

Supporting Information

Self-Brushing for Nanopatterning: Achieving Perpendicular Domain Orientation in Block Copolymer Thin Films

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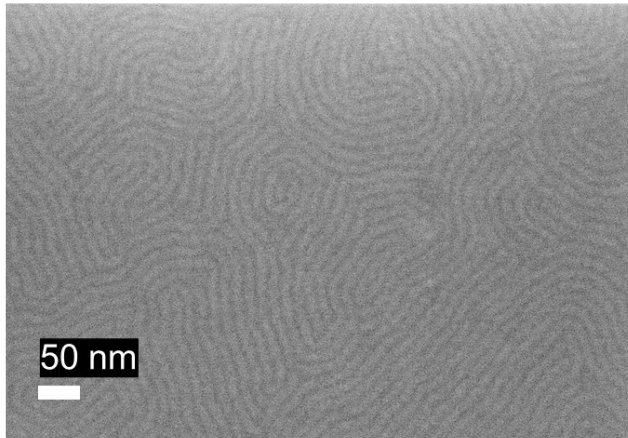
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(a)



(b)

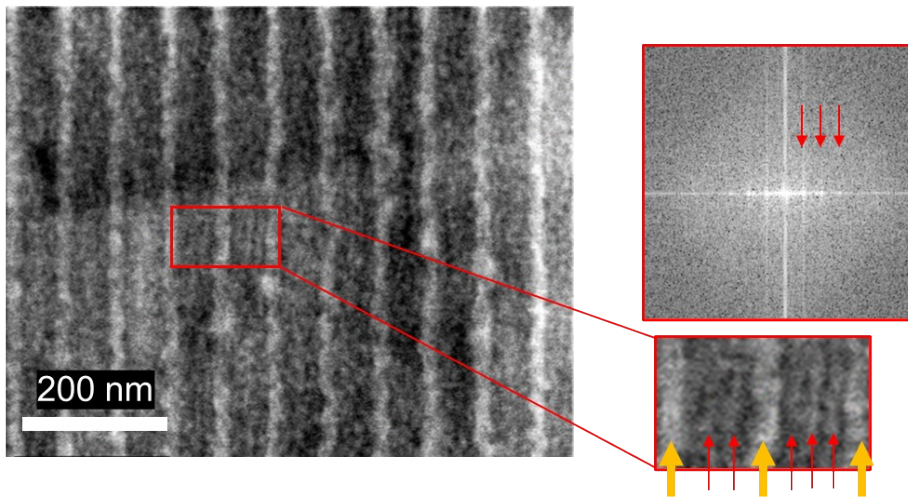


Figure S1. (a) Top-down SEM micrograph of S-*b*-G(TFET-*r*-2MP) with 400,000x magnification. The BCP was annealed on a piranha-treated Si surface. (b) Fourier Transform of post-rinse DSA sample. The red arrows indicate the periodic pitch of x-PS guide stripes. In zoom-in micrograph, red arrows indicate the residue SBL domain with pitch matching to the BCP. The orange arrows indicate the x-PS guide stripes. The relatively low contrast and waviness of the SBL layer is due to current induced film carbonization and defects in DSA.

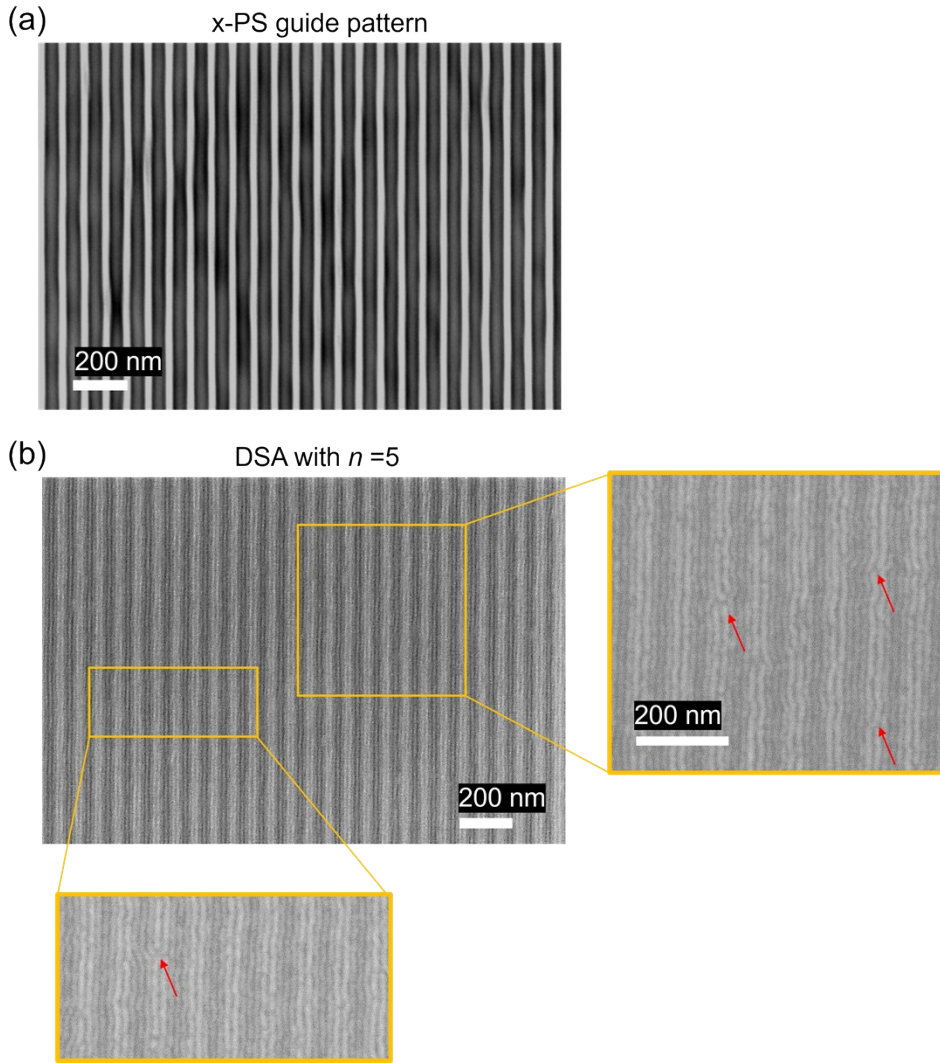


Figure S2. The potential of SBL for DSA. Top-down SEM micrograph of (a) the crosslinked polystyrene (x-PS) guide pattern with pitch $L_s=76$ nm and width $L_w=22$ nm; (b) DSA with $n = 5$ using self-brushing layer as the non-preferential brush. Two Zoom-ins on the selected region are also shown, where the red arrows indicate the presence of defects.

Table S1. Summarized literature values of surface tensions of substrates used in this work.

| Substrate ^a | Surface tension (mJ m ⁻²) | Reference |
|------------------------|--|-----------|
| S | 44.2 | 1 |
| Si | 1140-1900 | 2 |
| Au | 1175 | 3 |
| Pt | 2600-3500 | 4, 5 |
| Ti | 31-35 | 6 |
| SiN _x | 74 | 7 |
| AlN _x | 51 | 8, 9 |

^a S: polystyrene.

Table S2. Comparison of film thickness and grafting densities of SBL in this work and the summarized literature values of film thickness of ω -OH terminated polymer brushes.

| Polymer brush ^a | Reactive moiety to substrate | MW (kg mol ⁻¹) | Thickness (nm) | Grafting density (chain nm ⁻²) ^b | Reference |
|-----------------------------------|--|----------------------------|----------------|---|-----------|
| SBL in this work | Side chain secondary-OH (100 mol%) | 19.8 | 6.5 | 0.2 | N/A |
| S | ω -OH | 9.8 | 5 | 0.3 | 10 |
| P(S- <i>r</i> -M) with 45% S | ω -OH | 3.7 | 3.9 | 0.6 | 11 |
| P(S- <i>r</i> -M) with 58% S | ω -OH | 6.2 | 5-6 | 0.5 | 12 |
| P(S- <i>r</i> -M) with 62.5% S | ω -OH | 11.2 | 7.1 | 0.4 | 13 |
| P(S- <i>r</i> -M) with 62.4% S | ω -OH | 19.5 | 9.0 | 0.3 | 13 |
| P(S- <i>r</i> -M) with 72% S | ω -OH | 2.1 | 2.8 | 0.8 | 11 |
| PMMA | ω -OH | 8.0 | 5 | 0.4 | 10 |
| P(S- <i>r</i> -M- <i>r</i> -HEMA) | Side chain-OH (1-3 mol%) | 60.0-70.0 | 8 | 0.07-0.08 | 11 |

^a S: polystyrene; P(S-*r*-M) with #% S: poly(styrene-*random*-methyl methacrylate) with # mol% of S; PMMA: poly(methyl methacrylate); P(S-*r*-M-*r*-HEMA): poly(styrene-*random*-methyl methacrylate-*random*-hydroxyethyl methacrylate) copolymer.

^bThe grafting density is calculated using $\sigma = \frac{h\rho N_A}{M_n}$, where ρ is the density of the polymer (1.0 g cm⁻³ is used), N_A is the Avogadro's constant.

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