Supporting Information

Irreversible Physisorption of PS-*b*-PMMA Copolymers on Substrates for Balanced Interfacial Interactions as a Versatile Surface Modification

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Experimental

Materials: Nearly monodisperse ($M_w/M_n < 1.06$) and symmetric PS-*b*-PMMAs (20.3, 42.1, 93.5 and 232 kg/mol) were synthesized by living anionic polymerization in tetrahydrofuran (THF) using styrene (S) and methyl methacrylate (MMA) monomers at -78 °C. The process was carried out under purified argon environment. A *sec*-butyllithium was used as an initiator and LiCl (high purity, Aldrich) was dissolved into THF. The number-averaged molecular weight (M_n) and dispersity ($Đ = M_w/M_n$) was measured by size-exclusion chromatography (SEC) with multiangle laser light scattering (MALLS) detector. The volume fraction of PS (ϕ_{PS}) was characterized by ^{1}H NMR (Avance II, Bruker Biospin) based on the densities of the components (1.050 and 1.184 g/cm^3 for PS and PMMA, respectively). The equilibrium lamellar spacings (L_o) of bulk PS-*b*-PMMAs were measured by small-angle x-ray scattering (SAXS) at the beamline 4C of Pohang Accelerator Laboratory (PAL), Korea. Additionally,

two asymmetric PS-*b*-PMMAs such as PS-cylinder (ϕ_{PS}=0.28, 71.7 kg/mol) and PMMA-cylinder (ϕ_{PS} = 0.80, 73.3 kg/mol) forming samples were synthesized and characterized in the same manners as above.

Substrates: The standard silicon wafer with the native (2 nm) oxide layer was used as received. For H-passivated Si substrate, the native oxide substrate was immersed in 5 vol % of hydrogen fluoride (HF) aqueous solution for 30 min and was sequentially rinsed by ethanol and DI water. For wide-applicability test, the various substrates such as mica sheets (Ted Pella, Prod No.56, grade V1), glass (Corning, Cat. No. 2850-22), aluminum and gold (thermally deposited on silicon wafer in a thickness of 100 nm) were used.

Surface modification by irreversible adsorption: To form the adsorbed layer on the native oxide substrate, H-passivated Si substrate, mica, glass and deposited aluminum substrates, 93.5 kg/mol PS-*b*-PMMA solution (1.50 wt % in toluene) was spun cast to set ~ 30 nm thickness onto the substrates, followed by thermal annealing at 190 °C under vacuum which is above the glass transition temperatures of the two blocks (~ 100 °C for PS and ~ 105 °C for PMMA). In case of gold substrate, however, the adsorption process was carried out at 150 °C in order to prevent dewetting-induced inhomogeneity during adsorption process. Further, these films were immersed in toluene for 12 h to eliminate the unadsorbed chains, leading to the irreversibly adsorbed layers. Particularly for 42.1 kg/mol PS-*b*-PMMA films, the thermal annealing for irreversible adsorption was set at 160 °C under vacuum for 24 h.

Self-assembly of BCP thin film: 93.5 kg/mol PS-*b*-PMMA thin films were prepared onto various substrates by spin-casting the polymer solution in toluene. The solution concentration was varied in the range of 0.50 – 1.50 wt % and the process was operated at 2000 – 5000 rpm to fine-tune the film thickness. The films were thermally annealed at 190 °C under vacuum for 24 h, except for the films

supported on gold substrate (at 170 ºC for to prevent the onset of dewetting). In case of 42.1 kg/mol PS-*b*-PMMA films, the thermal annealing was set at 160 ºC under vacuum for 24 h.

Analysis for adsorbed layer and thin film: A Spectroscopic ellipsometry (SE-MG 1000, Nano-view Co.) was operated at an incidence angle of 69.7° to measure film thicknesses, where a deuterium−tungsten lamp (Hamamatsu Photonics) was used as the light source with the photon energy of $1.45 − 5.00$ eV ranging from the ultraviolet to visible ranges. Scanning force microscopy (SFM; Dimension 3100, Digital Instrument Co.) was used to examine the surface morphology of polymer films, which was operated in a tapping mode with the standard silicon nitride probe at 3 % offset below their resonance frequencies ranging from 250 to 350 kHz. The normal SFM phase images were acquired at a scanning rate of 7 μm/s. Grazing-incidence small-angle x-ray scattering (GISAXS) experiment was carried out at 9A beamline of Pohang Accelerator Laboratory (PAL), Korea. The typical operating conditions were set at a wavelength of 1.12 Å and a sample-to-detector distance of 6.5 m. The incidence angle (α_i) was set at 0.120º for the adsorbed layer and 0.140° for the BCP films, which are all above the critical angle (0.114°) to probe the entire film structures. 2D GISAXS patterns were recorded using a 2D detector (SX-165, Rayonix) positioned at the end of a vacuum guide tube with an exposure time of 12 s.
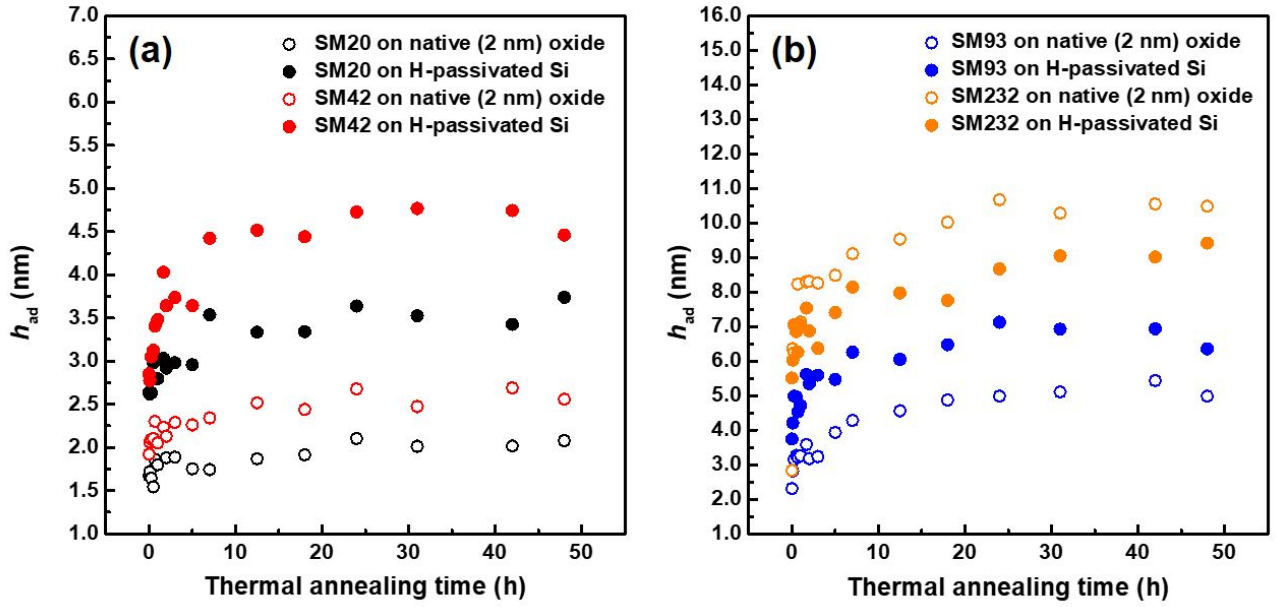
Figure S1. Thicknesses of the adsorbed layers (h_{ad}) onto the two kinds of substrates (native oxide substrate and on H-passivated Si substrate, respectively) as a function of annealing time. The thin ($\sim$ 30 nm) BCP films were thermally annealed at 190 °C under vacuum to generate the adsorbed layers onto the substrates, and the films were leached in toluene to remove the unadsorbed chains.
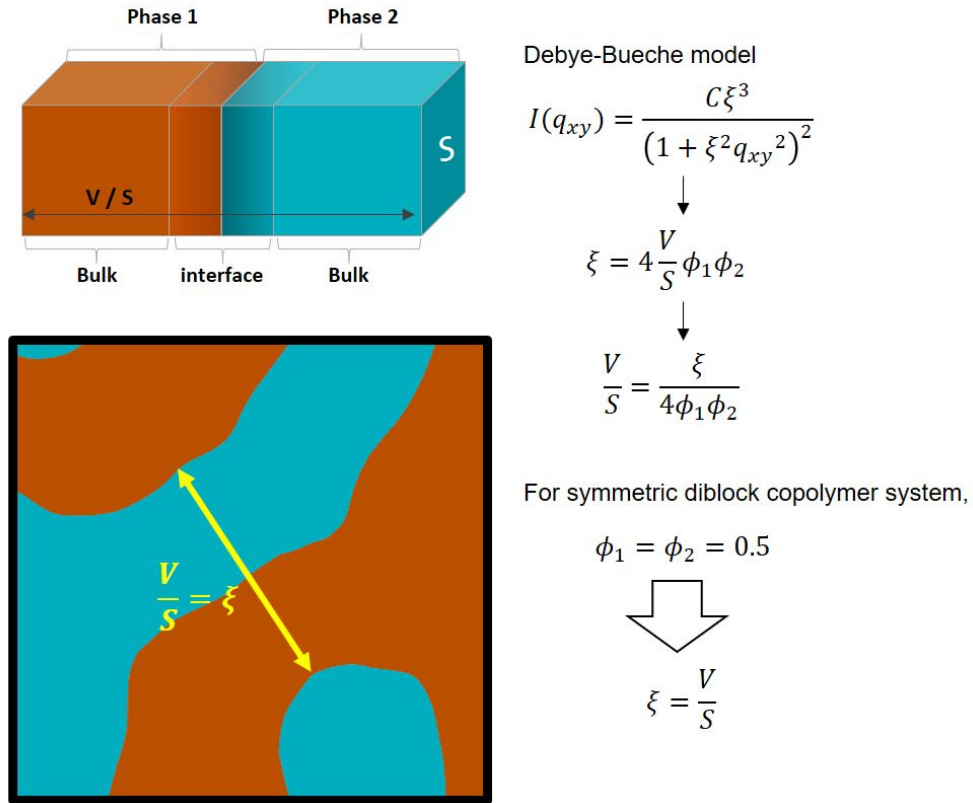

Debye-Bueche model

$$I(q_{xy}) = \frac{C\xi^3}{\left(1 + \xi^2 q_{xy}{}^2\right)^2}$$

$$\xi = 4\frac{V}{S}\phi_1\phi_2$$

$$\frac{V}{S} = \frac{\xi}{4\phi_1\phi_2}$$

For symmetric diblock copolymer system,

$$\phi_1 = \phi_2 = 0.5$$

$$\xi = \frac{V}{S}$$

Figure S2. Schematic description of the correlation length (ξ) of the adsorbed layers and the calculation of ξ based on the Debye-Bueche model. A nonparticulate two-phase model consisting of PS and PMMA is suggested, where a 3D unit region has volume (V), cross-section (S), and the average distance (V/S) between the two phases.

Figure S2 describes our adsorbed layers as a nonparticulate two-phase system model of which the two inhomogeneous phases are mixed irregularly but isotropically. According to Roe [1], a two-phase system (consisting of PS and PMMA) was presumed to have a 3D unit region with volume (V) and cross-section (S), and the average distance (V/S) between the two phases, respectively. The Debye-Bueche model was adopted to calculate the correlation length (ξ) between two phases by fitting the scattering intensity ($I(q)$) using the following equation

$$I(q) = \frac{C\xi^3}{(1 + \xi^2 q^2)^2} \tag{1}$$

where q and C are the scattering vector (in nm^{-1}) and a constant, respectively. Here, the ξ is defined as

$$\xi = 4\frac{V}{S}\frac{\langle \eta^2 \rangle}{(\Delta\rho)^2} \tag{2}$$

where $<\eta^2>$ is the mean square fluctuation of the electron density and $\Delta\rho$ is the electron density difference between the two phases. In this context, the invariant Q is expressed as

$$Q = V\langle \eta^2 \rangle = V(\Delta\rho)^2 \phi_1 \phi_2 \tag{3}$$

where ϕ_1 and ϕ_2 are the volume fractions of phase 1 and 2, respectively. By combining *eq* 2 and 3, we obtain the following relationship as

$$\frac{V}{S} = \frac{\xi}{4\phi_1\phi_2} \tag{4}$$

For a symmetric PS-*b*-PMMA system particularly with $\phi_{PS} = \phi_{PMMA} = 0.5$, one can calculate the ξ (equal to V/S) that defines the compositional randomness of our adsorbed layers.
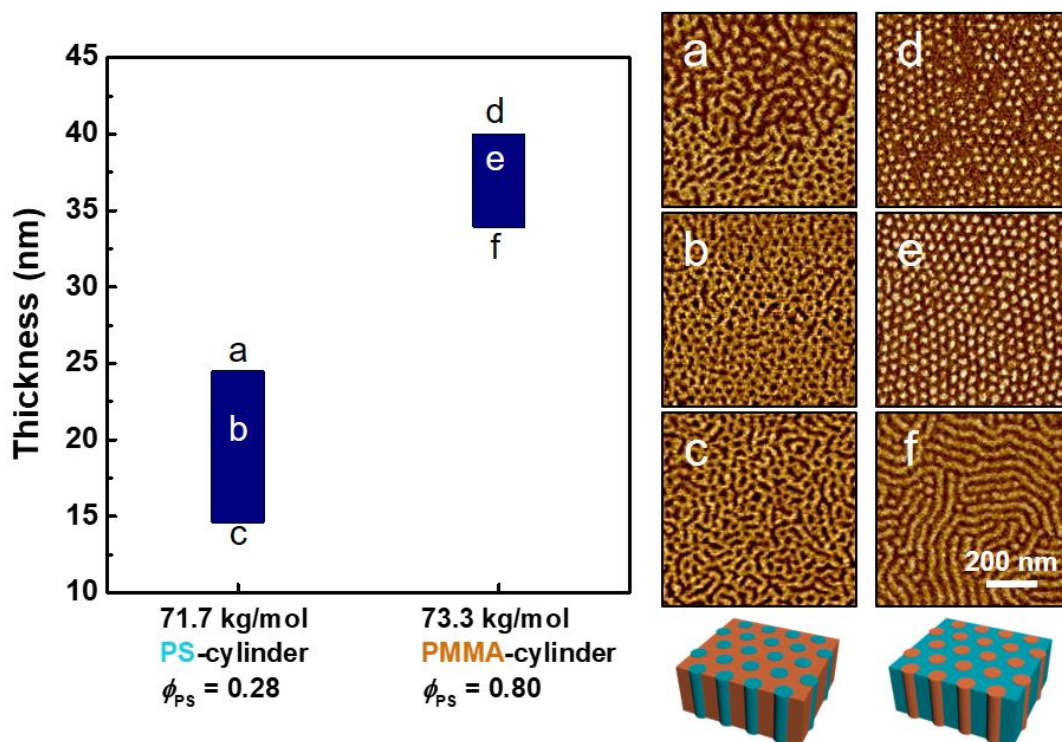
Figure S3. Thickness windows of perpendicular cylinders for asymmetric PS-*b*-PMMA films supported on the adsorbed layers of themselves. (a – c) SFM phase images of PS-cylinder forming BCP films (71.7 kg/mol, ϕ_{PS} = 0.28) at thicknesses of 25.3, 21.3, and 13.8 nm. (d – f) SFM phase images of PMMA-cylinder forming BCP films (73.3 kg/mol, ϕ_{PS} = 0.80) at thicknesses of 41.3, 37.8, and 33.0 nm, respectively. To ensure thermal equilibrium self-assembly, 71.7 kg/mol PS cylinder-forming and 73.3 kg/mol PMMA cylinder-forming PS-*b*-PMMA films were thermally-annealed at 200 and 170 °C, respectively, under vacuum for 24 h.
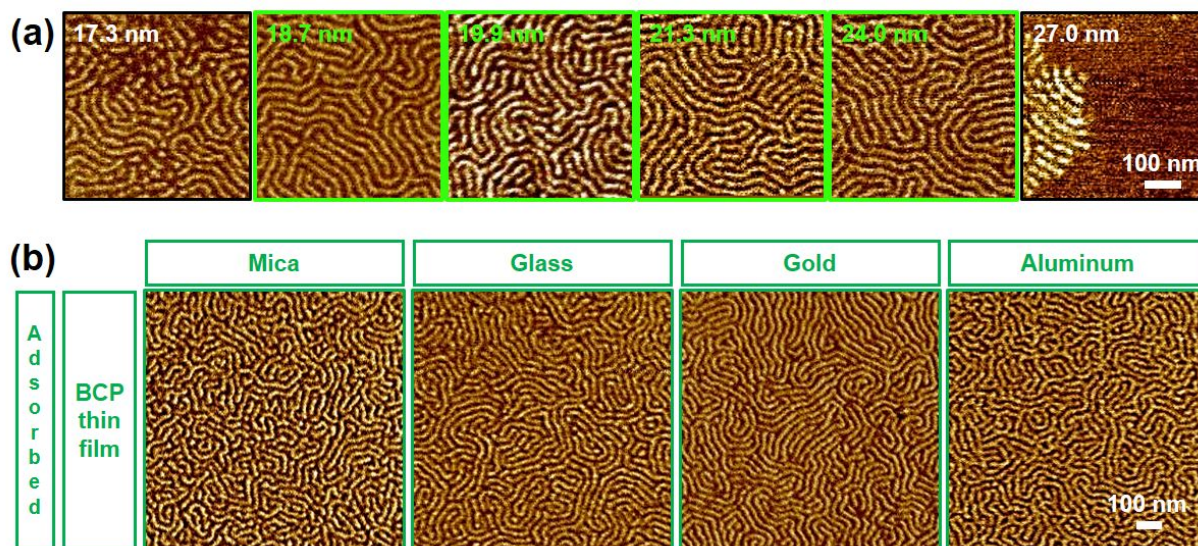

Figure S4. (a) Thickness window of perpendicular lamellae of the overlying SM42 on the adsorbed layer of its own using H-passivated Si substrates. (b) SFM phase images of SM42 films (~ 22 nm) supported on various substrates (mica, glass, gold, and deposited aluminum) with the irreversible adsorption of SM42 itself onto such substrates.

References

(1) Roe, R. J. *Methods of X-ray and neutron scattering in polymer science*; Oxford University Press: **2000**; p 174.