Supporting Information

Photocatalytic Printing of Inorganic Nanopatterns via Poly(styrene-*block*-carbosilane) Copolymer Thin Films on Titania Substrates

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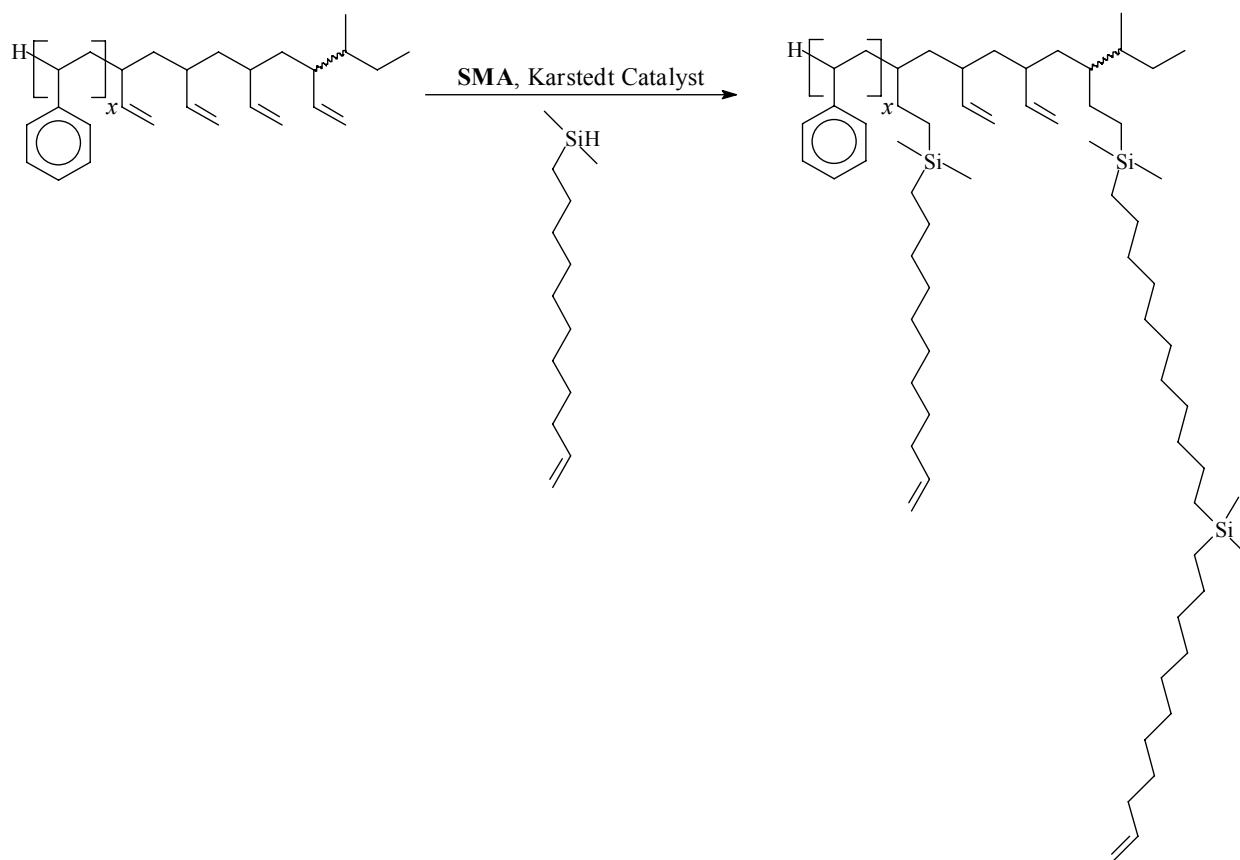
Figure S1. Synthesis of linear brush-like diblock copolymers by grafting of linear AB DMUS monomers from a short PBD-block of PS_x-*b*-PBD_y (The PBD block has an atactic configuration, although for simplicity the vinyl groups are depicted on one side).
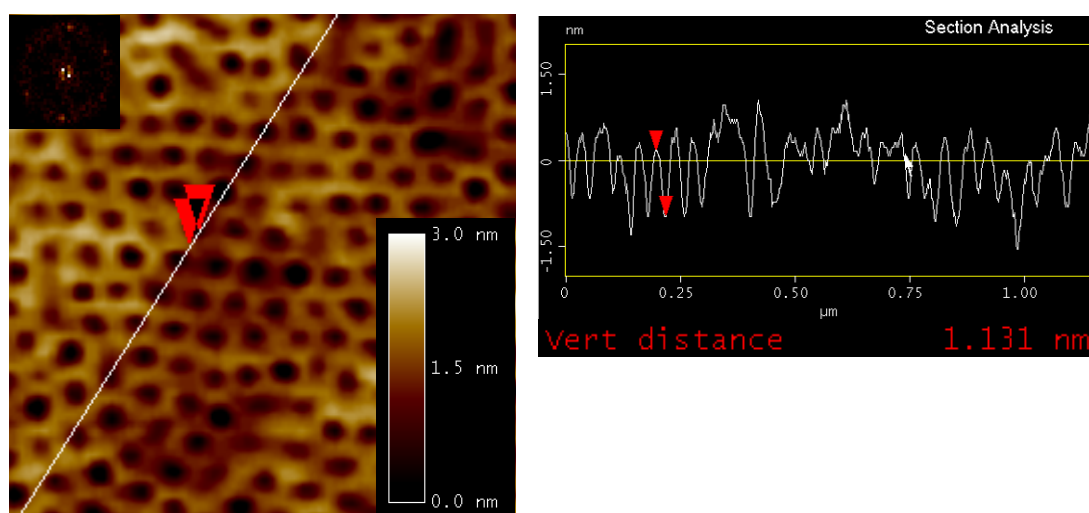
Figure S2. (left) A Magnified view of a selected region in Fig. 2(c). Image is 500 nm × 500 nm in size; (right) sectional profile of the surface of the film.
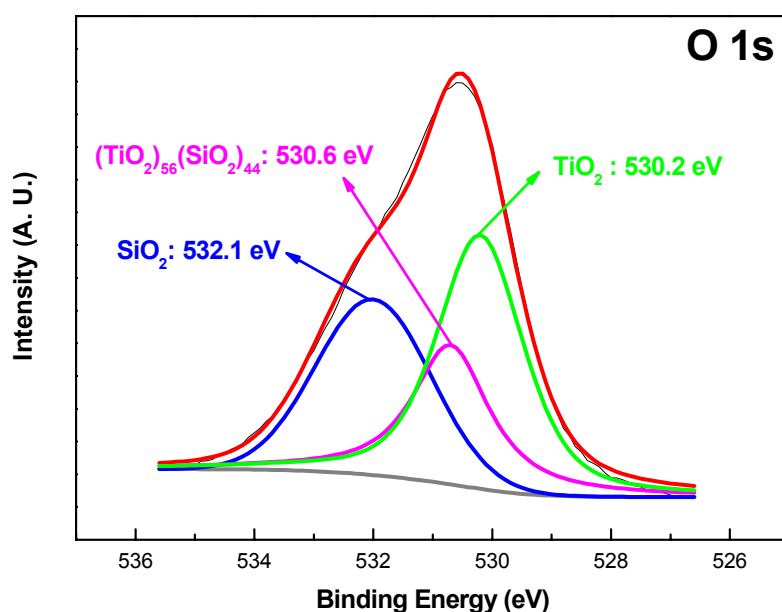
Figure S3. High resolution XPS O_{1s} spectrum of the silica nanodot arrays generated on a titania substrate.

Nomenclature. Linear brush-like diblock copolymers are denoted by PS_x-b-PCS_z, in which z indicates the DP_n of the polycarbosilane block (PCS). The short 1,2-PBD block from the parent linear diblock copolymer is regarded as being part of the final PCS block. This is

justified by the fact that the PBD-core in the final polymer architectures is indistinguishable from the linearly grafted carbosilane unit, as verified by DSC measurements.

Synthesis and Characterization of PS_{520}-*b*-PCS_{104}.

The synthesis of PS_{520}-*b*-PCS_{104} was carried out as follows: the monomer DMUS (0.35 g, 1.6 mmol) was dissolved in pentane (120 ml) and slowly added via a dosing pump to a solution of the diblock copolymer PS_{520}-b-PBD_{47} (1 g, 0.8 mmol PBD), with a number-average molecular weight (M_n) of 56,800 g/mol, in cis,trans-decahydronaphthalene (decaline, 10 mL) under a stream of argon containing 0.003 mmol of Karstedt catalyst (30 μL of the Pt solution). The reaction mixture was stirred at 70 °C to enable the constant removal of the pentane during the slow addition of the monomer. After addition of the monomer solution, the mixture was cooled down to room temperature and an aliquot taken for GPC analysis of the crude reaction product. The polymer PS_{520}-b-PCS_{104} was purified by fractionating precipitation. This was achieved by diluting the decaline reaction mixture with diethyl ether (ca. 100 mL), followed by the drop wise addition of methanol until the polymer precipitated. The supernatant fluid was decanted and the isolated polymer was washed several times with methanol and dried in vacuum at 40 °C. A polymer (0.83 g, 61 %) with a number average molecular weight (M_n) of 78,800 g/mol and with a polydispersity index (PDI) of 1.2 was obtained as determined by membrane osmometry (MO) and GPC measurements respectively.

1H NMR (400 MHz, $CDCl_3$): (ppm) -0.03 (Si-CH_3), 0.49 (-Si-CH_2), 1.05-1.6 (polymer backbone), 1.7 (m, CH_3-CH=CH-), 1.8-2.05 (m, -CH_2-CH=CH-CH_3 and polymer backbone), 2.2 (m, -CH_2-CH=CH_2), 4.9 (m, -CH=CH_2, PBD, PCSi), 5.3-5.7 (m, -CH=CH-, PCSi; -CH=CH_2, PBD), 5.9 (m, -CH=CH_2, PCSi), 6.3-7.4 (m, C_6H_5); 13C NMR (100 MHz, $CDCl_3$): (ppm) -2.97 (Si-CH_3), 13.1 (CH_3-CH=CH-, cis), 15.7 (Si-CH_2), 18.3 (CH_3-CH=CH-, trans), 24.3 (Si-CH_2-CH_2), 29.3, 29.5, 29.8, 29.9, 30, 34.1, 34.2, 39-47 (polymer backbone), 114.4 (CH_2=CH-, PBD, PCSi), 123.9 (CH_3-CH=CH-, cis), 124.8 (CH_3-CH=CH-, trans), 126.0 (C_6H_5), 128.3 (C_6H_5), 131.2 (CH_3-CH=CH-, cis), 132 (CH_3-CH=CH-, trans), 139.5 (CH_2=CH-, PCSi), 144.2 (CH_2=CH-, PBD), 145.6 (C_6H_5, Cipso); 29Si NMR (80 MHz, $CDCl_3$): (ppm) 2.4; IR (characteristic absorption bands): γ(cm-1) 1602 (stretching C=C mode), 1248 (stretching Si-CH_3 mode), 907 (terminal PBD and PCSi C=C deformation), 832 (bending CH_3-Si-CH_3 mode).