Supporting Information

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Fabrication of nanopatterned polymer brushes by combining ring-opening metathesis polymerization in the liquid and vapor phase with AFM anodization lithography – Supporting Information

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Experimental Details

AFM Anodization Lithography on Silicon Substrates. p-type silicon substrates were cleaned with piranha solution (H_2O_2:H_2SO_4 = 1:3) at 80 °C for 30 min (Caution: Piranha solution reacts violently with organic matter!), followed by extensive rinsing with water and ethanol, and drying in a stream of dry nitrogen. Cleaned silicon substrates were immersed in 0.1 M aqueous NaOH solution for

2 min and subsequently 0.1 M aqueous HNO_3 for 10 min to generate hydroxyl groups on the surface. Substrates were then rinsed with DI water and dried in a stream of dry nitrogen. Next, the substrate surface was incubated with 0.1 M octadecylmethyldiethoxysilane (ODMS, Gelest) in hexane for 12 h at 65 °C. After incubation, the substrate was sonicated in EtOH for 5 min and dried in a stream of dry nitrogen (Scheme 1(a)). Anodic oxide nanopatterns were generated by scanning probe lithography using a contact mode atomic force microscope (MultiMode III AFM, Nanoscope controller IIIa, Veeco Digital Instruments) and doped silicon cantilevers (spring constant ~ 0.1 N/m, NTMDT), by applying a positive voltage to the silicon substrate through the analog 2 channel of the AFM controller (Scheme 1(b)). Line patterns were generated at several applied bias voltages (6V – 10V), maintaining a constant 10 μm/s scanning speed and 4 scans (2 seconds) per line. The relative humidity ranged between 35% and 55% during lithography. The patterned samples were sonicated in EtOH for 5 min and then dried in a stream of nitrogen.

Surface-Initiated ROMP of COT and ENB. A 5-(Bicycloheptenyl) triethoxysilane (Nbn-$Si(OEt)_3$), *endo*/*exo* mixture of isomers was used as a ROMP tether.[1] Substrates were placed in a 0.1 M solution of Nbn-$Si(OEt)_3$ in toluene for 12 h at room temperature to yield Nbn-$Si(OEt)_3$ self-assembled monolayers (SAMs) on bare silicon oxide substrates and, selectively, on the oxide nanopatterns (Scheme 1(c)). Next, a ROMP catalyst was attached to the Nbn-$Si(OEt)_3$ by incubation with a 10 mM solution of ruthenium-based catalyst in dry CH_2Cl_2 (anhydrous, Sigma) for 1-3 h;[2] Grubbs' 1st generation catalyst was used for ethylidenenorbornene, (ENB, mixture of *endo*/*exo* isomers Sigma-Aldrich),[3] and Grubbs' 2nd generation catalyst was used for cyclooctatetraene (COT, Sigma-Aldrich)[4] (Scheme 1(d)). All initiator manipulations were performed under argon atmosphere to minimize surface oxidation. For solution phase polymerization, 0.1 mM of ENB and 1 M of COT in CH_2Cl_2 were used (Scheme 1(e)). It is important to note that ROMP of ENB with Grubbs' 1st

generation catalyst proceeds readily;[4] however, here we limited the extent of the reaction by using an extremely low concentration of ENB monomer (0.1 mM). This was done to match the height of polyCOT nanostructures on substrates patterned with both, polyENP and polyCOT. Approximately equal feature heights are required for EFM measurements (see below). For vapor phase polymerization, 25 ml ENB monomer were placed in a 250 mL glass bubbler and nitrogen gas was bubbled through the neat liquid at a flow rate of 60 cm^3/min and introduced into a 50 ml round-bottomed flask that contained the nanopatterned substrate, functionalized with tethered Grubbs' 1st generation catalyst (Scheme 1(e)). ENB was chosen as a monomer because it has a relatively high vapor pressure at room temperature (4.6 mmHg at 20 °C) and is known to be homo-polymerized with ruthenium-based ROMP catalysts.[5, 6] After polymerization, the sample surfaces were thoroughly rinsed and sonicated with dry CH_2Cl_2 and methanol to remove possible physisorbed monomer or polymer.

Characterization. The surface compositional changes after each reaction step were followed by X-ray photoelectron spectroscopy (XPS) on bulk samples, processed in the same way as nanopatterned samples. Survey scans were obtained with a Kratos Axis Ultra spectrometer using a monochromatic Al K-α source, scanning from 0ev to 1200ev with 1 eV stepsize, 200 ms dwell time, 90 degree take-off angle, and with the charge neutralizer switched on. The spectra were analyzed off-line with CasaXPS software (Casa Software Ltd., Ver. 2.2.79). Table S1 shows the atomic concentration (%) of major elements observed in the XPS survey scans. The survey spectra corresponding to samples (1), (2), (3), and (4) are shown in the relevant binding energy range from 0 to 600ev in Figure 1 in the paper.

	C 1s (%)	O 1s (%)	Si 2p (%)	B 1s (%)	P 2p (%)	Cl 2p (%)	I 3d (%)
(1) p-type Si-wafer	3.5	36.9	43.0	12.6	3.2	0.8	----
(2) Nbn-$Si(OEt)_3$ SAM	11.6	32.3	40.0	12.2	3.5	0.4	----
(3) Nbn-$Si(OEt)_3$ SAM + Grubbs' 2nd generation Ru catalyst	53.4	17.5	18.7	6.5	2.2	1.7	----
(4) polyCOT after 12h ROMP	84.4	13.1	2.6	----	----	----	----
(5) polyCOT after Iodine doping	84.8	11.5	1.5	----	----	----	2.2
(6) ODMS SAM	16.1	29.5	37.8	12.7	3.6	0.4	----
(7) ODMS SAM + Grubbs' 2nd generation Ru catalyst	19.5	31.4	33.1	12.9	2.9	0.4	----
(8) ODMS SAM + Nbn-$Si(OEt)_3$ + Grubbs' 2nd generation Ru catalyst	21.0	35.0	31.4	9.3	2.7	0.7	----
(9) ODMS SAM + Nbn-$Si(OEt)_3$ + Grubbs' 2nd generation Ru catalyst After 12 h ROMP	23.1	27.9	36.2	10.3	1.7	0.7	----

Table S1. Atomic concentration (%) of major elements obtained from XPS survey scans. (1) bare, p-type silicon substrate, (2) after incubation with Nbn-$Si(OEt)_3$, (3) after covalent immobilization of catalyst (Grubbs' 2nd generation), (4) after ROMP of COT for 12 h, (5) after Iodine doping. Control experiments: (6) ODMS SAM, (7) ODMS SAM after incubation with Grubbs' 2nd generation catalyst, (8) ODMS SAM incubated first with Nbn-$Si(OEt)_3$ and then with Grubbs' 2nd generation catalyst, (9) the same substrate as in (8), after 12 h ROMP in 1M COT.

Comparison of the compositional data obtained from the XPS survey spectra (3) and (4) reveals a significant increase in the surface concentration of carbon (C 1s) and a concomitant decrease in the surface concentration of Si (Si 2p) and O (O 1s) after the ROMP step, indicating that a polymer film was generated on the p-type (significant B 1s amount) Si/SiO_2 substrate (1). The Ru 3d peak, expected to occur after incubation of (2) with catalyst, is problematic to detect and quantify by XPS when C is present and when Ru occurs only in small amounts. Since the Ru 3d5/2 and the Ru 3d3/2 peak

positions are located within 5 eV of the C 1s peak, they can not be sufficiently de-convoluted in survey spectra.[3] Thus we focused on the presence of Cl as a quantitative reporter for the presence of catalyst. The Cl 2p appeared significantly (1.7%) above baseline contamination only in survey scan (3), indicating the successful immobilization of the catalyst. We also performed several control experiments to ascertain the level of spurious catalyst immobilization on ODMS SAMs (survey scans (6-9)). Control substrates (7-9) where all subjected to an indentical cleaning procedure: a CH_2Cl_2 rinse step followed by 10 min sonication in ethanol and then drying in a stream of dry nitrogen gas. The compositional analysis of scans (6) and (7) suggests that catalyst does not physisorb to a measurable extent on the ODMS SAM because the Cl (Cl 2p) surface concentration is not affected; however, some small amount of adventitious carbon, likely from the ethanol sonication, seems to have deposited on the ODMS SAM after the incubation and rinse step (C1s goes from 16.1% in (6) to 19.5% in (7)). Another control experiment was aimed to ascertain whether pinholes in the ODMS resist SAM could lead to significant, unwanted immobilization of Nbn-Si$(OEt)_3$ and thus, after a reaction step with the catalyst, to polymer growth.[7] Compositional analysis of survey scans (6) and (8) suggests that a small amount of Nbn-Si$(OEt)_3$ may have backfilled in pinholes of the ODMS resist SAM and enabled a trace amount of catalyst to be tethered to the surface because the surface carbon (C 1s) composition increased from 16% to 21%, and the Cl concentration (Cl 2p) increased from 0.4% to 0.7%. However, the small increase in the Cl concentration is considered to be still within the baseline contamination level. Considering that the surface carbon concentration changes only slightly after 12 h of ROMP (survey scans (8) and (9)), we conclude that any polymer formation on the ODMS resist must be insignificantly small. This is also consistent with the only small background contamination visible in AFM height images of polymer patterned substrates.

Nanopatterned samples were imaged by TappingMode™ AFM and by electric force microscopy (EFM). For EFM, n-doped silicon cantilevers (MESP probe, Veeco) were used and a positive DC bias voltage (+10V) was applied to the sample surface, while the interleave scan mode

allowed control over lift height. EFM was used to characterize the electronic state of the sample surface. The technique uses standard tapping mode atomic force microscopy (AFM) to get the topographic information of the sample surface; the tip is then lifted up to a fixed height to detect long-range electrostatic force (LiftMode^{TM}) while eliminating topographic interference and any other short-range forces. When an electric potential is applied to the conductive cantilever or the sample surface, a vertical electrostatic interaction between the conductive tip and the sample surface causes changes in resonance frequency of the cantilever and therefore the system detects frequency and phase shift due to electrostatic interaction. There are two main EFM modes: EFM-phase mode (or scanning conductance microscopy) and surface potential microscopy (or Kelvin probe microscopy). In our experiments on p-type Si/SiO_2 substates, the background surface electronic state is semiconducting, and thus only a relative comparison between a polymer pattern and the background should be considered. The magnitude of the phase gradient was gradually increased by increasing the applied voltage. A negative phase shift corresponds to a long-range attractive force gradient, described by equations (1) and (2) [8]:

(Phase shift) $$\Delta \boldsymbol{f} = -\arcsin\left(\frac{Q}{k}\frac{dF}{dz}\right), \quad (1)$$

(Force gradient) $$\frac{dF(z)}{dz} = \frac{1}{2}\frac{d^2C}{dz^2}(\Delta U)^2, \quad (2)$$

where Q is the quality factor, k is the spring constant, z is the distance between the tip and the surface, C is the capacitance, and ?U is the potential difference between the tip and the surface.

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