Hierarchical Patterns of Three Dimensional Block-Copolymer Films Formed by Electrohydrodynamic Jet Printing and Self-Assembly

Supplementary Information


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Figure S1. **Effect of the weight % of BCP in the ink and printing speed on the thickness of printed lines.** a) Thickness of printed lines as a function of the weight % of PS-\textit{b}-PMMA in the ink. The data points in the plot correspond to the average thickness of the ~3 \( \mu \)m lines printed with a 5 \( \mu \)m internal diameter nozzle. b) The height profiles of printed lines as a function of printing speed. The printing was performed using a 1 \( \mu \)m internal diameter nozzle.
**Figure S2. Mixing of printed BCPs on the surface.** SEM image shows the morphology of two crossing lines of different molecular weight BCPs. First a linear pattern of 37-37 K (vertical direction) and then 25-26 K (horizontal direction) PS-\(b\)-PMMA was printed. Thermal annealing was performed at 220 °C for 5 min.
Figure S3. Island/hole formation in printed BCP films. AFM image (after annealing) and cross-sectional height profile of printed 25-26 K PS-b-PMMA on a preferential wetting substrate.
Figure S4. Schematic of the terrace formation on preferential wetting substrates. The schematic is based on the height profile given in Figure 4c of the manuscript and the previously proposed mechanism for a BCP droplet.¹
Figure S5. The effect of thermal annealing on the cross-sectional height profiles of individual printed BCP lines. The molecular weight of PS-b-PMMA and printing speed are given at the top of the plots. The substrate is neutral wetting for the all cases.
Figure S6. Effect of the annealing time on the height profile of printed BCP films. AFM image of 20 µm wide square films of 25-26 K PS-b-PMMA printed on a neutral wetting substrate. a) Before annealing, b-e) After annealing at 220 °C for b) 2 min, c) 5 min, d) 15 min, e) 1 h and f) 5h.
**Figure S7. BCP films near the edge of a printed square.** SEM images were taken at the edges of the films presented in Figure 4 of the manuscript. a) ~30 nm film of 37-37 K (Fig 4a), b) ~30 nm film of 25-26 K (Fig 4b), c) ~70 nm film of 25-26 K (Fig 4d) PS-\textit{b}-PMMA. The substrate is neutral wetting for the all cases.
Figure S8. Printed BCP lines near the wall. SEM images of individual printed lines near the edge of the topographical patterns, for MWs of (a) 37-37 K and (b) 25-26 K. c) Movement of 37-37 K PS-\(b\)-PMMA microns away from to the central axis of the line near the wall. The wall is 70 nm high and preferential wetting to the PMMA block. The bottom substrate is neutral wetting.

References