-SET-LRP using a copper wire or plate.

Reuse of the reaction solution and the copper plate: SI-SET-LRP was performed for 1 h at room temperature using 2 mL MMA in 1 mL DMSO and 36.8 μL PMDETA with a copper plate facing the substrate at a distance of 0.5 mm. After the first reaction the substrate was removed and the PMMA brush layer thickness determined by AFM. A new substrate was sandwiched with the same copper plate (rinsed with DMSO but otherwise untreated) and the placed in the same reaction solution. The procedure was repeated for 5 times in total.

Table S1. Brush layer thickness for the comparison of SI-SET-LRP catalyzed by a copper plate or wire as well as SI-ATRP.

	PSPMA	PNIPAAM	PMMA	PS	P4VP
SI-ATRP	97 nm	69 nm	10 nm	4 nm	16 nm
SI-SET-LRP(Cu wire)	15 nm	15 nm	29 nm	5 nm	4 nm
SI-SET-LRP(Cu plate)	289 nm	210 nm	88 nm	31 nm	56 nm

Table S2 Grafting density of PNIPAAM brush surfaces.

	h_{dry} (nm)	σ (chains/nm^2)
ellipsometry	230 ± 11^{a}	0.85
AFM	220 ± 7^{b}	0.81

a The value was averaged over measurements at ten different spots on PNIPAAM brush surfaces. *b* The value was averaged over measurements at three different spots on PNIPAAM brush surfaces.

The dry thickness (h_{dry}) of the PNIPAAM brush surfaces (~4 cm^2) after SI-SET-LRP in 1 h was characterized using ellipsometry (SENTECH Instruments GmbH, Germany). With KOH (30%),[4] we carefully removed the grafted PNIPAM brushes from the substrate and analyzed the polymer by GPC (PSS, Germany). GPC analysis gave an M_n = 207 kg/mol and a very narrow dispersity of Đ = 1.07. With M_n = 207 kg/mol, the grafting density, σ, was determined by $\sigma = h_{dry}\rho N_A/M_n = 764.21\ h_{dry}/M_n$,[5] where M_n is the number average molar mass of PNIPAAM as determined by GPC, N_A is the Avogadro's number, and ρ (= 1.269 g/cm^3) the density of a PNIPAAM dry film. The dry brush thickness, h_{dry}, was additionally confirmed by AFM analysis of the original PNIPAAM brush using the section analysis at inflicted scratches

by a clean and sharp needle. Please note that AFM measurements of the dry PNIPAAM film thicknesses are slightly lower than those determined by ellipsometry (Table S1). Other groups investigating PNIPAAM brushes on gold[6] and silicon[7] substrates observed similar discrepancies between these two methods because of the different physical principles of the measurements. Especially, it is suggested that the adhesion between the PNIPAAM and AFM tip dampened the tip oscillation and increased the hysteresis in the force-distance curve. This could introduce systematic errors in the film thickness determinations.[8] In addition, both measurements were performed under ambient conditions and slight differences of the air humidity could lead to a slightly different swelling of the PNIPAAM brush and thus to a different thickness. However, both h_{dry} values calculate to extremely high grafting densities being $\sigma = 0.85$ chains/nm (ellipsometry) and $\sigma = 0.81$ chains/nm^2 (AFM).
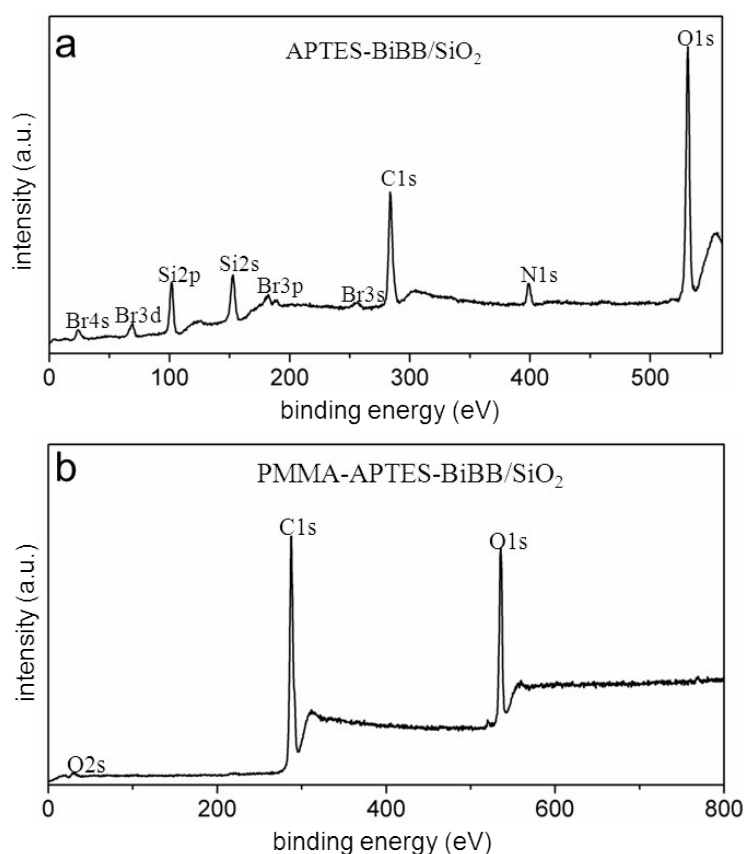

Figure S1. a) XPS survey spectrum of monolayer BiBB modified SiO_2/Si substrate. The N1s peak at the binding energy of about 402.1 eV is attributed to the O C–N species. The presence of the Br3d peak at the binding energy of about 68.7 eV and the appearance of the O C–N peak component indicate that the initiator species for the subsequent SI-ATRP reaction has been successfully immobilized on the SiO_2 surface *via* silanization and acylation reaction. b) The XPS survey spectrum of PMMA brush grown from APTES-BiBB-SiO_2/Si substrate.
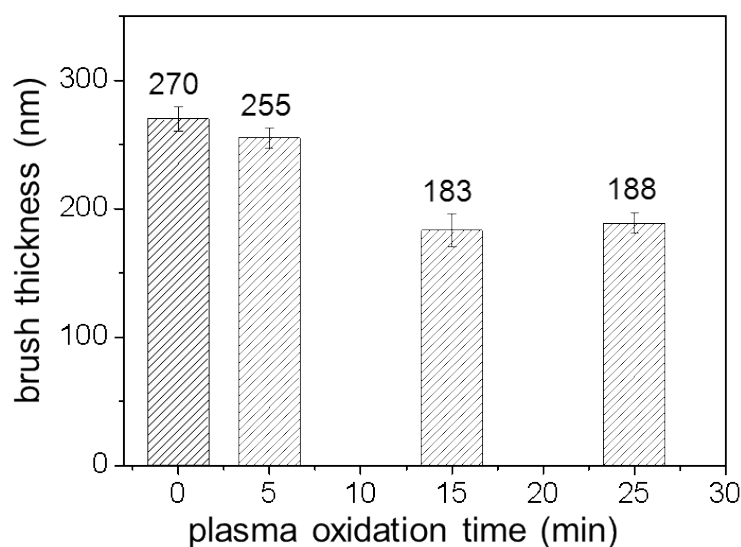
Figure S2. SI-SET-LRP with fresh and oxidized copper plates. Copper plates were treated by oxygen plasma for indicated times for oxidation, and afterwards the oxidized Cu plates were used for SI-SET-LRP of SPMA. Plot shows resulting brush thicknesses vs. time of plasma treatment for the copper plate used in the experiments. Even strongly oxidized copper was able to catalyze the polymerization to yield a 188 nm thick PSPMA brush on the facing substrate.

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