Supporting information

Structural Evolution and Nanodomain Formation in Blend Films of a Block Copolymer and Homopolymer.

Ya-Sen Sun[1], Yi-Qing Jian[2], Shin-Tung Yang[2], Pei-Hsuan Chiang[2], and Chun-Jen Su[3]*

1. *Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan*
2. *Department of Chemical and Materials Engineering, National Central University, Taoyuan 32001, Taiwan*
3. *National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan*

*corresponding author: Y. S. Sun (Email: yssun@gs.ncku.edu.tw)

Quantitative Analysis of Yoneda Streaks and Peaks

It has been well known that a combined effect of refraction and reflection inevitably gives rise to Yoneda streaks and its resonance X-ray waveguides[S1-S5]. Thus, the positions of Yoneda peaks depend on the materials' scattering length densities (SLD). The correlation of the Yoneda peak's position with material SLD is given as follows,

$$q_{\perp} = \frac{2\pi}{\lambda}[\sin(\alpha_{c,f/s}) + \sin(\alpha_i)] \quad \text{(S1)}$$

In Equation (S1), $\alpha_{c,f/s}$ denotes a critical angle for film (f) or substrate (s), given by

$$\alpha_c = \sqrt{\delta} \quad \text{(S2)}$$

with $\delta = \frac{\lambda^2}{2\pi} r_o \rho_e$ where r_o is the classical radius of the electron (r_o=2.818×10^{-15} m) and ρ_e denotes the number density of electrons. Equation (S2) indicates that the critical angle of a material is related to the SLD (i.e., $r_o\rho_e$). Because the SLD of a polymer film is much less than the SLD of SiO_x/Si, the low-$q_{\perp}$ Yoneda peak is reflected from the film, and the high-$q_{\perp}$ Yoneda peak is reflected from SiO_x/Si.

Based on the positions of the Yoneda peaks, the SLD values of the thin film and

substrate were estimated as 9.46×10^{10} cm^{-2} and 19.07×10^{10} cm^{-2}, respectively, in agreement with theoretically calculated SLD values (Table S1) based on λ=1.24 Å, $\rho_{SiOx/Si}$=2.33 g/cm^3, ρ_{PS}=1.06 g/cm^3, and ρ_{PMMA}=1.15 g/cm^3. For brevity, the two Yoneda peaks are labeled as Y_f and Y_s.

Table S1. Parameters of the materials used for the quantitative analysis of GISAXS.

E = 10 keV; $\lambda = 1.24\times10^{-8}$ cm							
	$r_o\rho_e[10^{10}\ cm^{-2}]$[a]	$\mu/\rho[cm^2/g]$[b]	$\rho[g/cm^3]$	$\mu_x\ [cm^{-1}]$	δ	β	α_c[radian]
vacuum	0.0000			0	0	0	0
PS	9.6900	2.2190	1.060	2.35214	2.37×10^{-6}	2.32×10^{-9}	0.00218
PMMA	10.5520	3.3570	1.150	3.86055	2.58×10^{-6}	3.81×10^{-9}	0.00227
PS_{21k}-b-$PMMA_{21k}$[c]	10.1210	2.7880	1.105	3.1063	2.48×10^{-6}	3.06×10^{-9}	0.00223
$B_{75}H_{25}$ films[c]	10.0133	2.6458	1.094	2.9178	2.45×10^{-6}	2.88×10^{-9}	0.00221
Si	19.9830	33.8900	2.330	78.9637	4.89×10^{-6}	7.79×10^{-8}	0.00313

a. SLD can be calculated at https://www.ncnr.nist.gov/resources/activation/; b. mass absorption coefficient can be calculated at https://www.nist.gov/pml/x-ray-mass-attenuation-coefficients; c. The estimation of the SLD and mass absorption coefficient is based on the mass fractions of PS and PMMA in PS-b-PMMA and its blend with PS.

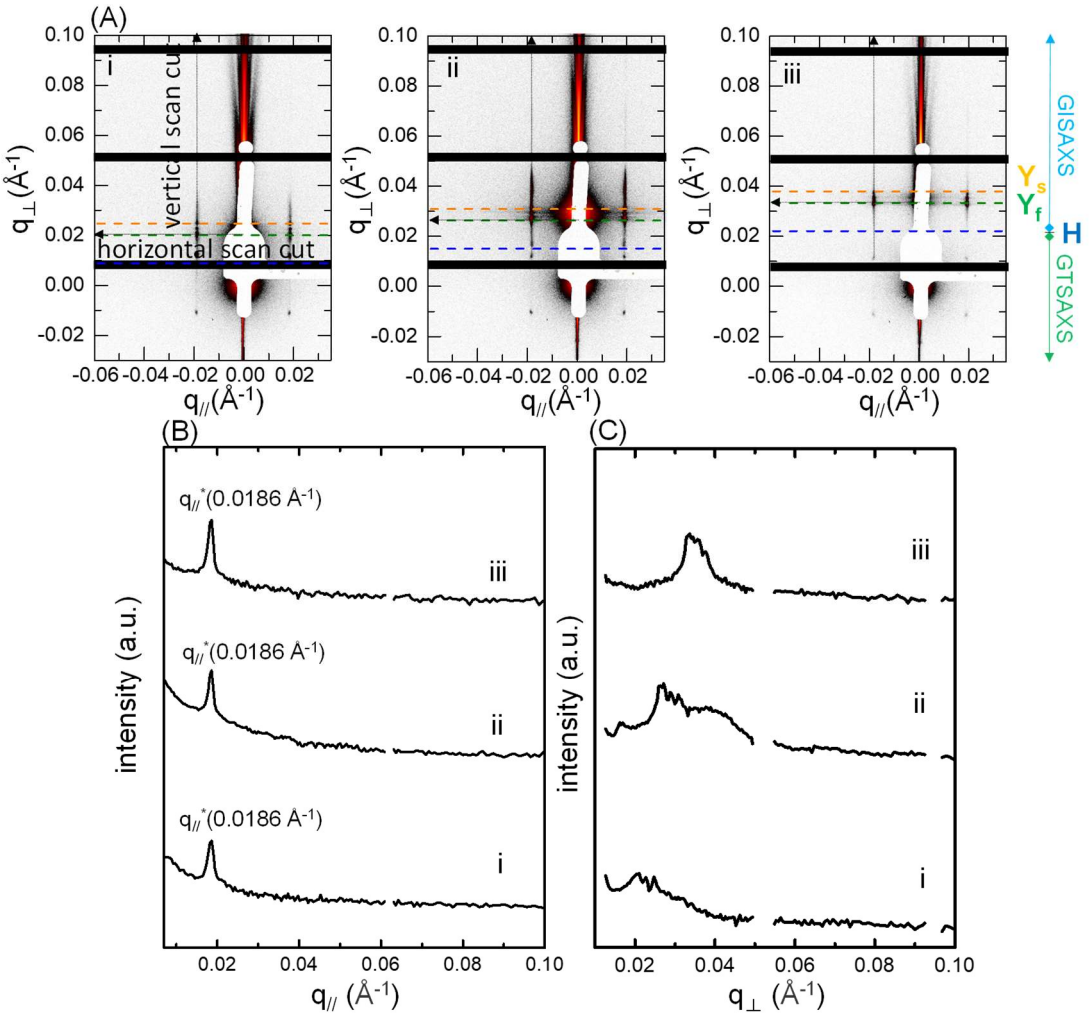

Figure S1. (A) GISAXS 2D patterns, (B) in-plane, and (C) out-of-plane GISAXS 1D profiles measured at α_i= (i) 0.1°, (ii) 0.17°, and (iii) 0.25° for the thin $B_{75}H_{25}$-205 film cooled to room temperature. In (A), Horizon (H) and Yoneda streaks (Y_s and Y_f) are indicated by blue, green, and orange dashed lines. GISAXS regions are above H, and GTSAXS regions are below H. Vertical and horizontal scan cuts are indicated by vertical and horizontal arrows.

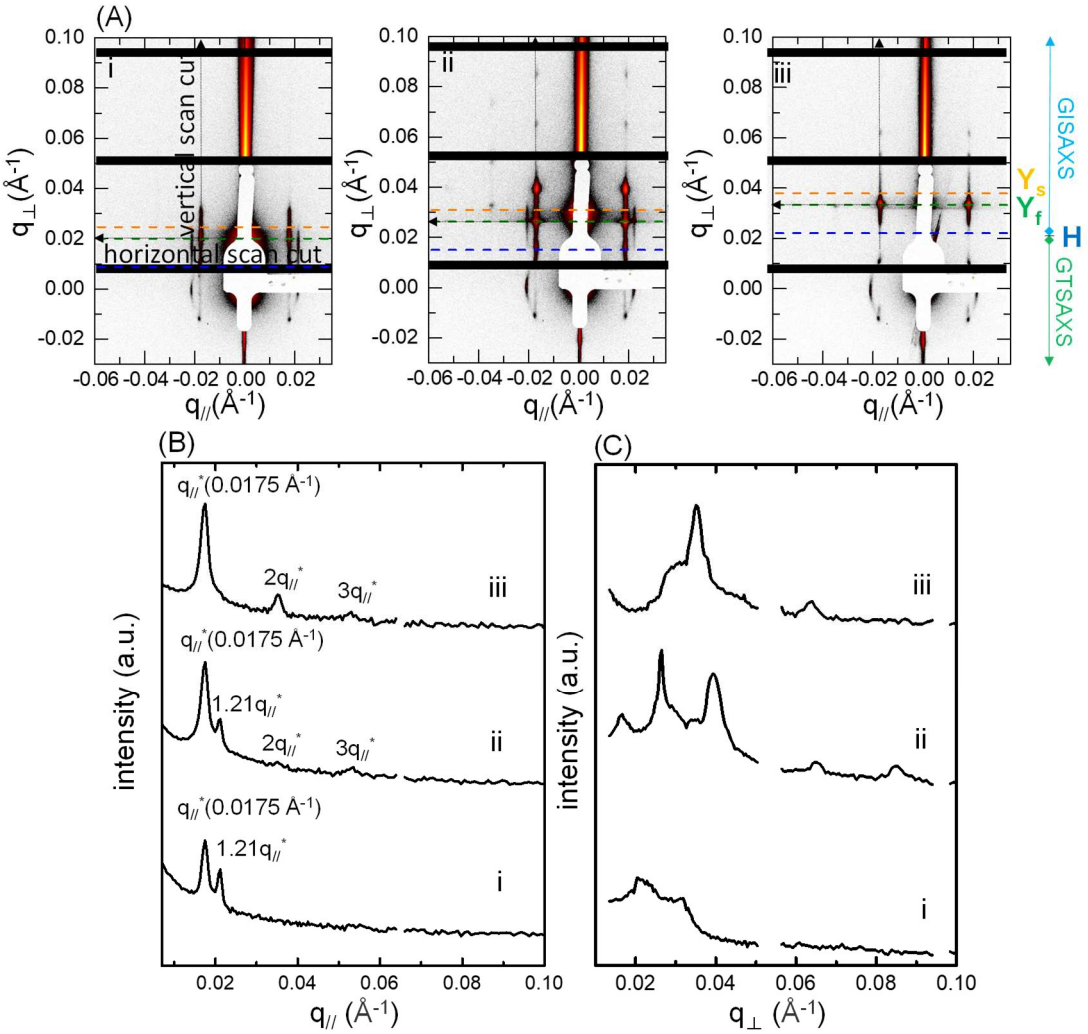

Figure S2. (A) GISAXS 2D patterns, (B) in-plane, and (C) out-of-plane GISAXS 1D profiles measured at α_i = (i) 0.1°, (ii) 0.17°, and (iii) 0.25° for the thick $B_{75}H_{25}$-205 film cooled to room temperature. In (A), Horizon (H) and Yoneda streaks (Y_s and Y_f) are indicated by blue, green, and orange dashed lines. GISAXS regions are above H, and GTSAXS regions are below H. Vertical and horizontal scan cuts are indicated by vertical and horizontal arrows.

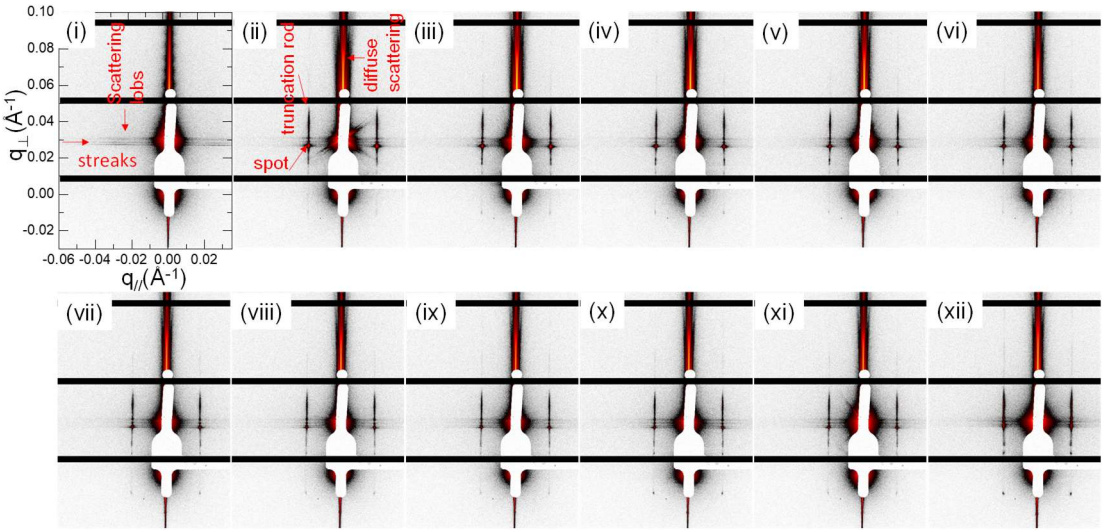

Figure S3. A series of GISAXS 2D patterns collected for a thin B75H25 blend film (h_i = 82 ± 1 nm). Patterns (i) and (xii) were measured at room temperature before and after isothermal annealing at 205 °C for 60 minutes, respectively. Patterns (ii)-(xi) were measured in-situ by GISAXS at different times during isothermal annealing at 240 °C: (ii) 10, (iii) 15, (iv) 20, (v) 25, (vi) 30, (vii) 35, (viii) 40, (ix) 45, (x) 50, and (xi) 55 minutes. The direct and transmission beams are blocked by three beam stoppers, resulting in the white shadow.

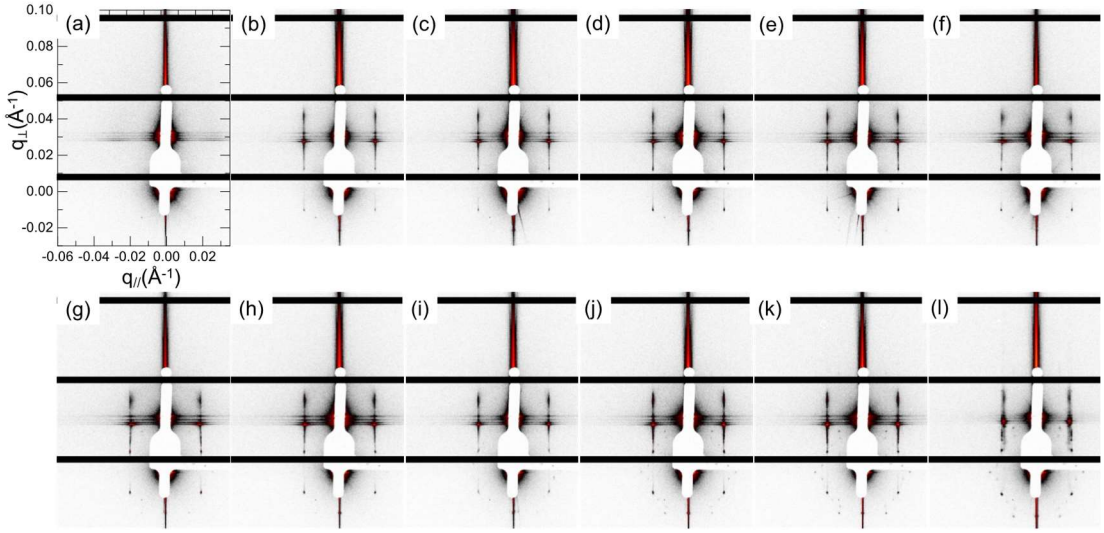

Figure S4. A series of ex-situ and in-situ GISAXS 2D patterns collected for a thin $B_{75}H_{25}$ blend film (h_i=82±1nm). Patterns (a) and (l) were measured ex-situ at room temperature before and after isothermal annealing at 240 °C. Patterns (b)-(k) were measured in-situ by GISAXS at different intervals during isothermal annealing at 240 °C: (b) 10, (c) 15, (d) 20, (e) 25, (f) 30, (g) 35, (h) 40, (i) 45, (j) 50, and (k) 55 minutes. The direct and transmission beams are blocked by three beam stoppers, resulting in the

white shadow. The reflection beam, Yoneda streak, and Horizon are denoted as orange R, green Y, and blue H, respectively.

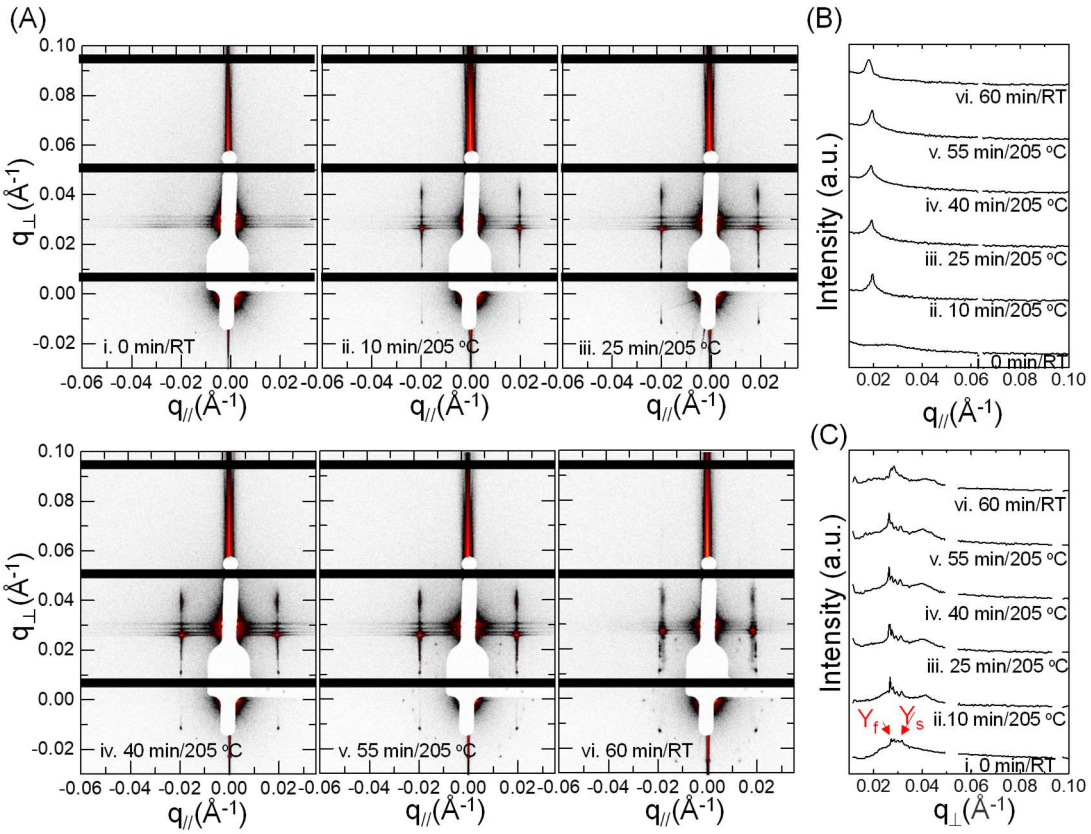

Figure S5. (A) In-situ GISAXS 2D patterns, (B) in-plane 1D profiles, and (C) out-of-plane profiles collected for a thin $B_{75}H_{25}$ blend film. The in-plane profiles, showing intensity as a function of $q_{//}$, were obtained by horizontal scan cuts along the Yoneda streak. The out-of-plane GISAXS profiles, showing intensity as a function of $q_{\perp}$, were obtained by vertical scan cuts at $q_{//} = 0.0194$ Å^{-1}. Annealing times and temperatures are indicated in the figures, along with several prominent scattering features (Yoneda streak, scattering lobe, truncation rod, diffraction spot, and meridian diffuse scattering). The direct and transmission beams are blocked by three beam stoppers, resulting in the white shadow seen in (A).

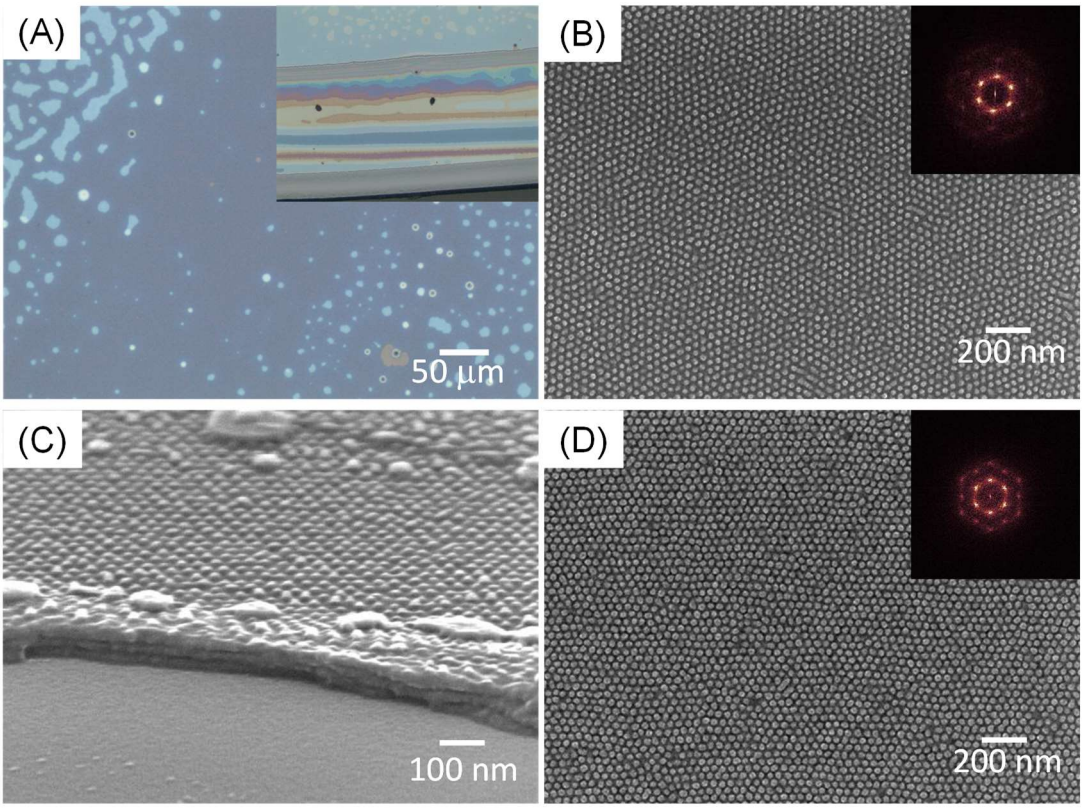

Figure S6. (A) OM, (B, D) top-view SEM, and (C) side-view SEM images (collected at a 25°-tilted stage) of the thin $B_{75}H_{25}$-240 film after in-situ GISAXS measurements at 240 °C. The inset in (A) shows an OM image of thick edge beads collected at the periphery. The insets in (B) and (D) show FFT patterns. Before SEM characterization, the film was cut with a diamond knife and then etched with oxygen plasma for 15 seconds. Image (D) was collected at the periphery.

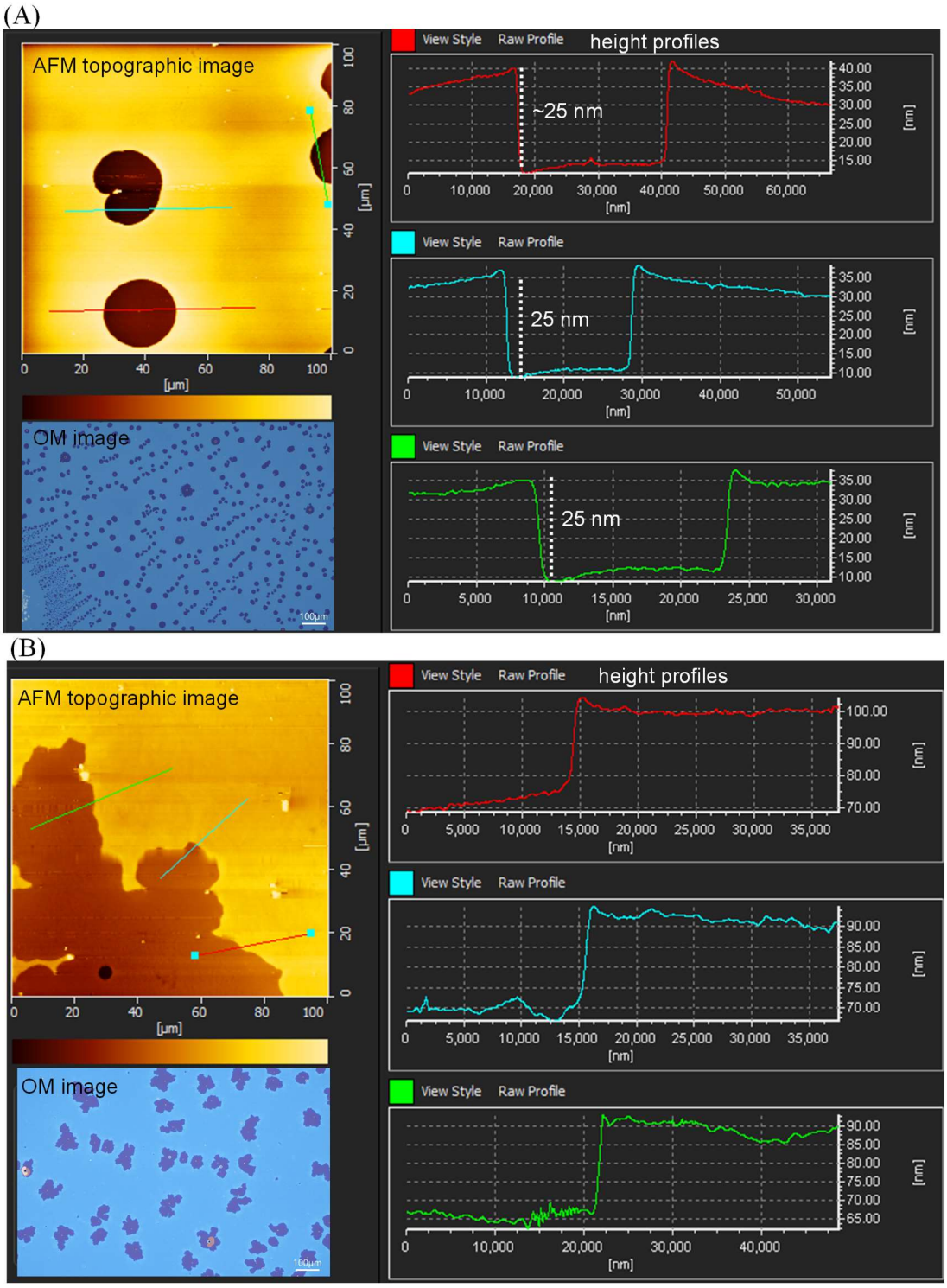

Figure S7. AFM topographic images, OM images and height profiles of (A) thin $B_{75}H_{25}$-205 and (B) thin $B_{75}H_{25}$-240 films after prolonged annealing was performed at 205 or 240 ºC for 24 hours.

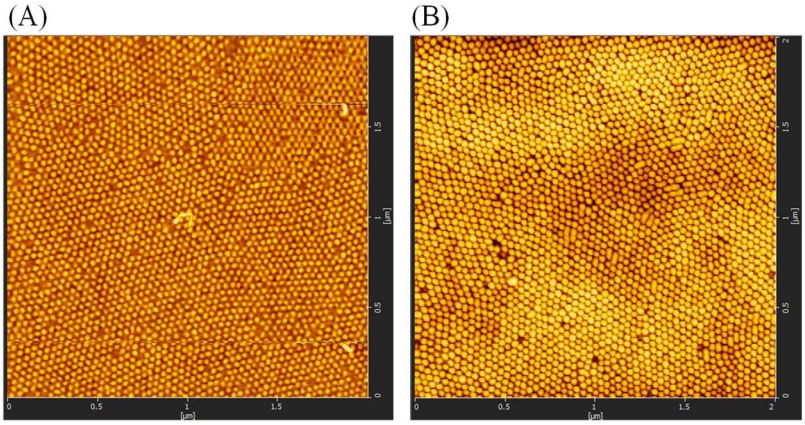

Figure S8. 2 μm×2 μm AFM topographic images of (A) thin $B_{75}H_{25}$-205 and (B) thin $B_{75}H_{25}$-240 films after prolonged annealing was performed at 205 or 240 ºC for 24h, followed by oxygen plasma etching.

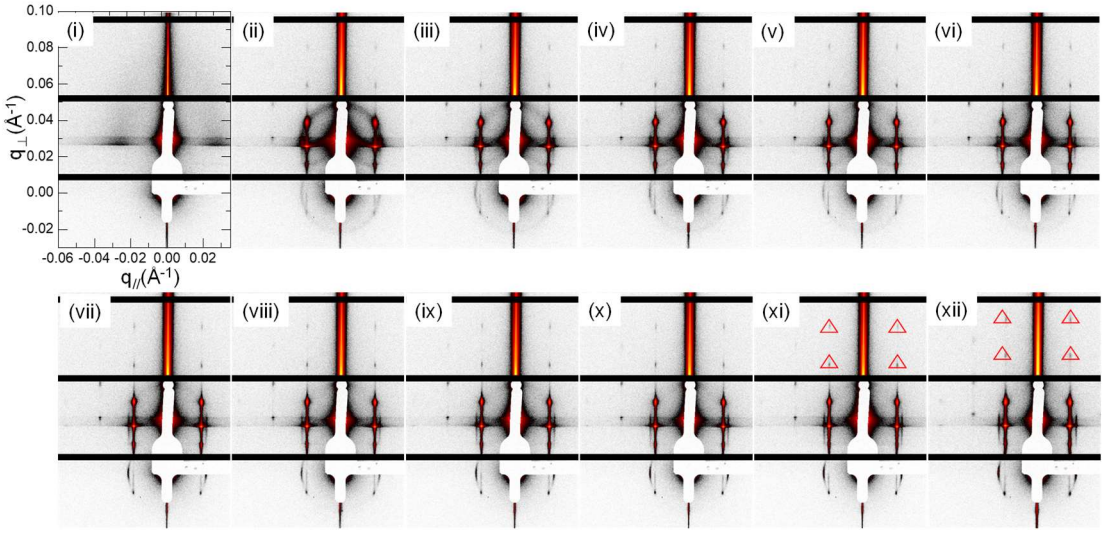

Figure S9. A series of GISAXS 2D patterns collected for a thick $B_{75}H_{25}$ blend film (h_i =282±2 nm). Patterns (i) and (xii) were measured at room temperature before and after isothermal annealing at 205 °C for 60 minutes, respectively. Patterns (ii)-(xi) were measured in-situ by GISAXS at different times during isothermal annealing at 205 °C: (ii) 10, (iii) 15, (iv) 20, (v) 25, (vi) 30, (vii) 35, (viii) 40, (ix) 45, (x) 50, and (xi) 55 minutes. The direct and transmission beams are blocked by three beam stoppers, resulting in the white shadow.

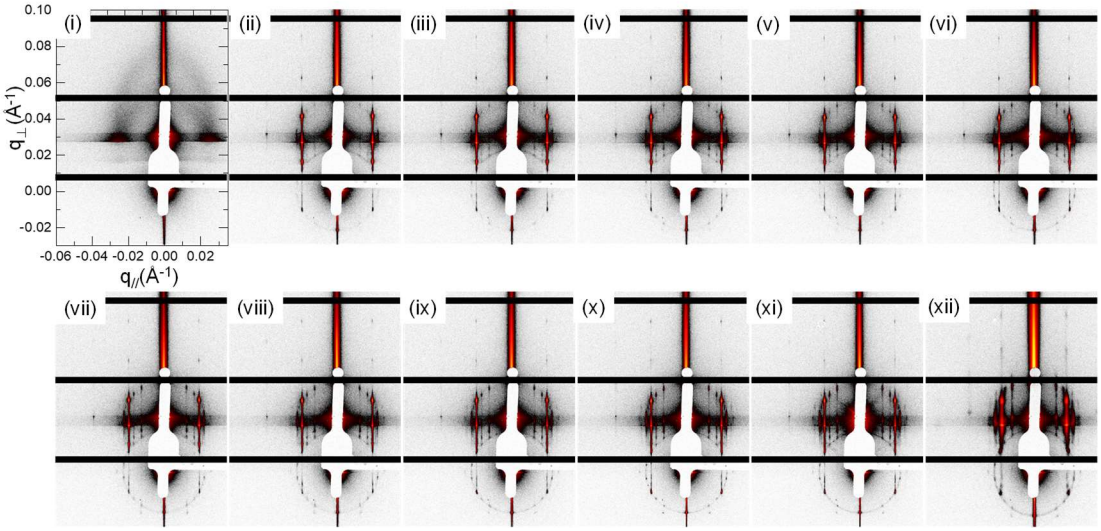

Figure S10. A series of GISAXS 2D patterns collected for a thick $B_{75}H_{25}$ blend film (h_i=282±2 nm). Patterns (i) and (xii) were measured at room temperature before and after isothermal annealing at 240 °C for 60 minutes, respectively. Patterns (ii)-(xi) were measured in-situ by GISAXS at different times during isothermal annealing at 240 °C: (ii) 10, (iii) 15, (iv) 20, (v) 25, (vi) 30, (vii) 35, (viii) 40, (ix) 45, (x) 50, and (xi) 55 minutes. The direct and transmission beams are blocked by three beam stoppers, resulting in the white shadow.

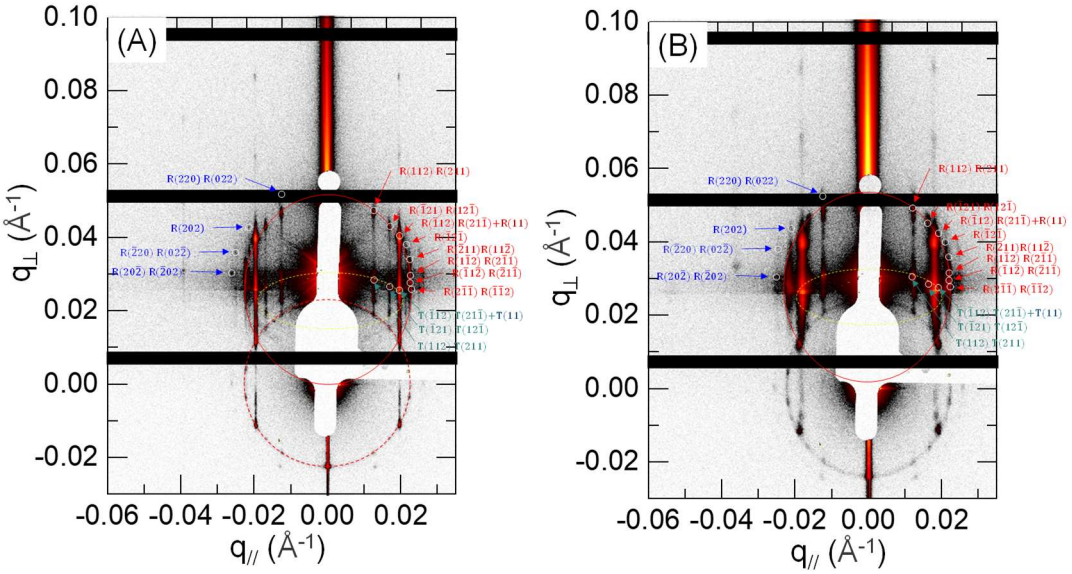

Figure S11. Indexed GISAXS patterns for (A) Figure $S8_{xi}$ and (B) Figure $S8_{xii}$.

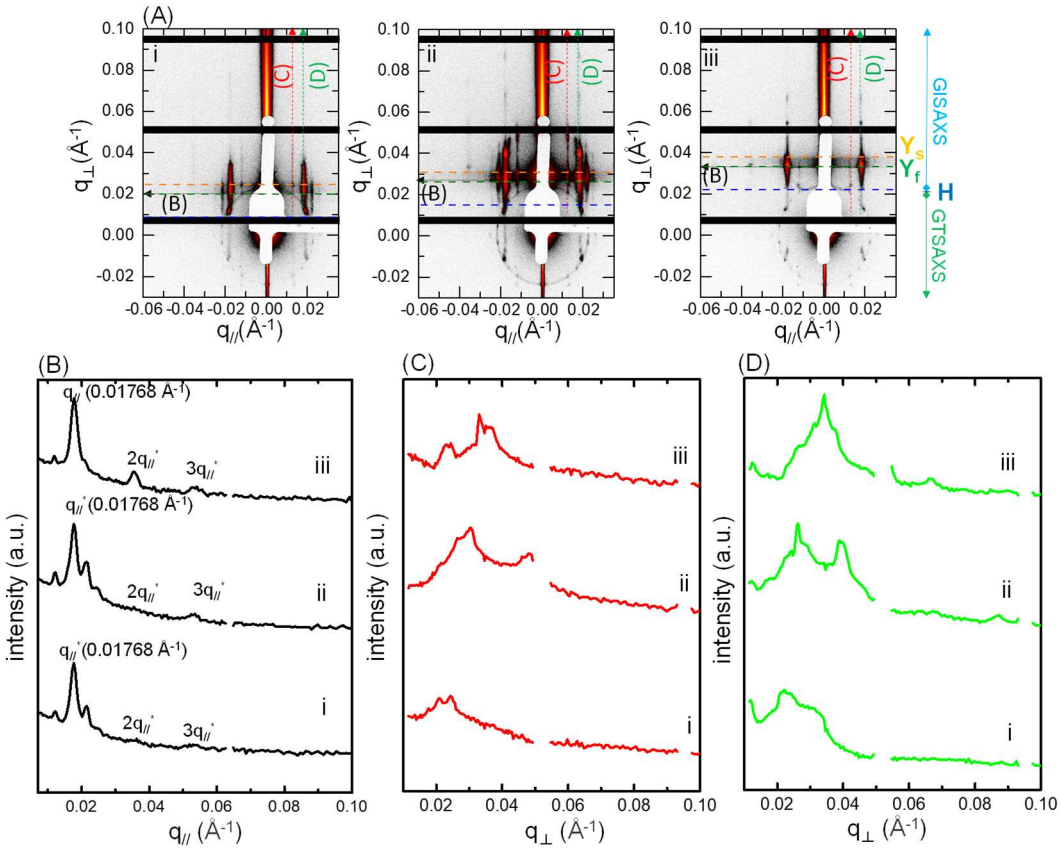

Figure S12. (A) 2D patterns, (B) in-plane and (C, D) out-of-plane 1D profiles measured at α_i= (i) 0.1, (ii) 0.17, and (iii) 0.25° for the thick $B_{75}H_{25}$-240 film cooled to room temperature. The profiles in (B) were obtained by a horizontal scan cut on the orange lines. The profiles in (C) were obtained by a vertical scan cut on the red lines, whereas those in (D) were obtained by a vertical scan cut on the green lines.

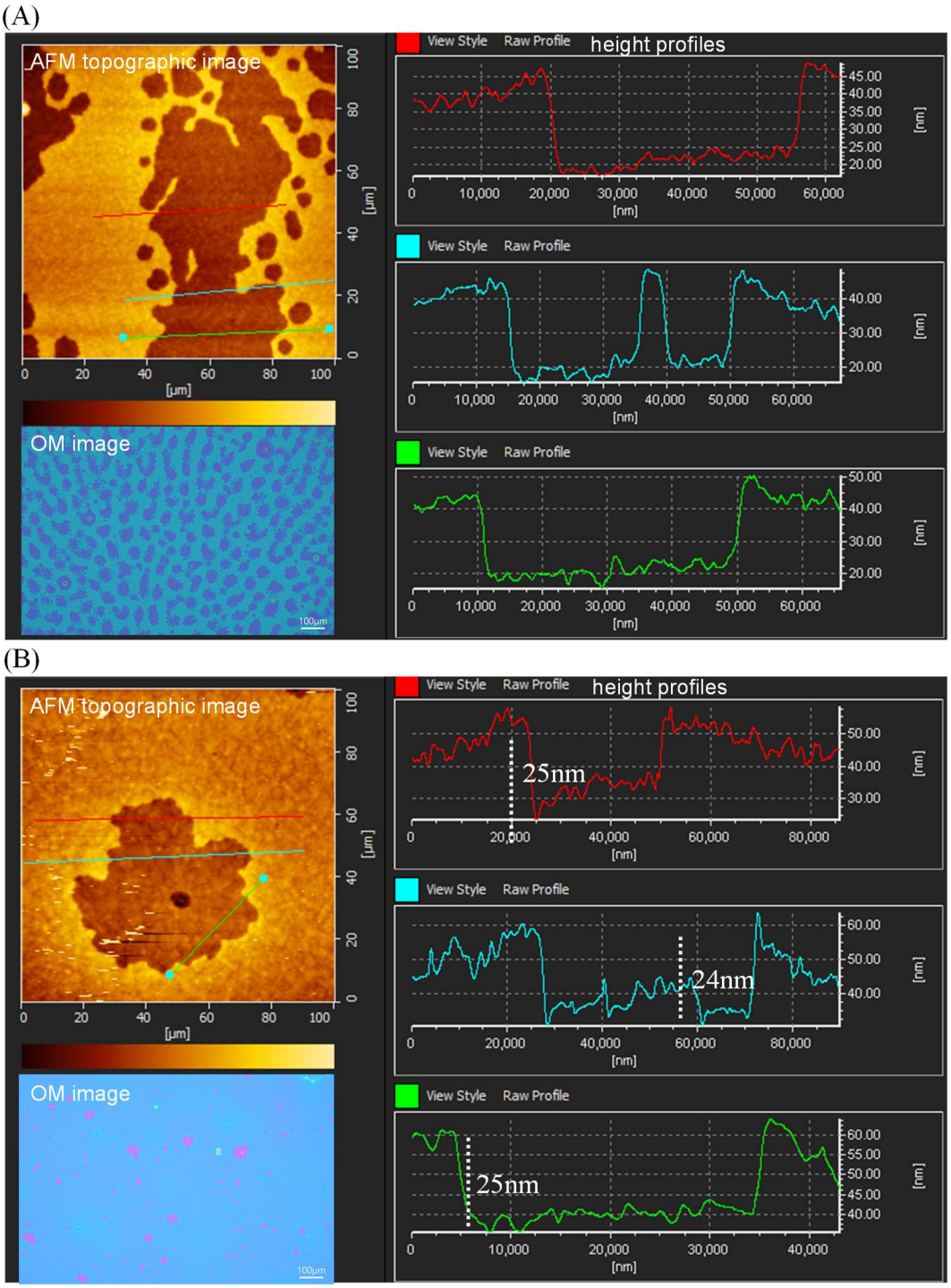

Figure S13. AFM topographic images, OM images and height profiles of (A) thick $B_{75}H_{25}$-205 and (B) thick $B_{75}H_{25}$-240 films after prolonged annealing was performed at 205 or 240 ºC for 24 hours.

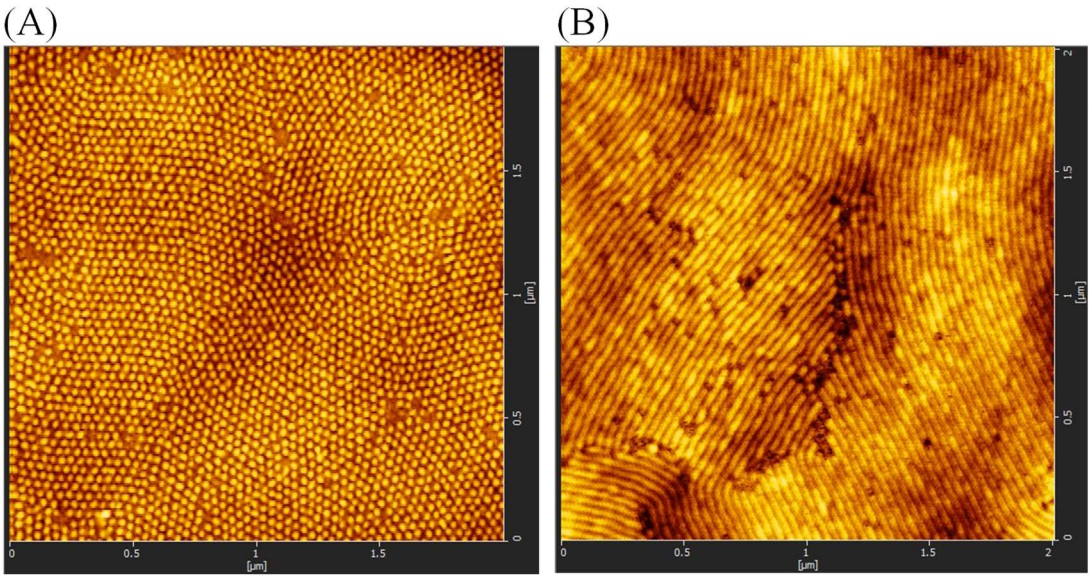

Figure S14. 2 µm×2 µm AFM topographic images of (A) thick $B_{75}H_{25}$-205 and (B) thick $B_{75}H_{25}$-240 films after prolonged annealing was performed at 205 or 240 ºC for 24h, followed by oxygen plasma etching.

References:

(S1) S. Narayanan, D. R. Lee, R. S. Guico, S. K. Sinha, J. Wang, *Physical Review Letters* 2005, **94**, 145504.

(S2) S. Narayanan, D. R. Lee, A. Hagman, X. Li, J. Wang, *Physical Review Letters* 2007, **98**, 185506.

(S3) J. Wang, M. J. Bedzyk, M. Caffrey, *Science* 1992, **258**, 775-778.

(S4) Y. P. Feng, S. K. Sinha, H. W. Deckman, J. B. Hastings, D. P. Siddons, *Physical Review Letters* 1993, **71**, 537.

(S5) Z. Jiang, D. R. Lee, S. Narayanan, J. Wang, S. K. Sinha, *Physical Review B,* 2011, ***84***, 075440.