Electronic Supplementary Information

Periodic Nanoscale Patterning of Polyelectrolytes over Square Centimeter Areas Using Block Copolymer Templates

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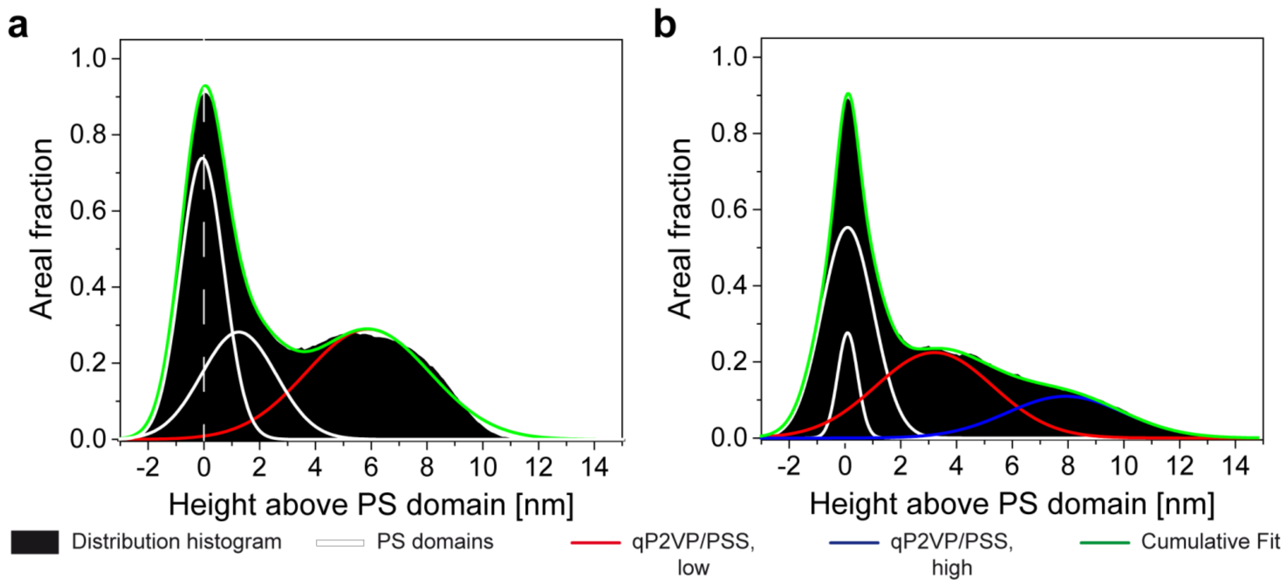

Figure S1. Representative height distribution histograms of $PS_{124}P2VP_{61}$ ESA template after 30 min dipping in PSS solution of the (a) smooth and (b) coarse pattern. Two Gaussians are used to fit the PS domains (white curves). The qP2VP/PSS domains were fitted to one Gaussian function (red curve) in the case of the smooth deposition pattern (a; fitting to 2 Gaussian functions showed marginal contribution of the tallest features) and to two Gaussian functions (red and blue curves) in the case of the coarse deposition pattern (b; Figure S5b below shows that both low and high features contribute significantly to the distribution).

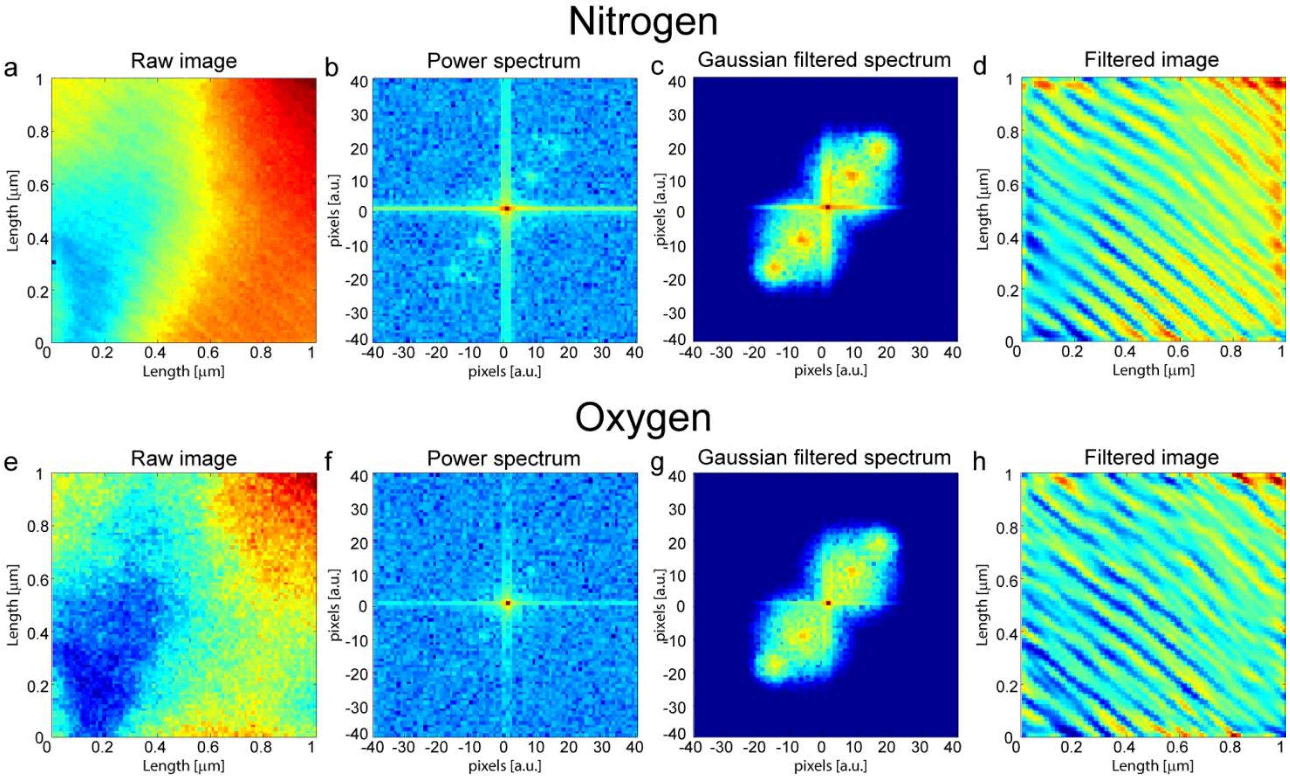

Figure S2. STXM images of nitrogen (a-d) and oxygen (e-h) for the $PS_{124}P2VP_{61}$ ESA templates after 30 min PSS deposition. (a,d) Raw images; (b,f) power spectra obtained from the two-dimensional Fourier analysis of the raw image; (c,g) filtered power spectra using Gaussian functions; (d,h) filtered images after applying the reverse Fourier transform.

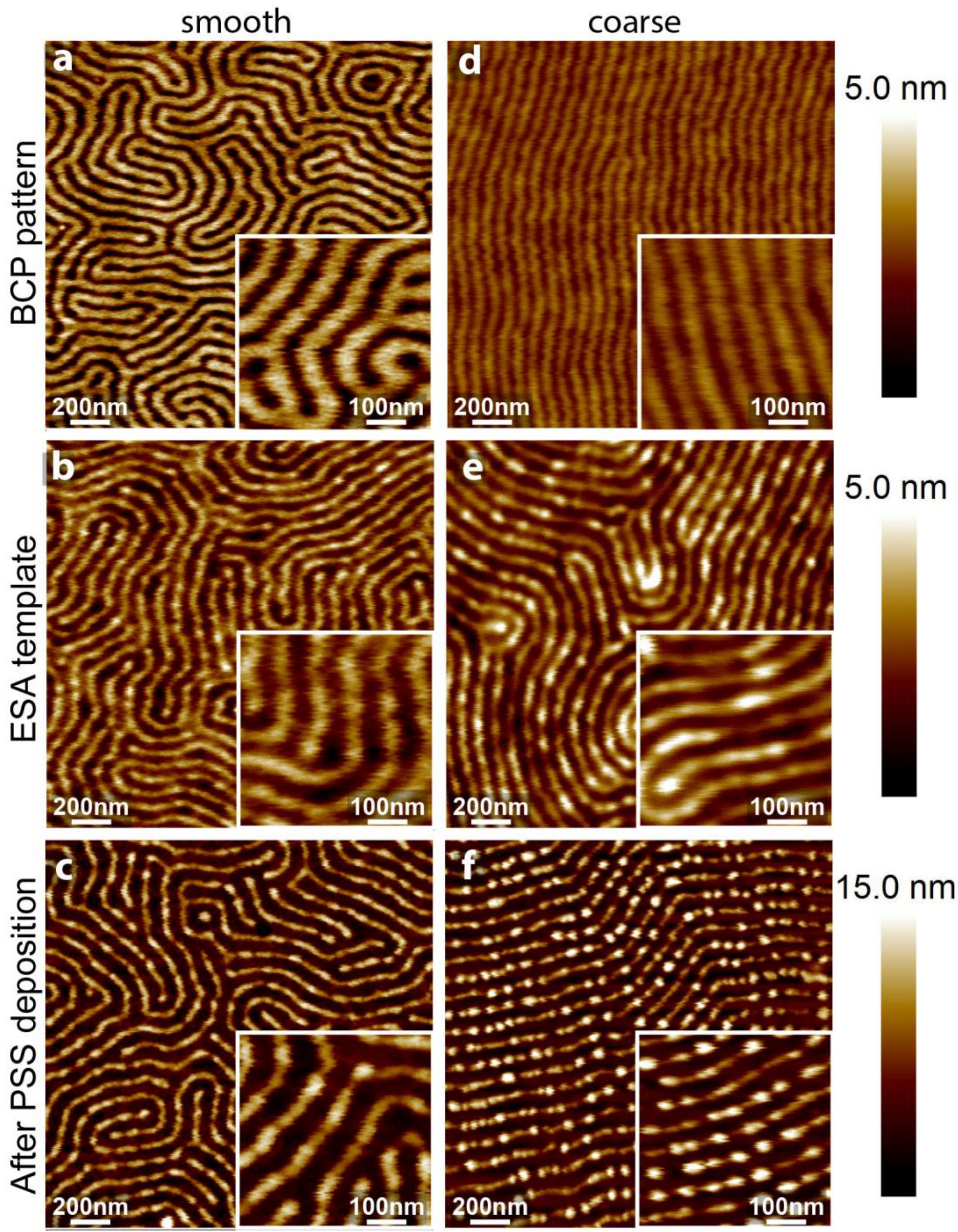

Figure S3. AFM height images of the two $PS_{124}P2VP_{61}$ patterns (smooth and coarse; a,d), the corresponding ESA templates (b,e), and the ESA templates after PSS deposition for 30 min (c,f). The higher domains in b,c,e,f are identified as the P2VP domains.

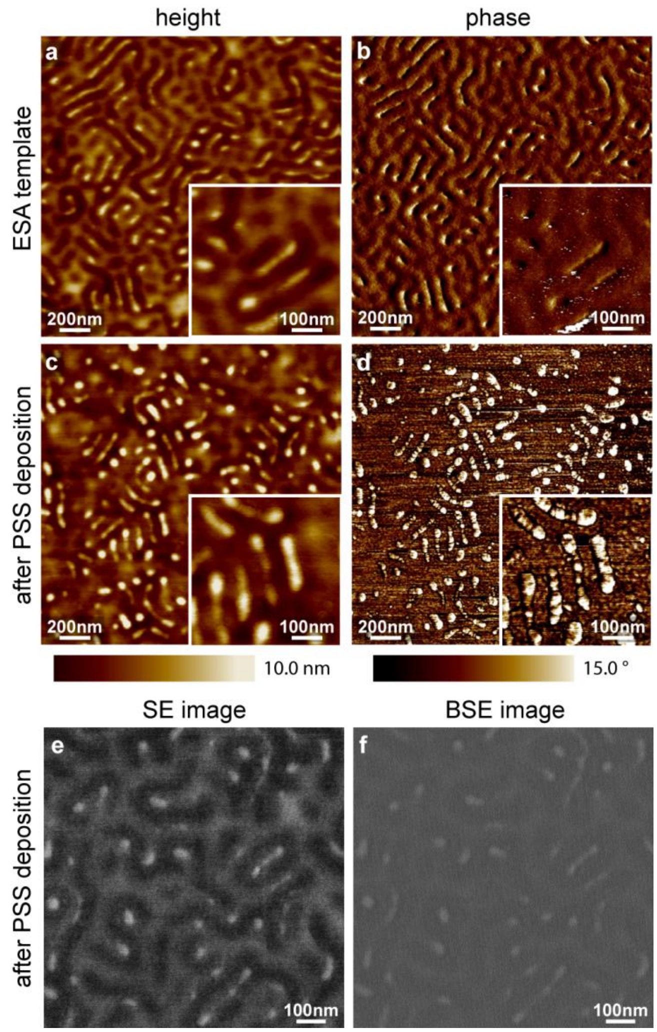

Figure S4. Height and phase AFM images of $PS_{106}P2VP_{115}$ template featuring partially exposed qP2VP domains before (a,b) and after (c,d) PSS deposition. (e,f) XHR-SEM images correspond-ing to the sample in (c) obtained using (e) secondary electrons detector and (f) back-scattered electrons detector. The correlation between the higher domains (brighter tone in (e)) and the high electron density domains (brighter tone in (f), attributed to PSS) confirms the selectivity of PSS to the qP2VP domains.

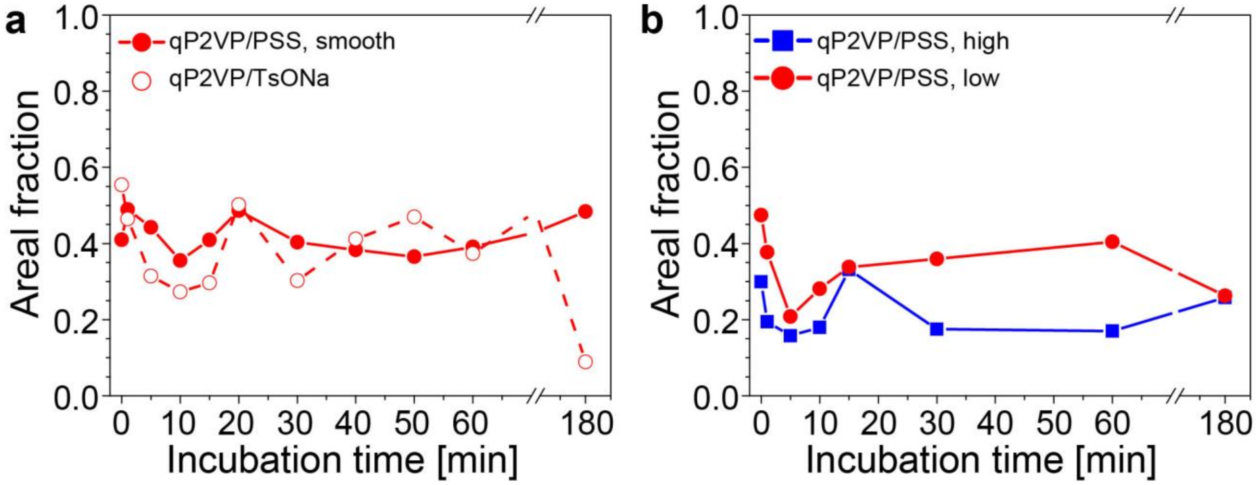

Figure S5. Complementary data for Figure 6, showing largely invariant areal fractions for each height feature with deposition time for both the (a) smooth and (b) coarse deposition patterns.

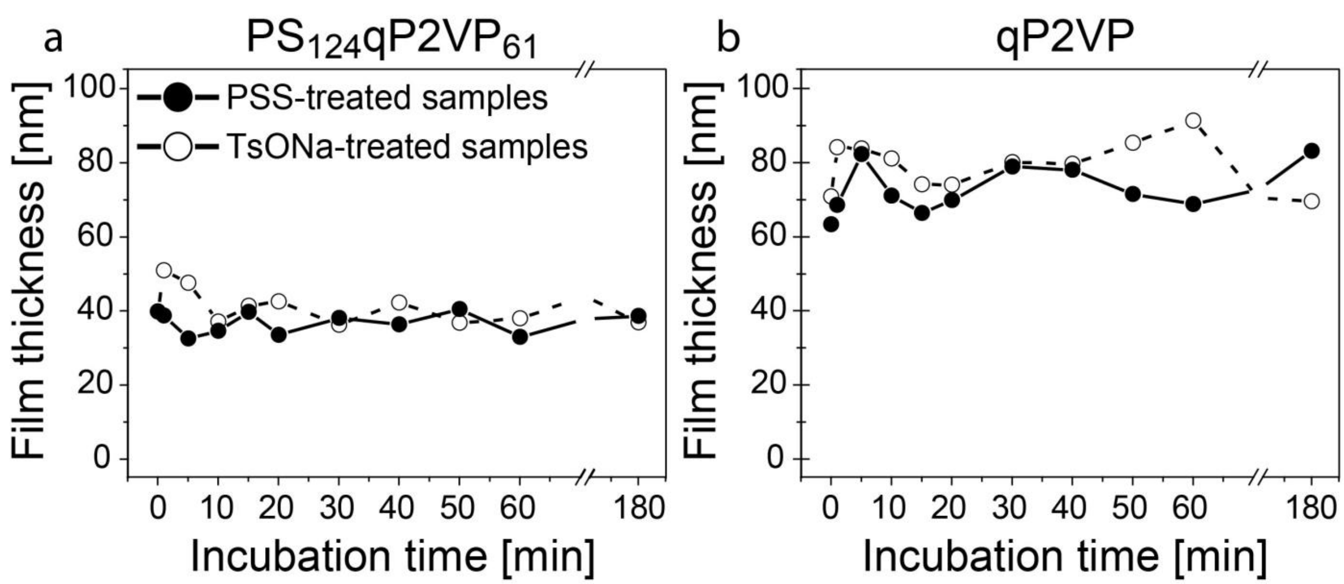

Figure S6. Total film thicknesses of (a) $PS_{124}P2VP_{61}$ ESA template, and (b) qP2VP homopolymer films, after dipping in PSS (filled circles) or TsONa (empty circles) solutions for different time intervals, determined by AFM scratch profiling.

Additional control experiments

The importance of pyridine alkylation. In principle, transforming the P2VP domains into ESA substrates may be induced simply by protonation by the slightly acidic PSS solution (pH 4.7).[1] To address the question regarding the necessity of alkylation, non-quaternized $PS_{124}P2VP_{61}$ patterns were dipped into PSS solution for 30 min. **Figure S7** presents spectroscopy images and XPS spectra of the resulting morphologies. The sulfur XPS spectra (**Figure S7**e) show that PSS deposition indeed occurred under these conditions. Microscopy images (**Figure S7**a-b) show that PSS deposition is indeed selective toward the protonated P2VP domains (denoted as P2VP-H^+ in this section). Nonetheless, comparing the SEM images **Figure S7**a and Figure 2c reveals a much less uniform deposition along the stripes; AFM images shows that PSS formed much wider, globular aggregates over the P2VP-H^+ domains (**Figure S7**b), which conform less to the P2VP stripes compared with PSS deposited over DIB-treated qP2VP domains (**Figure S3**c,f). This suggests that protonation leads to smaller charge densities at the surface of the P2VP domains compared with alkylated pyridines.

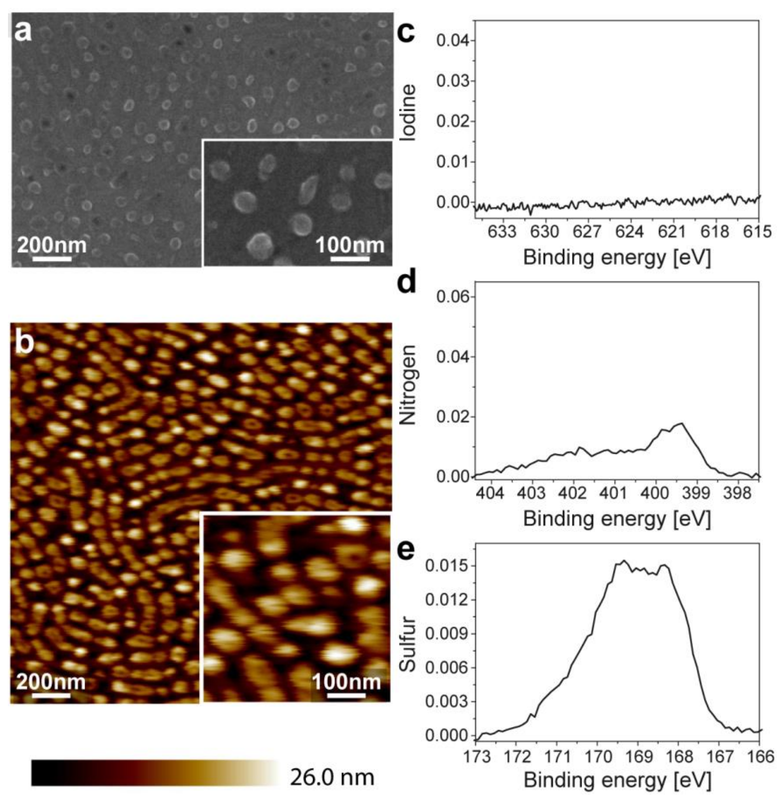

Figure S7. (a) SEM and (b) AFM height images and (c-e) corresponding XPS spectra of a $PS_{124}P2VP_{61}$ pattern that was not treated with DIB, after 30 min dipping in a PSS solution.

The importance of cross-linking the P2VP domains. DIB was chosen as the alkylating agent not only because it enables creating permanent charges by irreversible alkylation, but also because it cross-links the P2VP domains and thus hinders morphological changes during PSS deposition. To probe the necessity for cross-linking, ESA templates were created using 1-iodobutane (IB) as a mono-functional alkylating agent. **Figure S8** presents the morphologies of the $PS_{124}P2VP_{61}$ film after reaction with IB and subsequent PSS deposition. Although the morphology is maintained after IB treatment, PSS deposits non-uniformly along the qP2VP stripes.

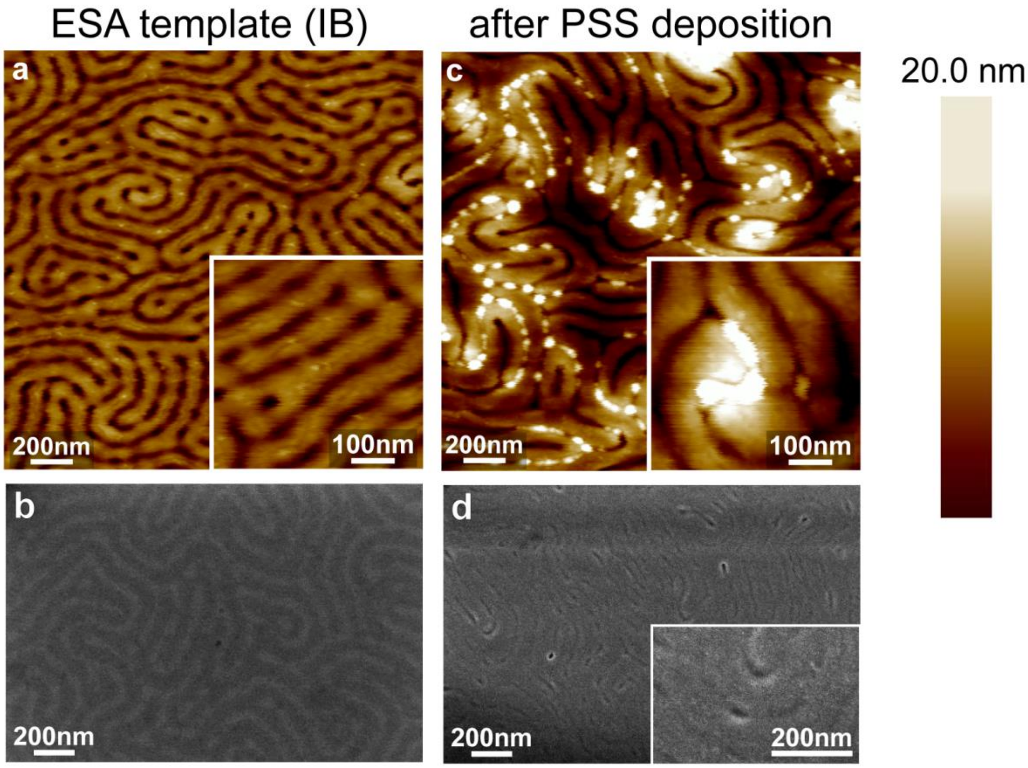

Figure S8. AFM and SEM images of $PS_{124}P2VP_{61}$ ESA template formed after treatment with 1-iodobutane (IB) before (a,b) and after (c,d) 30 min PSS deposition. Lack of cross-linking leads to considerable P2VP domain swelling and less uniform PSS deposition.

References

1 D. Nepal, M. S. Onses, K. Park, M. Jespersen, C. J. Thode, P. F. Nealey and R. A. Vaia, *ACS Nano*, 2012, **6**, 5693-5701.