Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information for:

Real-time and *in-situ* observation of structural evolution of giant block copolymer thin film under solvent vapor annealing by atomic force microscopy

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Section ESI.1: Defect density analysis

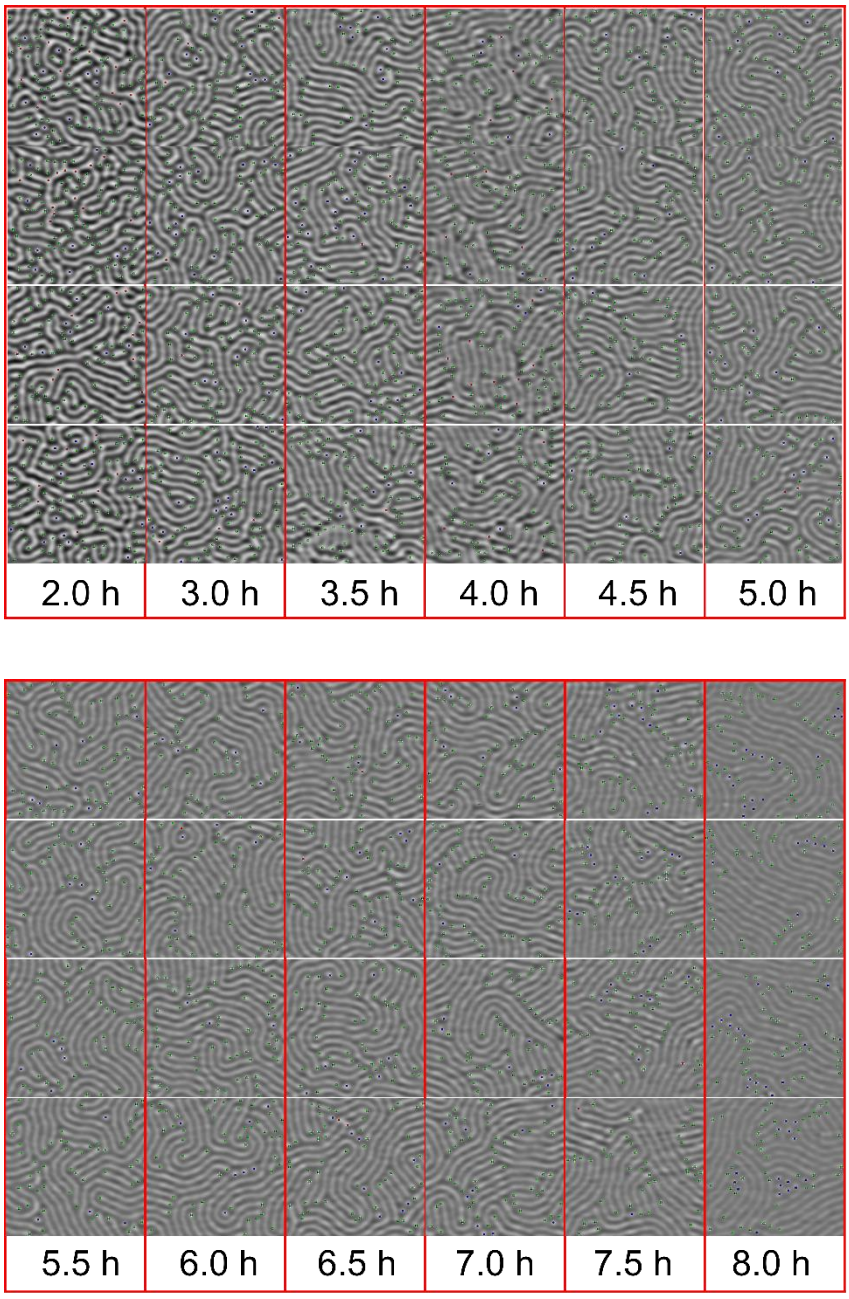

Fig. S1: Defect density analysis. Dots: blue, Terminal: green, and Junction: red.

Section ESI.2: Experiments for the data validation of *in-situ* AFM measurement

a) Materials and sample preparation

The homopolymers selected had molecular weights very close to that of the BCP (PS: PMMA = 510:500 kg mol^{-1}) used in this study. The PS (mfd. by Tosoh Corporation) had a M_n of 427 kg mol^{-1} and PDI of 1.02, and the PMMA (mfd. by Showa Denko K.K.) had a M_n of 505 kg mol^{-1} and PDI of 1.02. Both were used as received. The PS was spin-cast from a toluene solution, while the PMMA was cast from a propylene glycol monomethyl ether acetate (PGMEA) solution, due to its being insoluble in toluene. All substrates were dried under vacuum overnight to remove residual solvent.

b) Solvent vapor annealing using reflectometry

Before performing solvent vapor annealing (SVA), the refractive index dispersions of the polymers (BCP, PS homopolymer, and PMMA homopolymer) were determined by using ellipsometry to measure a film of each polymer cast onto a bare Si substrate. For SVA, each polymer was spin-cast onto a Si wafer that was previously polymer brush grafted.

The polymer-casted substrates were placed into an aluminum SVA chamber with a glass lid, THF was introduced, and the swelling ratio of the films were adjusted by way of the N_2 flow rate. The swollen film thickness was measured by reflectometry using a built-in function of the F-50, by fitting the reflective spectra with the changing n and thickness.

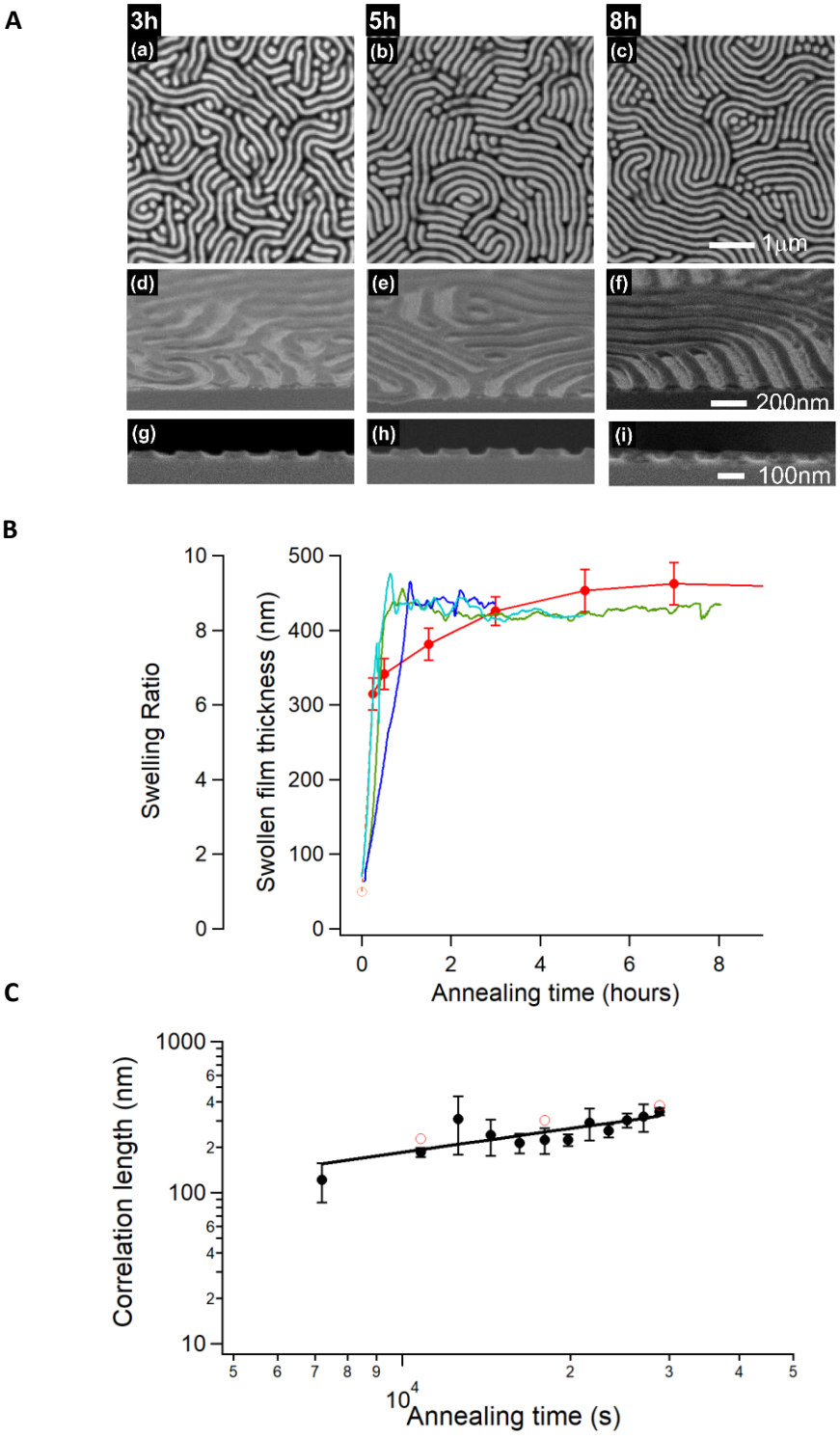

Fig. S2: Solvent vapor annealing in a different SVA chamber for 3, 5 or 8 hours.

A: AFM (dry, before selective etching) and cross-sectional Tilt-SEM (after selective etching) images

B: Temporal swelling ratio measured by reflectometry. (overwritten onto Fig. 3B)

C: Correlation length of each AFM image in dry condition (red circle, overwritten onto Fig. 5A)

c) The selective swelling of PS and PMMA homopolymers in THF

To prevent dewetting, the dry film thickness was set at around 300 nm. The substrates were placed close to each other, and the swollen film thickness of PS was measured first. After saturating, 10 data points (in 10 seconds) were collected as the average swollen film thickness at that condition, and PMMA thin film is measured right after that. This set of measurements was repeated 7 times at different N_2 flow rates. Higher swelling ratios could not be obtained due to dewetting. The obtained swollen film thickness of each polymer was divided by the original dry film thickness and shown as the swelling ratio T on the left axis in Fig. S3. The swelling selectivity, T_{PS}/T_{PMMA}, was plotted on the right axis of Fig. S3.

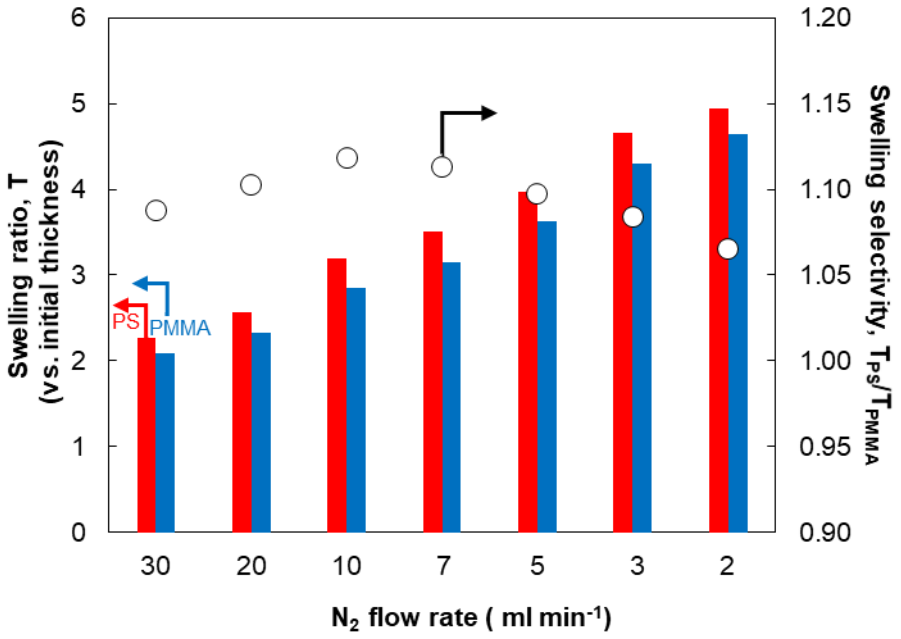

Fig. S3: THF swelling selectivity of PS and PMMA homopolymer thin films

d) The structural periods observed in the *in-situ* AFM images

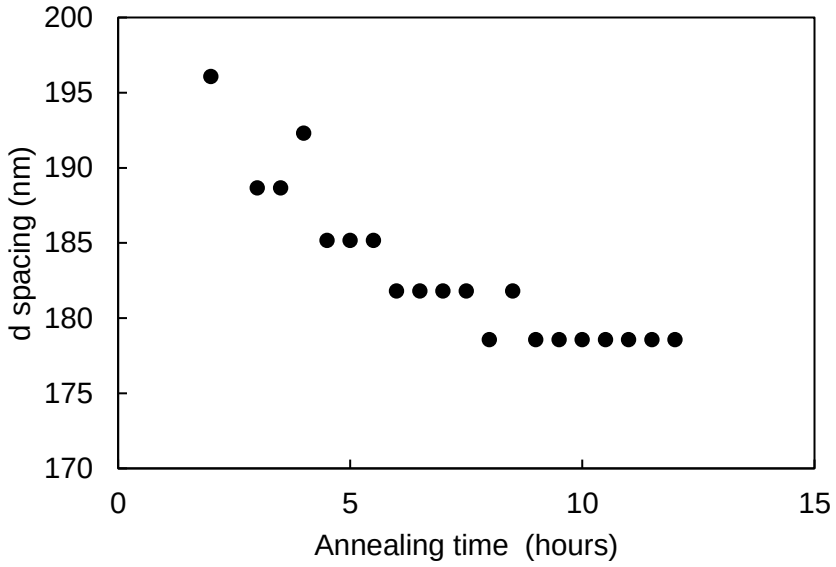

Fig. S4: Periodicities from AFM tapping images under swollen state
(obtained by FFT of images in Fig. 4). The resolution of 4.66 nm pixel^{-1} of AFM yields the steps.

e) Ultra Small-Angle X-ray Scattering (USAXS) measurement of bulk BCP phase-separated pellets

100 mg of BCP was dissolved in 10 g of THF, filtered (0.2 μm pore) and slowly dried (30 mg h^{-1}) at room temperature. The microphase separated pellets were dried at room temperature under vacuum overnight, after which half was then additionally thermally annealed (240°C, 3h under vacuum).

USAXS (L= 41 m) measurement was performed on both pellet types using a synchrotron light source (Spring-8, BL19B2). The scattering peaks we picked are shown as arrows in Fig. S5.

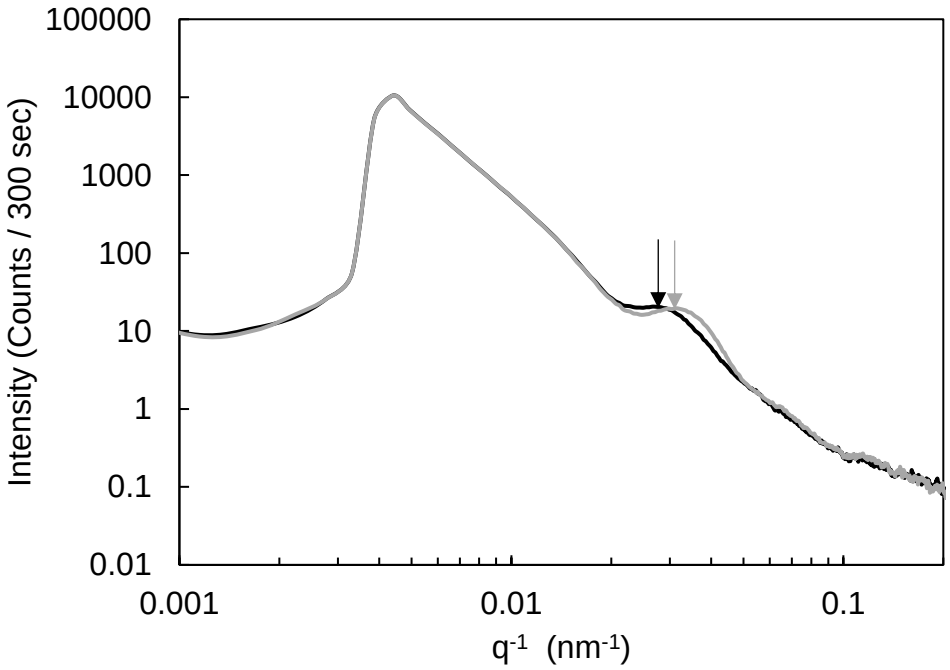

Fig. S5: USAXS of bulk BCP phase-separated pellets. Black: as prepared (before thermal annealing), gray: after thermal annealing (240°C, 3h)