

Electronic Supplementary Information

Polymer brush patterning using self-assembled microsphere monolayers as microcontact printing stamps

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Experimental Section

Materials: NIPAAM (99%), Copper (I) bromide (CuBr, 99.9%), and Methanol (MeOH, 99.9%), Ethanol were obtained from Sigma-Aldrich (Milwaukee, WI). Milli-Q (Millipore, Billerica, MA) water (18MΩ/cm) and methanol were used as polymerization solvents. N,N,N,N,N-Pentamethyldiethylenetriamine (PMDETA) was used as received from Acros Organics (Hampton, NH). The thiol initiator (BrC(CH₃)₂COO(CH₂)₁₁SH) was synthesized as reported. ^[1] Polystyrene microspheres (5 μm and 10 μm, Thermofisher, Waltham, MA) were donated by Dr. R.M. Erb at Duke University. The microspheres are crosslinked with divinylbenzene (DVB) and contain a slight anionic charge from sulfate ester. To immobilize the initiators for surface-initiated polymerization, gold substrates with an average grain diameter of 45 nm were prepared by thermal evaporation under a vacuum of 4×10^{-7} Torr. For this purpose an adhesion layer of chromium (50 Å) followed by a layer of gold (450 Å) was evaporated onto silicon wafers. Before deposition, silicon wafers were cleaned in a mixture of H₂O₂/H₂SO₄ (1:3, v/v) at 80°C (“piranha solution”) for 10 min and washed thoroughly with Milli-Q-grade water. (Caution: Piranha solution reacts violently with organic matter!).

SMM Stamp Preparation: After the polystyrene microspheres were transferred from aqueous suspension (0.5mL) into ethanol (1.0mL) with a subsequent shake, they were first centrifuged

and then the mixed solvent was removed. The residual was then re-dispersed in ethanol (0.5mL) for a subsequent pipetting onto a slightly tilted silica wafer (~10 deg.). Upon drying at room temperature the microspheres self-assembled to form regions of hexagonally close-packed monolayers via gravitation induced sedimentation combined with solvent evaporation. ^[2]

μCP of Initiator using SMM Stamp: The SMM stamp was prepared by inking the stamp features with an ethanol solution of thiol initiator (~2 mM) for 3 min and subsequent drying with nitrogen. Gold coated silica substrates were then brought into contact with the dry SMM stamp for printing, using a range of applied load (20 to 100 g) via gently placing “balancing weight” onto the surface and corresponding contact times (10 to 60 s) during printing.

SI-ATRP: The polymer brushes were prepared according to our previous procedures. ^[3] Briefly, the polymerization solution was prepared by adding a solution of NIPAAM monomer to an organometallic catalyst. The organometallic catalyst was formed in a nitrogen atmosphere by adding CuBr (1.8 mg, 0.013 mmol) and PMDETA (14 μL, 0.064 mmol) in a 1:5 molar ratio to 1.0 mL of MeOH as solvent. The mixture was then sonicated for 2 min to facilitate the formation of the CuBr/PMDETA complex. Next, 1.5 g (17 mmol) of NIPAAM monomer dissolved in 5 mL of Milli-Q water was filtered into the catalyst-complex solution through a 0.45 μm Millipore Millex filter. The polymerization solution was then transferred into flasks containing the sample substrates with immobilized patterned initiator. The flasks were sealed with rubber septa and kept at room temperature under nitrogen. After 4 hours the substrates were removed from the polymerization solution, substrates were removed from the polymerization solution, exhaustively rinsed with water to remove all traces of the polymerization solution, and subsequently dried in a stream of nitrogen.

Characterization: The substrates with the patterned polymer brush microstructures were rinsed with Milli-Q-grade water, dried under a stream of nitrogen, and mounted on steel sample disks

prior to AFM measurements. AFM topographic images were collected in contact mode using V-shaped silicon nitride cantilevers (Nanoprobe, Veeco, spring constant 0.12 N/m; tip radius 20-60 nm) using a MultiMode atomic force microscope (Veeco, Digital Instruments, Santa Barbara, CA). Topographic imaging was performed in air, water and water/methanol. The AFM topographic images were obtained under low applied normal forces to minimize compression and lateral damage of the polymer brushes.

We found (Fig. S1) that with increasing contact time, the initially radially symmetric, conical cross-sectional profiles of the brushes become rougher, with an increasing loss of radial symmetry. We presume that this morphology progression results from unequal diffusion of the thiol ink onto the gold substrate surface, and from an inhomogeneous depletion of ink on the sphere surface.

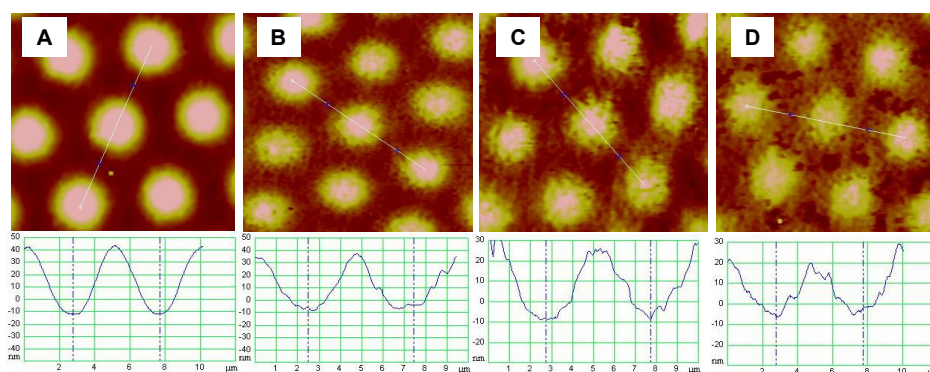


Figure S1, (A-D) Contact-mode AFM height images ($15\ \mu\text{m} \times 15\ \mu\text{m}$) of patterned PNIPPAM brush microstructures imaged at RT in air and the corresponding height profiles. Print force was 50 g for all samples, and the contact time was 10 s, 20 s, 40 s, and 60 s, for images (A-D), respectively. The polymerization conditions were identical for all samples.

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- [3] S. J. Ahn, M. Kaholek, W. K. Lee, B. LaMattina, T. H. LaBean, S. Zauscher, *Adv. Mater.* **2004**, *16*, 2141.