Supplementary Material (ESI) for Soft Matter

Electronic Supplementary Information

Phase transition behavior in thin films of block copolymers by use of immiscible solvent vapors

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Table S1. The swelling degrees, vapor pressures, and vapor compositions in equilibrium at 17 ^{o}C and 22 ^{o}C.

	Swelling degree (t/t_0)			Vapor Pressure (mmHg)			Vapor Composition (%)	
	Benzene	Benzene/Water w/o preswelling	Benzene/Water w/ preswelling	Benzene	Water	Benzene/Water	Benzene	Water
17 ^{o}C	1.51	1.69	1.82	70.6	14.5	85.1	83	17
22 ^{o}C	1.65	1.74	1.88	88.4	19.8	108.2	82	18

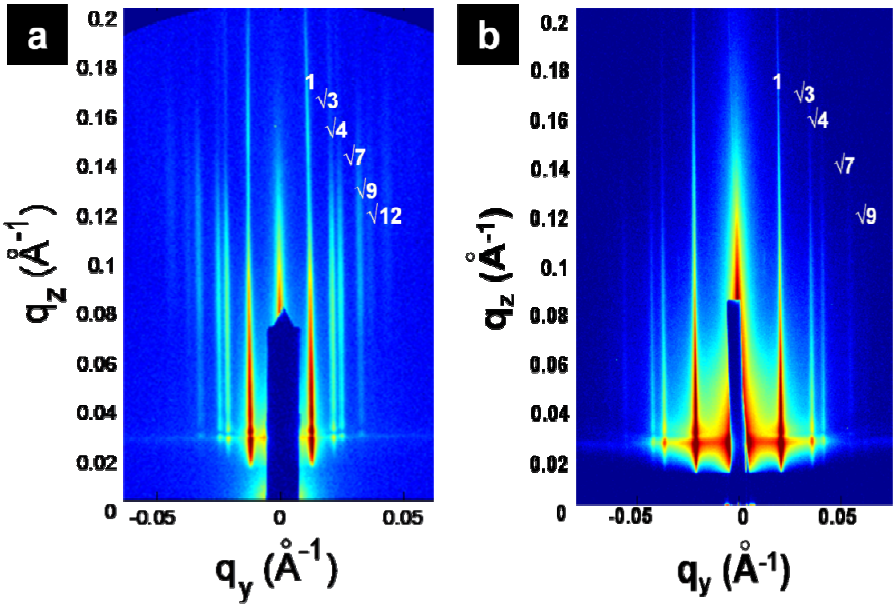

Fig. S1. The GISAXS patterns (incidence angle of 0.2^{o}) of PS-*b*-PEO thin films annealed in benzene/water vapor at (a) 17 ^{o}C and (b) 22 ^{o}C for 10 hr. Significantly enhanced lateral orderings of cylindrical microdomains oriented normal to the surface were confirmed by the presence of multiple high-order peaks.

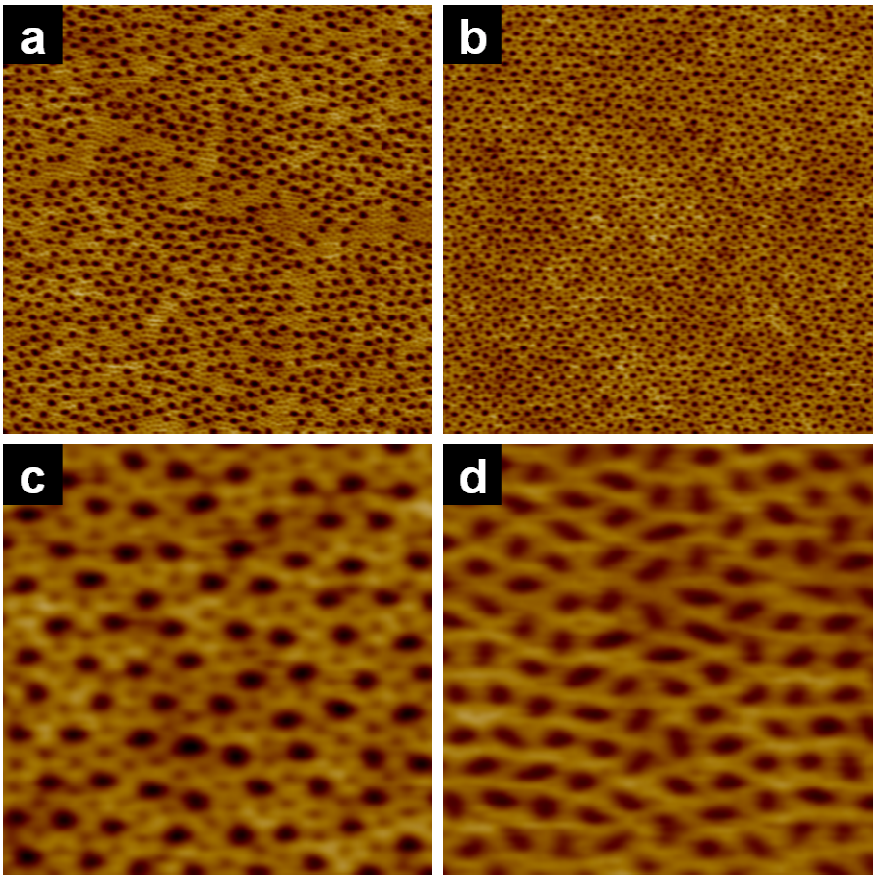

Fig. S2. The SFM height images of solvent-annealed PS-*b*-PEO films at 17 ^{o}C (a) for 50 min and (b) 1 hr (scale: 3 μm × 3 μm). (c) and (d) are the magnified image (scale: 750 nm × 750 nm) of Fig. S1 (b) and Fig. 3 (c), respectively. In the Fig. S1 (a) and (b), the numbers of larger PEO domains increase but those of smaller PEO domains decrease. Smaller PEO domains were absorbed to larger ones, as clearly seen Fig. S1 (c) and (d).

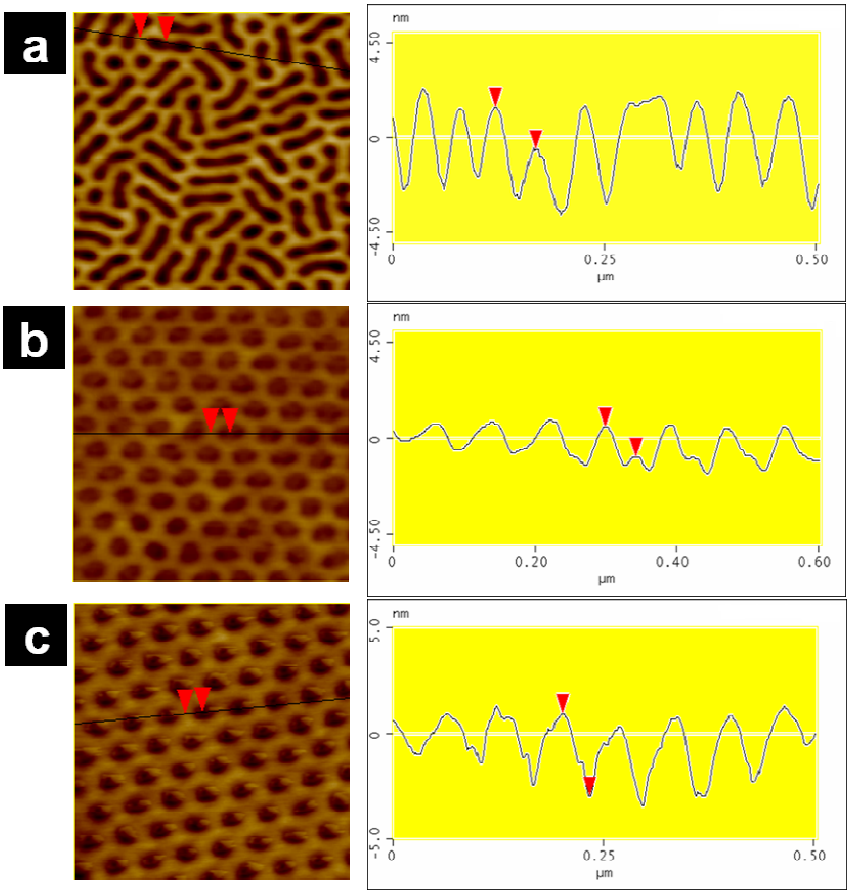

Fig. S3. The SFM height images and corresponding height profiles of solvent-annealed PS-*b*-PEO films at 17 ^{o}C for (a) 180, (b) 360, and (c) 600 min. In height profiles, red arrows represent the height steps between top surfaces of PS matrixes and center of PEO domains. Different height steps can be clearly observed.

We used orientational correlation function to calculate quantitatively two dimensional (2D) order of the PS-*b*-PEO thin film. The orientational correlation function is defined as[1]

$$G_6(r) = < \varphi_6^*(0)\varphi_6(r) > \quad (1)$$

where

$$\varphi_6(r_j) = \frac{\sum_{j=1}^{NN} \exp(6i\theta(r_{ij}))}{NN} \quad (2)$$

and $\varphi_6^*(0)$ indicates the complex conjugate of the order parameter of the cylindrical microdomains which is designated as the origin, index *j* counts the nearest-neighbors, *NN*, of cylinder *i* and $\theta(r_{ij})$ is the angle made between the bond connecting cylinders *i* and *j* and an arbitrarily chosen reference axis. Each cylinder is used as the origin for one calculation, and the angular brackets indicate an average over all cylinders. $G_6(r)$ has a value between 0 and 1 for all *r*. For a perfect hexagonal crystal, a plot of $G_6(r)$ vs. *r* will have a value of 1 and will only exist when *r* = *na*, where *n* has a integer value. In a real crystal, the maximum value of this graph will not be 1.0 due to fluctuations in lattice positions even for a well ordered 2D crystal. The local bond orientational order of solvent-annealed PS-*b*-PEO films at 17 ^{o}C and 22 ^{o}C is 0.95 and 0.97, respectively, which is close to 1, the value of a perfect lattice, as seen in Fig. S5. $G_6(r)$ decays very little over large distances, which implies the presence of long range orientational order.

[1] R. A. Segalman, A. Hexemer, R. C. Hayward, E. J. Kramer, *Macromolecules,* 2003, **36,** 3272-3288.

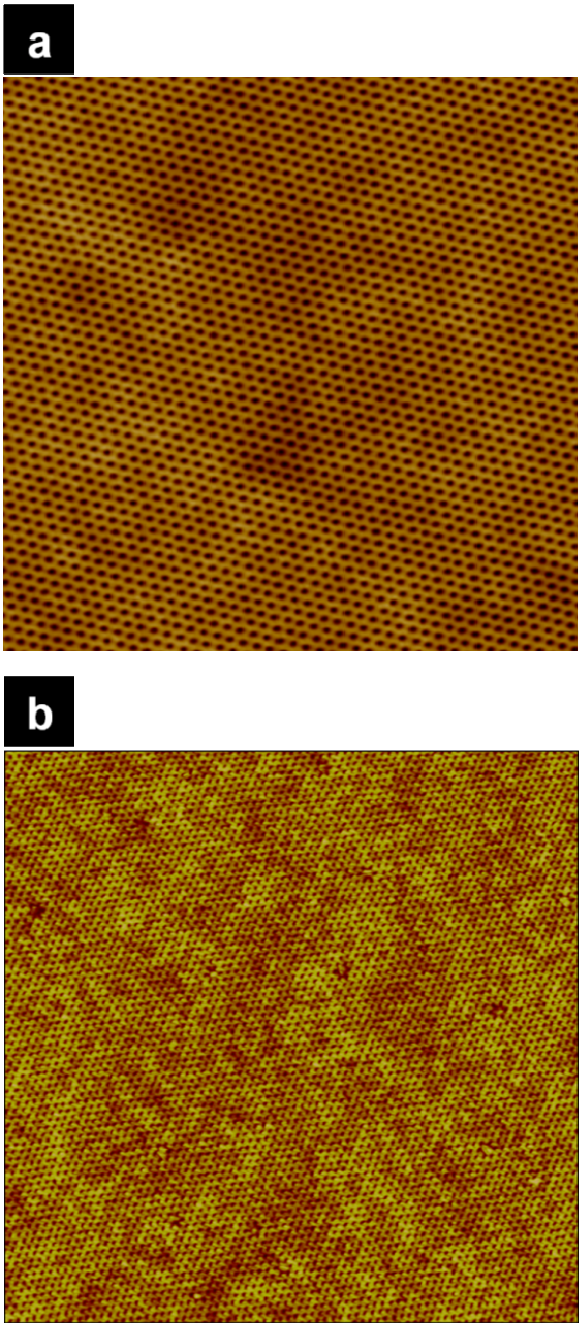

Fig. S4. The SFM height images of solvent-annealed PS-*b*-PEO films at (a) 17 ^{o}C and (b) 22 ^{o}C for 10 hr (scale: 3 μm × 3 μm). Highly ordered PEO cylindrical microdomains with interdomain distances of 61.6 and 34.4 nm were obtained from PS-*b*-PEO thin films annealed in benzene/water vapor, respectively.

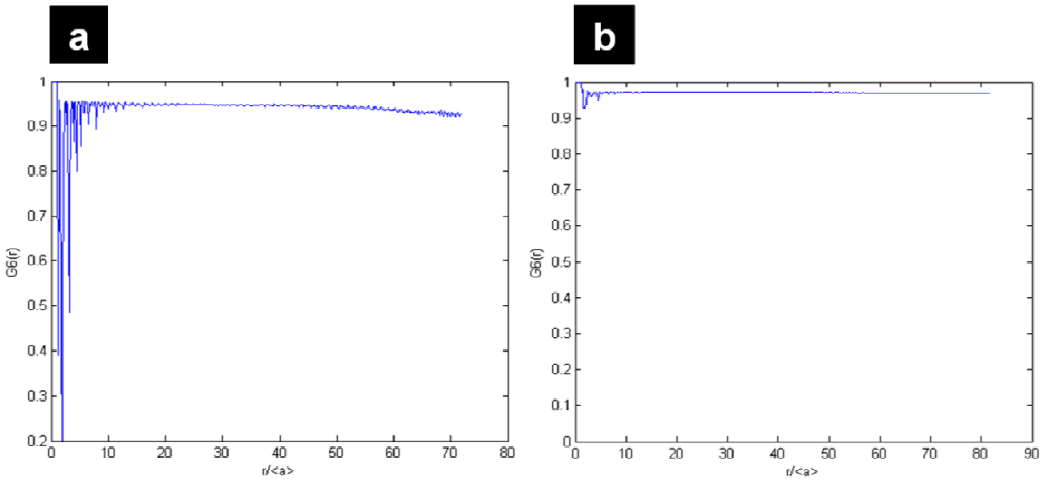

Fig. S5. Orientational order calculation from Fig. S5 (a) and (b) corresponding to solvent-annealed PS-*b*-PEO films at (a) 17 ^{o}C and (b) 22 ^{o}C for 10 hr, respectively.

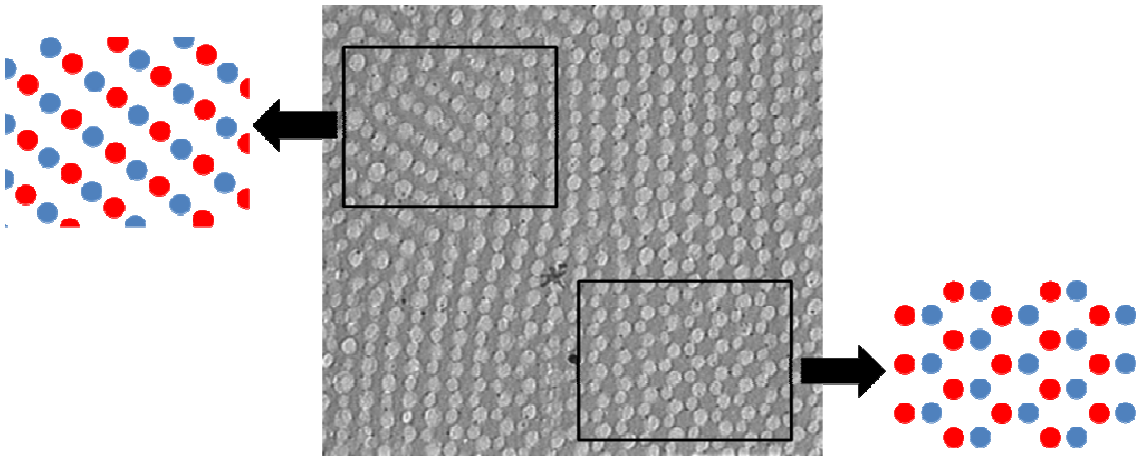

Fig. S6. TEM in-plane view image of the PS-*b*-PEO thin film annealed in benzene/water vapor at 22 ^{o}C and the schematic representation for the projection of two superimposed hexagonal lattices.