

Supplementary Information for

Automated Solvent Vapor Annealing with Nanometer Scale Control of Film Swelling For Block Copolymer Thin Films

Hanna Hulkkonen^{1*}, Turkka Salminen² & Tapio Niemi^{1*}

¹Nanophotonics, Faculty of Engineering and Natural Sciences,
Tampere University, 33101 Tampere, Finland

²Tampere Microscopy Center,
Tampere University, 33101 Tampere, Finland

Locality of the vapor saturation

In the SVA system, the relative solvent saturation P/P_{eq} can be modulated near the substrate by either heating or cooling the local environment. To demonstrate the effect, the sample stage was heated or cooled and the relative saturation of water vapor measured in different locations inside the annealing chamber using a Sensirion Humidity logger. Figure S2 displays the measured relative saturation of water vapor (i.e. relative humidity) on the sample stage and approximately 1 cm above the stage. When the stage temperature was decreased, the relative saturation increased in the vicinity of the stage compared to the chamber space above (Figure S2a, $T_{stage} = 18^\circ\text{C}$, $T_{\text{H}_2\text{O}} = 21^\circ\text{C}$). Figure S2b shows the difference between the P/P_{eq} values that were measured on stage and above the stage at different stage temperatures. While the P/P_{eq} measured above the stage was largely unaffected by the stage temperature, on the stage even $\pm 1^\circ\text{C}$ a difference changed the obtainable relative saturation significantly.

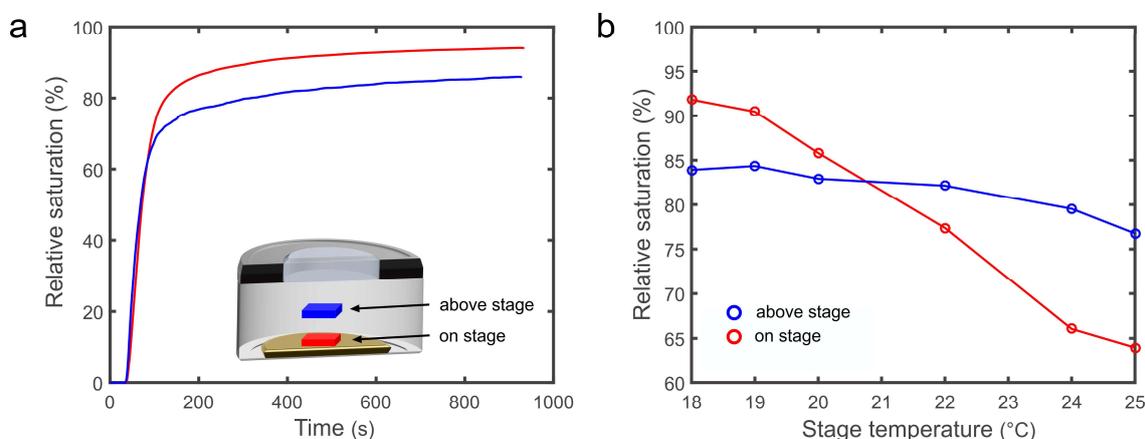


Figure S1. (a) The relative water vapor saturation in the chamber in two different locations. Bubbler flow (0.1 l/min) switched on at 30 s, after which the P/P_{eq} begins to increase as the chamber is filled with the H_2O vapor. Vapor temperature $T = 21^\circ\text{C}$ and stage temperature $T = 18^\circ\text{C}$. (b) The spatial difference in the relative saturation of H_2O vapor when the sample stage is heated or cooled. Measurements were done at constant stage temperature after waiting 10 min for the chamber atmosphere to stabilize. The lines are a guide to the eye.

BCP thin film swelling

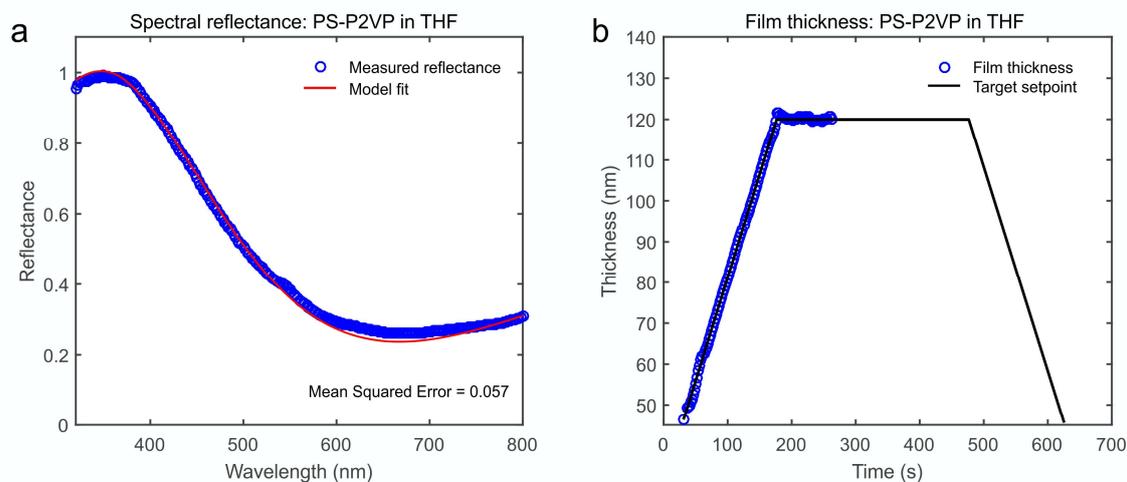


Figure S2. Screenshot of the video SV1. (a) Real-time reflectance modeling and (b) film thickness determination during SVA of PS-P2VP in THF. The reflectance and model data are stored every 1-2 s while the duration of each control loop is 30 ms. The film swelling follows an annealing profile with a swelling rate +30 nm/min, dwell time 5 min at a thickness of 120 nm and a deswelling rate of -30 nm/min.

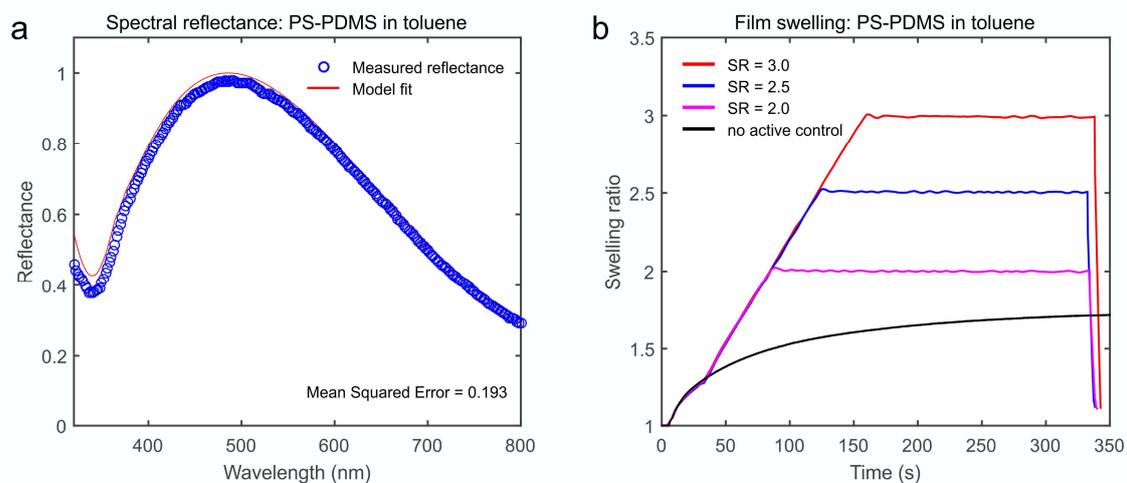


Figure S3. (a) Spectral reflectance modeling during automated SVA of high-molecular weight PS-PDMS in toluene (at $t = 125$ s, $SR = 2.5$). (b) Controlled and uncontrolled swelling of 172 kg/mol PS-PDMS ($M_{PS} = 61$ kg/mol, $M_{PDMS} = 111$ kg/mol) in toluene. The PS-PDMS was spincoated onto unmodified Si wafers from a 1% cyclohexane solution. Uncontrolled SVA was performed with a constant vapor flow rate and stage temperature ($T = 20^\circ\text{C}$). The film swelling in feedback-controlled SVA followed the predetermined swelling profile with the SR set to 3.0, 2.5 and 2.0.

Order-disorder transition of PS-P2VP

BCPs with different molecular weights have an order-disorder transition (ODT) at different polymer concentrations (i.e. swelling ratios). The order-disorder limit for cylinder-forming BCPs ($f_A = 0.23$) has been estimated using self-consistent field theory as $(\chi N)_{ODT} = 18.63$, where N is the degree of polymerization and χ the Flory-Huggins interaction parameter.¹ For PS-P2VP, the Flory-Huggins parameter has been reported as²

$$\chi = \frac{63}{T} - 0.033$$

When the BCP is swollen by a neutral solvent, the effective interaction parameter is given as $\chi_{eff} \sim \chi\phi^\beta$, where $\beta = 1.3 - 1.6$.³ The polymer concentration ϕ at ODT can then be estimated from the combined approximation:

$$\chi\phi^\beta N = (\chi N)_{ODT} = 18.63$$

For 258 kg/mol PS-P2VP ($N \sim 2480$) at $T = 20^\circ\text{C}$ and $\beta = 1.6$, this gives an ODT concentration of $\phi_{PS-P2VP} = 0.136$ corresponding to a swelling ratio of $SR = 7.33$.

Directed self-assembly and large-area order

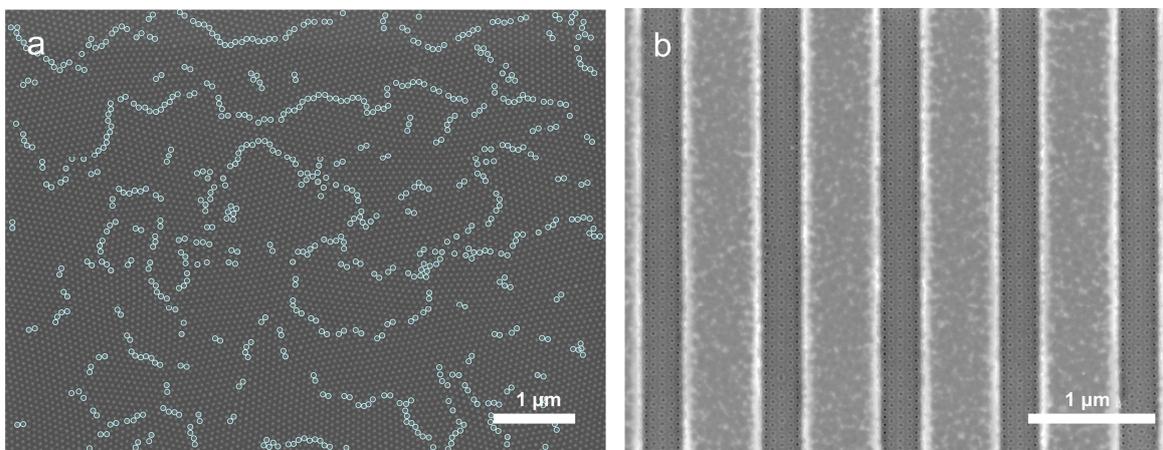


Figure S4. (a) A representative SEM image of 258 kg/mol PS-P2VP on an unmodified silicon substrate annealed in THF ($SR = 3.53$, dwell time = 25 min). The PVP domains were stained with a platinum salt for imaging. The lattice defect locations obtained from the image analysis are circled in light blue. (b) An example of directed self-assembly of high-molecular weight PS-P2VP on a lithographically pre-patterned silicon template. Long-range alignment of perpendicular cylinders can be achieved in the 355 nm-wide trench pattern after 15 min of controlled SVA in THF. The PVP domains were selectively removed by dipping in ethanol for SEM imaging contrast.

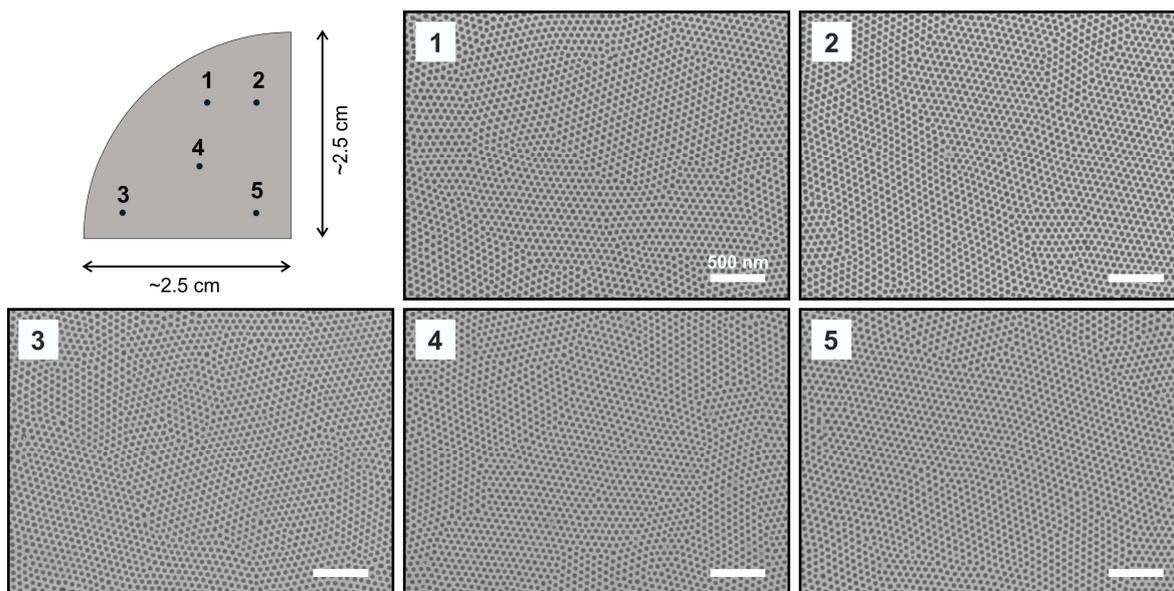


Figure S5. Large-area self-assembly of high molecular weight PS-P2VP on unmodified quarter 2-inch Si wafers using feedback-controlled SVA in THF (SR = 3.15, dwell time = 10 min). The cylinder pattern was shallowly etched into the Si surface using SF_6/O_2 dry etching. The top-down SEM images 1-5 are from five different locations on the etched wafer as depicted in the illustration.

References

- 1 S. Kim, W. Li, G. H. Fredrickson, C. J. Hawker and E. J. Kramer, *Soft Matter*, 2016, **12**, 5915–5925.
- 2 K. Dai and E. J. Kramer, *Polymer (Guildf)*, 1994, **35**, 157–161.
- 3 T. P. Lodge, K. J. Hanley, B. Pudil and V. Alahapperuma, *Macromolecules*, 2003, **36**, 816–822.