Supporting Information

Non-Native Square Packing and Structural Arrangement of Ultrahigh Molecular Weight Diblock Copolymer from One-step Solvent Vapor Annealing

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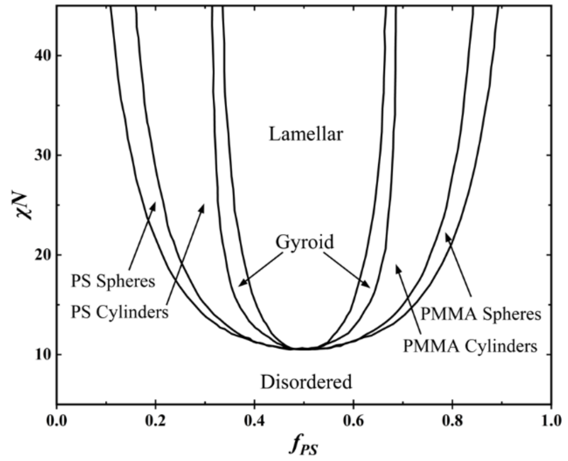

$$N_{PS-b-PMMA(537k-265k)} = \frac{M_{w_{PMMA}}/\rho_{PMMA} + M_{w_{PS}}/\rho_{PS}}{M_{S_{PS}}/\rho_{PS}} = 7832$$

$$N_{PS-b-PMMA(140k-60k)} = \frac{M_{w_{PMMA}}/\rho_{PMMA} + M_{w_{PS}}/\rho_{PS}}{M_{S_{PS}}/\rho_{PS}} = 1943$$

$$f_{PS-b-PMMA(537k-265k)} = \frac{M_{w_{PMMA}}/\rho_{PMMA}}{M_{w_{PMMA}}/\rho_{PMMA} + M_{w_{PS}}/\rho_{PS}} = 30.5\%$$

$$f_{PS-b-PMMA(140k-60k)} = \frac{M_{w_{PMMA}}/\rho_{PMMA}}{M_{w_{PMMA}}/\rho_{PMMA} + M_{w_{PS}}/\rho_{PS}} = 30.0\%$$

$$\chi N_{PS-b-PMMA(537k-265k)} = 0.043 \times 7832 = 337$$

$$\chi N_{PS-b-PMMA(140k-60k)} = 0.043 \times 1943 = 84$$

Figure S1. A typical phase diagram of PS-b-PMMA diblock copolymer and basic parameter of two PS-b-PMMA block-copolymer used in this study

$$\delta_{PS} = 18.6MPa^{0.5}$$

$$\chi = \frac{V_{solvent}}{RT}(\delta_{solvent} - \delta_{polymer})^2 + 0.34$$

$$\delta_{PMMA} = 19.0MPa^{0.5}$$

Solvent	VP(kPa) at 25°C	$\delta_{solvent}$(MPa$^{0.5}$)	V_s(ml/mol)	χ_{PS-S}	χ_{PMMA-S}
THF	**21.6**	**19.5**	**81.3**	**0.34**	**0.88**
Acetone	**30.7**	**19.9**	**73.7**	**1.1**	**0.29**
Chloroform	**26.7**	**18.9**	**80.2**	**0.34**	**0.34**
PGMEA	**0.5**	**17.4**	**136**	**0.42**	**0.48**
TCE	**9.1**	**17.5**	**89.7**	**0.39**	**0.43**

Table S1. Polymer-solvent Flory-Huggins interaction parameters.

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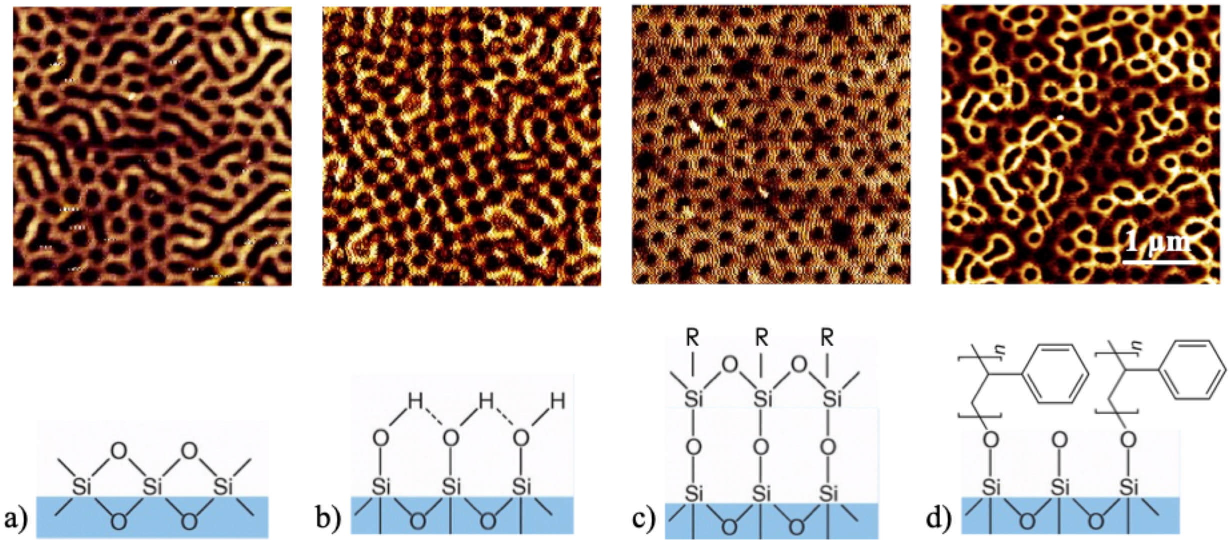

Figure S2. AFM images of SVA 110 nm PS-b-PMMA film with the different silicon substrate treatments: (a) IPA rinsed, (b) piranha cleaned, (c) OTS modified, (d) grafted PS-brush.

Calculation of the Natural Period L_0 of PS-b-PMMA (537k-265k) & (140k-60k)

Using strong-segregation theory (SST) [1–3], the equilibrium natural period L_0 of microphase-separated diblock copolymer is set by the balance between chain stretching and interfacial segregation energies, which yields the SST scaling form:

$$L_0 \approx CaN^{\frac{2}{3}}\chi^{\frac{1}{6}}$$

Where a is an effective statistical segment length that maps the coarse-grained Gaussian-chain description to a real-space length scale, N is the total degree of polymerization, χ is the Flory–Huggins interaction parameter for PS/PMMA, and C is an order-unity perfector that weakly captures morphology- and composition-dependent geometric factors that are not resolved in the scaling law. For PS-b-PMMA (537k-265k), the volume fraction $f = 30.5\%$, consistent with PMMA cylinders in a PS matrix. An effective value $a = 0.695$ nm was adopted for ultra-high molecular weight as a representative segment-length scale for PS/PMMA to convert the SST scaling relation into a dimensional estimate of L_0. The prefector was set to $C \approx 1$ for it is expected to be for unity and the present calculation is intended as a first order estimate for thickness normalization rather than a parameter-free prediction. substituting these values yields:

$$L_{0(537k-265k)} \approx 0.695 \times 7835^{\frac{2}{3}} \times 0.043^{\frac{1}{6}}\, nm \approx 163 nm$$

Similarly, for PS-*b*-PMMA (140k-*b*-60k), the volume fraction $f = 30.5\%$, consistent with PMMA cylinders in a PS matrix. The same values of $a = 0.695$ nm and $C \approx 1$ were used for calculation consistency. Substituting values of PS-b-PMMA (140k-60k) system, the estimated natural period is:

$$L_{0(140k-60k)} \approx 0.695 \times 1943^{\frac{2}{3}} \times 0.043^{\frac{1}{6}}\, nm \approx 64nm$$

So, the value $L_{0(537k-265k)} \approx 163nm$ and $L_{0(140k-60k)} \approx 64nm$ are used to normalize film thickness as t/L_0 in the subsequent analysis.

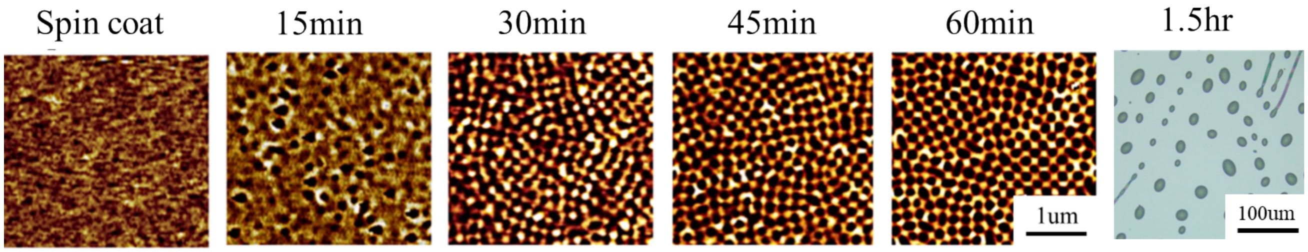

Figure S3. AFM images of the structure evolution of 110 nm thick PS-b-PMMA film during SVA.

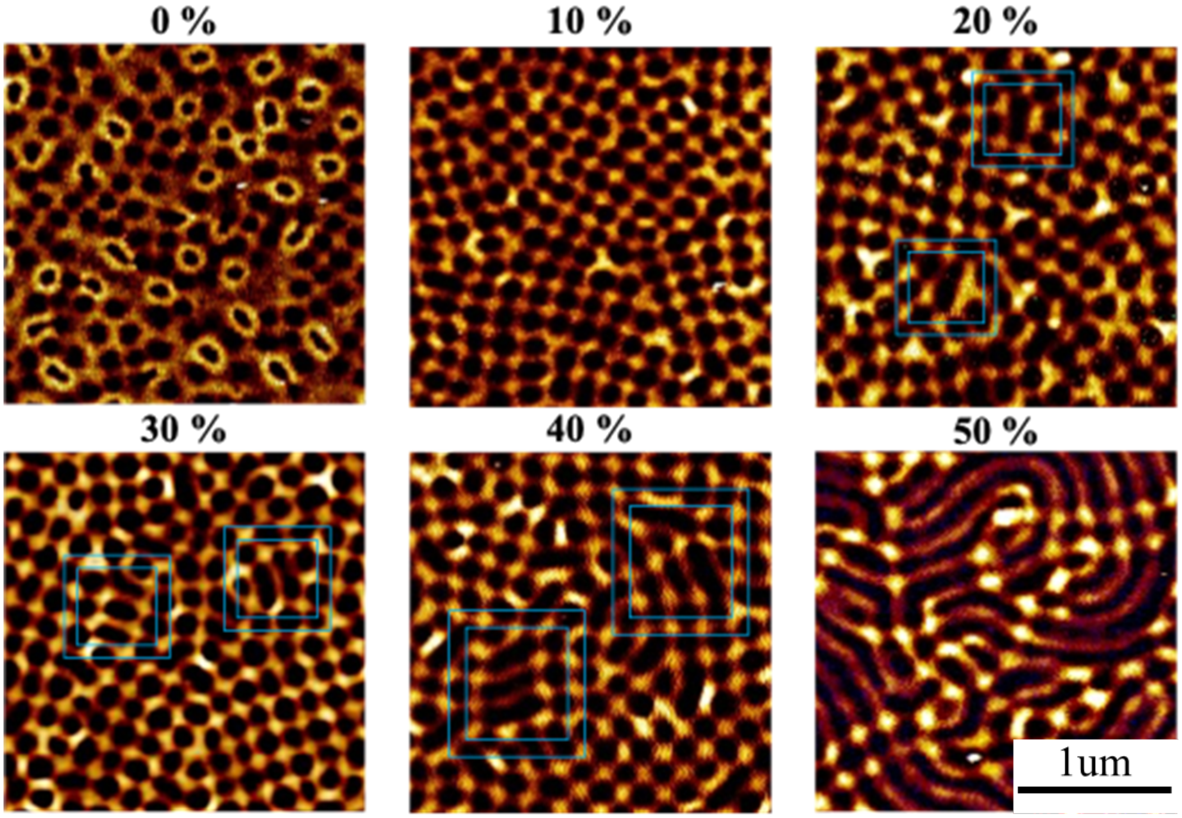

Figure S4. Enlarged AFM images of 110nm 1-hour SVA PS-b-PMMA film with 0-50 wt% of PMMA homopolyer.

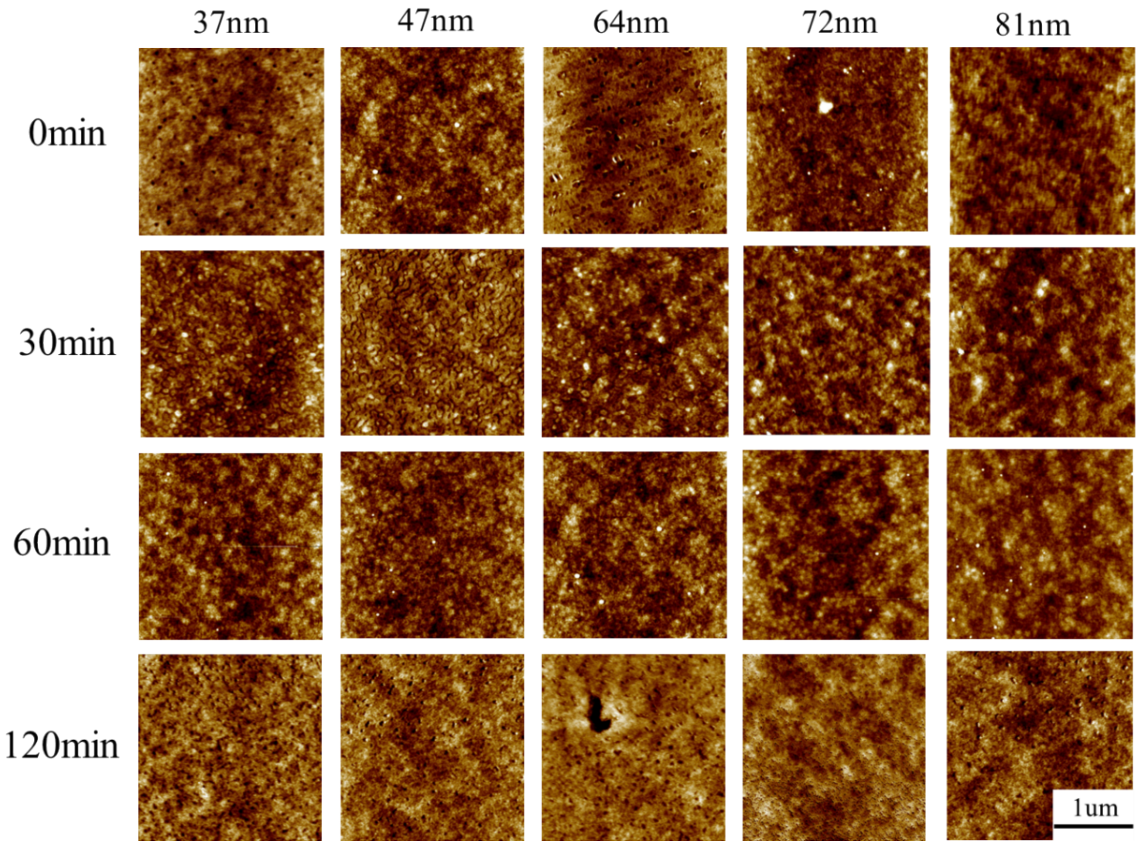

Figure S5. AFM height images of PS-b-PMMA (140k-60k) structural evolution. Films with different thicknesses (37nm-81nm) correspond to 0.57-1.3L_0 range after solvent vapor annealing (SVA) in saturated TCE vapor for varying times, all AFM images are shown at same scale.

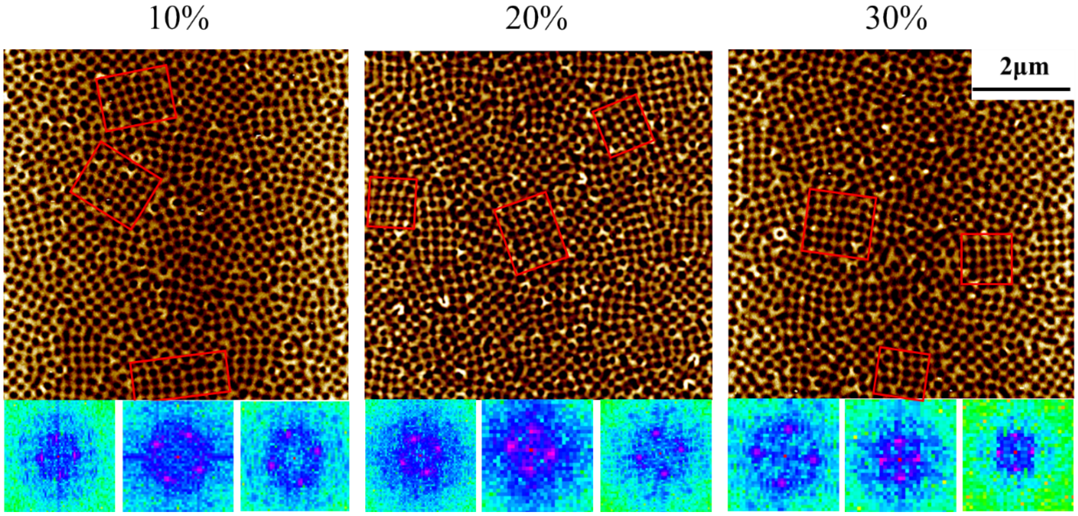

Figure S6. Representative square array pattern formed by 10-30% homopolymer addition. The 2D FFT pattern corresponds to highlighted square array domains.

Reference

1 G. Fredrickson, *The Equilibrium Theory of Inhomogeneous Polymers*, DOI:10.1093/acprof:oso/9780198567295.001.0001.
2 M. W. Matsen and M. Schick, *Phys. Rev. Lett.*, 1994, **72**, 2660–2663.
3 F. S. Bates and G. H. Fredrickson, *Annu. Rev. Phys. Chem.*, 1990, **41**, 525–557.