Supporting Information

Self-assembled Copolymer Adsorption Layer-Induced Block Copolymer Nanostructures in Thin Films

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A. Experimental details

Materials Polystyrene-\textit{b}-poly(2-vinylpyridine) (PS-\textit{b}-P2VP) and polystyrene-\textit{b}-poly(methyl methacrylate) (PS-\textit{b}-PMMA) were purchased from Polymer Source, Inc. The molecular weights of PS-\textit{b}-P2VP are 30,000-\textit{b}-8,500 g/mol (30-8.5k, polydispersity index (PDI) = 1.06), 30,000-\textit{b}-12,500 g/mol (30-12.5k), 44,000-\textit{b}-18,500 g/mol (44-18.5k, PDI = 1.07), and 79,000-\textit{b}-36,500 g/mol (79-36.5k, PDI = 1.05). The molecular weights of PS-\textit{b}-PMMA are 64,000-\textit{b}-35,000 g/mol (64-35k, PDI = 1.09), and 35,000-\textit{b}-37,000 g/mol (35-37k, PDI = 1.09). P2VP/PS homopolymers (37,500/35,000 g/mol) were purchased from Sigma-Aldrich (37.5k/35k). Chloroform (Sigma-Aldrich, HPLC grade, 99.9%), Toluene (Sigma-Aldrich, anhydrous, 99.8%), Ethanol (Sigma-Aldrich, 99.8%), Isopropanol (Sigma-Aldrich, anhydrous, 99.5%), Heptane (Sigma-Aldrich, HPLC grade, ≥99%), Hexane (Sigma-Aldrich, HPLC grade, ≥99.5%), Tetrahydrofuran (Sigma-Aldrich, HPLC grade, ≥99.9%) were used in this study. Deionized water (18.2 MΩcm) was obtained by purification of distilled water with a Millipore Milli-Q Gradient system. (100) Si wafers (purchased from Waferbiz) were employed as substrates. 0.5 wt % ruthenium tetroxide (RuO\textsubscript{4}) aqueous solution were purchased from Fisher Scientific.

| Underlying layer (SCAL) | Upper layer |
|-------------------------|-------------|
| notation                | morphology  | notation | morphology            |
|                         | bulk        | air/water interface | hole                  |
| PS-\textit{b}-P2VP      | cylinder    | dot (without confinement) | dot-filled hole        |
| (44-18.5k)              |             |            | perpendicular cylinder |
|                        |             |            | perpendicular cylinder with some parallel one |
| PS-\textit{b}-PMMA      |             | strand (with confinement) | dot-filled hole        |
| (64-35k)                | cylinder    |             | density-multiplied dot patterns |
| PS-\textit{b}-PMMA      |             | narrow strand (with confinement) | dot-filled honey comb |
| (35-37k)                | lamella     |             | perpendicular lamell   |
| PS-\textit{b}-P2VP      | cylinder    | wide strand (with confinement) | trench                |
| (79-36.5k)              |             |             | dotted-line            |

Table S1. Morphology and structure information for all block copolymers used in this study. The strand forming SCAL was obtained with area-confinement previously reported.\textsuperscript{1}
Atomic Force Microscopy (AFM) AFM (Veeco Dimension 3100) was used in a tapping mode with Bruker tips (RTESP), which have a drive frequency of 300 kHz, a spring constant of 40 N/m, a cantilever length of 125 μm, and a tip radius of 8 nm.

Scanning Electron Microscopy (SEM) Hitachi S-4800 field emission scanning electron microscope (high vacuum, 1 keV) were used. For the cross section images, the BCP thin films were exposed to the saturated vapor from 0.5 wt % ruthenium tetroxide (RuO₄) aqueous solution for 30 min to stain the PS domains and thereby increase the interdomain contrast.

Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) Depth profiles were obtained using ToF-SIMS (ION TOF, Germany), with a 25 keV Bi³⁺ analysis beam and a 0.25 keV Cs sputtering beam. The raster sizes for analysis and sputtering were 90 and 300 μm, respectively. The target currents of the analysis and sputtering beams were 0.4 pA and 11.0 nA, respectively. The ToF-SIMS instrument was operated in the noninterlaced mode, and negative secondary ions were detected to analyze the composition along the out-of-plane direction. The depth distributions of PS, PMMA, and P2VP are represented by C₆H−, CH₃O−, and C₂N− ions, respectively.

Grazing Incident Small Angle X-ray Scattering (GISAXS) GISAXS measurements were performed at the PLS-II 6D UNIST-PAL and 9A U-SAXS beamline of the Pohang Accelerator Laboratory (PAL) in Korea. For the GISAXS measurements in 6D UNIST-PAL, the energy of the X-rays was 10.0 keV (wavelength, λ = 1.2398 Å), the incident angle was 0.13°, and the sample-to-detector distance was 3088.86 mm. For the GISAXS measurements in 9A U-SAXS, the energy of the X-rays was 11.025 keV (wavelength, λ = 1.12454 Å), the incident angle was 0.12°, and the sample-to-detector distance was 6367.87 mm. Scattering patterns were collected using a 2D CCD detector (MX225-HS, Rayonix L.L.C., USA).

Langmuir-Blodgett (LB) instrument Langmuir trough having a maximum size 273 cm² (a computer controlled KSV NIMA KN 2002 Langmuir Blodgett instrument with a platinum Wilhelmy plate) was employed. Temperature of water in a trough was kept constant at room temperature. Every symmetric barrier compression was proceeded with a barrier speed of 5 mm/min (3.75 cm²/min) and LB films were deposited on clean Si wafers at a speed of 5 mm/min. Every surface pressure – area (π–A) isotherm curve was confirmed by repeats more than three times.

X-ray Photoelectron Spectroscopy (XPS) Thermo Scientific Model K-Alpha XPS instrument were used for XPS analysis. The chemical state of all the elements in P2VP film were determined by XPS analysis using an Al Kα X-ray source (1486.6 eV). All samples were analyzed with a 900 μm X-ray spot size.

The typical pressure in the analysis chamber was 2 × 10⁻⁷ mbar. 3 - 10 scans were performed for each measurement at 0.1 eV/step.

Film thickness measurement The thickness of films was measured using a spectroscopic ellipsometer (M-2000V, J.A. Woollam Co.).

Interfacial Self-Assembly (ISA) of BCPs The interfacial assembly of PS-b-P2VP at the air/water was investigated with varying molecular weight and relative block fraction of PS-b-P2VP. BCPs and P2VPs were
dissolved in chloroform at a concentration of 1 mg/ml. 30 μL of solutions were spread on a deionized water (Milli Q) surface as 6 drops in a medium Langmuir trough having a maximum size 273 cm². After a complete spreading-solvent evaporation (more than 20 min), LB films were compressed laterally with a symmetric barrier (5 mm/min) and subsequently deposited on a clean Si wafer.

**Spreading area-dependent morphology transition for strand-forming SCALs** For the strand-forming SCALs in Figure 6b, c and d, 10 μL of a 1 mg/mL of chloroform solution for PS-b-P2VP (30-12.5k, 44–18.5k, and 79-36.5k, respectively) were spread onto water surface in a 6 cm diameter Petri dish. After a complete spreading-solvent evaporation (more than 20 min), interfacial self-assembled BCPs were transferred onto a clean Si wafer.

**Thermal annealing (TA)** Every TA in this study was conducted at 190 °C, for 24 hours, under vacuum.

**Sample preparation for SCAL-induced self-assembly** PS-b-PMMA (64-35k and 35-37k) were spin-coated from toluene solution of 0.5 – 1 wt% on the SCALs, thus forming a 23 – 25 nm thick film. The spin-coated films were thermally annealed at 190 °C, for 24 hours, under vacuum.

**Sample preparation for irreversibly adsorbed layers from spin-coated P2VP film** Guiselin’s approach² were utilized to obtain the irreversibly adsorbed layer of P2VP (37.5k). 300 nm-thick P2VP (37.5k) films were spin-coated from chloroform solution of 3 wt%. 300 nm-thick P2VP films were immersed in a few hundreds of ml of fresh chloroform for 30 minutes three times, and the irreversible adsorbed layers were achieved. The processes are shown in Table S2a, b, c and d in section J.

**Safety Statement** No unexpected or unusually high safety hazards were encountered.
B. SCALs replacing the natural adsorbed layer

Figure S1. SEM images of PS-b-PMMA (64-35k) adsorbed layer after toluene-washing of the spin-coated PS-b-PMMA (64-35k) film on (a and b) a bare Si wafer and (c and d) PS-b-P2VP (44-18.5k) SCALs.
C. GISAXS 2D images for the stability of SCALs

Figure S2. GISAXS 2D images of PS-\(b\)-P2VP (44-18.5k) SCALs in Figure 1a before (pristine) and after the immersion in various solvents and/or thermal annealing.
D. PS-b-PMMA SCALs and its stability

Figure S3. The stability of SCAL. SEM images of PS-b-PMMA (50-100k) SCAL (a) transferred at 2 mN/m on a O2 plasma treated Si wafer and (b) after toluene-washing.
E. Langmuir film of PS homopolymers (35k) and its stability

![SEM images of transferred LB film of PS homopolymer](image)

**Figure S4.** SEM images of (left) transferred LB film of PS (35 kg/mol) homopolymer at 5 mN/m on a wafer, and (right) after toluene washing.

In our main experiments, the SCAL was transferred and additional BCP was spin-coated without thermal annealing, where SCAL remains stable. However, the PS aggregates in the LB film of PS homopolymers on the substrate were washed away with toluene without thermal annealing indicating a weaker adsorption of the PS aggregates compared to that of P2VP. Thus, we consider that the P2VP in SCAL firstly contribute to the adsorption. However, during the additional thermal annealing process in SCAL-induced self-assembly, the PS domain in SCAL starts to be irreversibly adsorbed on the substrate via the van der Waals interaction or π···H–O interaction of PS chains to the substrates.
F. $\pi$–$A$ isotherm curve for the P2VP (37.5k)

Figure S5. $\pi$–$A$ isotherm curve of P2VP (37.5k). The prepared films at the pressures marked with red triangles were transferred to Si substrates and used for XPS analysis. The XPS spectra of these films were given in Figure 1c in the main manuscript. The samples are listed in Table S2 as ‘e’, ‘f’, ‘g’, and ‘h’.
G. Discussion on XPS analysis

Fourteen different samples of P2VP homopolymers (37.5 k) were used for the XPS analysis, and the details of samples used for XPS analysis are listed in Table S2.

When the P2VP chains are in bulk, only one main peak is shown in the N 1s spectra at 399.1 ± 0.1 eV, attributed to the single nitrogen atom of pyridine (Figure S6m and n). Whereas, all the other P2VP adsorbed layers show two additional peaks at 401.5 and 397.8 ± 0.1 eV (Figure S6a, b, c, d, e, f, g, h, i, j, k, and l).

According to previous researches,\textsuperscript{3-6} N 1s peak at 401.5 eV is assigned to the hydrogen bonded nitrogen atom of N⋯H–O feature. This peak is prominent in P2VP(LB) at 2, 5, 10, and 15 mN/m, as shown in Figure S6e, f, g and h, respectively. The results correspond to our prediction that transferred P2VP chains from the air/water interface can adsorb onto a silicon wafer as forming a H-bonding between a nitrogen atom of a pyridine ring and a hydroxyl group of a native oxide layer (Figure 1b). Against additional thermal annealing (P2VP(LB)\textsubscript{TA}), the peaks at 401.5 eV from hydrogen bonded nitrogen atom remained unchanged as shown in Figure S6i, j, k and l. This implies that the H-bonding for adsorption was strong enough not to change the chain conformation during thermal annealing even considering such a harsh annealing condition at high temperature.

On the other hand, a shoulder peak of N 1s at 397.8 eV appears in P2VP(spin) of Figure S6a and b, and becomes dominant in P2VP(spin)\textsubscript{TA} of Figure S6c and d. This peak informs that the nitrogen atoms of the pyridine rings not involved in the hydrogen bonding of N⋯H–O is clearly present; different type of interaction may govern the irreversible adsorption of P2VP chains in films prepared by the Guiselin’s approach.\textsuperscript{2} We carefully investigated whether the chemical states of other atoms were changed or not in accordance with the increasing peaks of N 1s at 397.8 eV. Interestingly, we found that the core level shifts of C 1s occur proportional to increasing peaks of N 1s at 397.8 eV: black arrows in Figure S7a, b, c, and d show increasing core level shifts with N 1s peaks at 397.8 eV in Figure S6a, b, c, and d, respectively. Note that those changes in C 1s or N 1s are correlated with the change in a chemical state of pi-bond in a pyridine ring. Taken together, we postulated that the silanol or siloxane groups of the native oxide layer interact with the pi bond in the aromatic pyridine ring, thus forming H-bonding of pi⋯H–O or pi⋯O. Thus, the H-bonding of pi⋯H–O or pi⋯O is found to be main origin of irreversible adsorption of P2VP chains in P2VP(spin)\textsubscript{TA} while the H-bonding of N⋯H–O is the main contribution to the great stability of the SCAL.

These results correspond to the previous studies; the polymer chains in irreversibly adsorbed layer undergo flattening process as their aromatic ring moieties tend to be parallel to a substrate by forming the H-bonding of pi⋯H–O between the aromatic ring and a surface hydroxyl group of the quartz surface.\textsuperscript{7,8}

It is striking that the origins of the H-bonding for adsorbed layers are differed depending on how the adsorbed layers are formed: whether they are transferred from air/water interface or obtained from spin-coated film.

At the air/water interface, P2VP chains spread on the water surface two-dimensionally and form an H-bonding between an electron lone pair on nitrogen in pyridine and a water molecule owing to their great mobility, which overcomes the steric hindrance from the ortho-position of the nitrogen. This chain conformation of P2VP including the H-bonding of N⋯H–O is preserved during the transferring process.
Whereas, a spin-coating provides different chain conformations of P2VP chains in the adsorbed layer. When P2VPs are spin-coated on substrates, the P2VP chains are kinetically trapped with disordered chain conformations driven by the rapid solvent evaporation. Therefore, pyridine rings of the P2VP chains in the adsorbed layer are randomly oriented on the SiO-H substrate, thus having both of N···H–O and pi···H–O, as shown in Figure S6a and b. While further thermal annealing may relax the chain conformation, we found that the pyridine ring prefers the pi···H–O rather than N···H–O due to the bigger steric hindrance in N···H–O.
H. XPS spectra of N 1s for P2VP (37.5k) adsorbed layers

Figure S6. XPS spectra of N 1s for p2vp homopolymer (37.5 k). The adsorbed layers were created either from spin-coating or film transfer from the air/water interface. Samples are briefly labeled in each figure and the detailed procedure for each is given in Table S2 in Section K.

P2VP adsorbed layers were created by (a) spin-coating of films and washing the non-adsorbed polymers with chloroform, (b) spin-coating, residual solvent removal and washing with solvent (c) spin-coating,
thermal annealing and washing with solvent, (d) spin-coating, residual solvent removal, thermal annealing, and washing with solvent.

P2VP adsorbed layers were also created by the film transfer of P2VP monolayer formed at air/water interface at different pressures. (e) 2 mN/m, (f) 5 mN/m, (g) 10 mN/m, and (h) 15 mN/m. (i), (j), (k), and (l) are the samples which underwent additional thermal annealing after the transfer at (e), (f), (g) and (h), respectively.

For comparison, XPS spectra of bulk P2VP were also obtained by (m) spin-coating of P2VP at 300 nm thickness and (n) spin-coating of P2VP and residual solvent removal process. The raw data is in black open scatters. The fitted curves are in red and the base line is in black, which mostly are hidden by the deconvoluted peaks in blue).
I. XPS spectra of C 1s for P2VP (37.5k) adsorbed layers

Figure S7. XPS spectra of C 1s for p2vp homopolymer (37.5 k) adsorbed layers described in Figure S6 and Table S2 in Section J. Here, the black arrow indicates the core level shift of C 1s.

P2VP adsorbed layers were created by (a) spin-coating of films and washing the non-adsorbed polymers with chloroform, (b) spin-coating, residual solvent removal and washing with solvent (c) spin-coating, thermal annealing and washing with solvent, (d) spin-coating, residual solvent removal, thermal annealing, and washing with solvent.

P2VP adsorbed layers were also created by the film transfer of P2VP monolayer formed at air/water interface at different pressures. (e) 2 mN/m, (f) 5 mN/m, (g) 10 mN/m, and (h) 15 mN/m. (i), (j), (k), and (l) are the samples which underwent additional thermal annealing after the transfer at (e), (f), (g) and (h), respectively.
For comparison, XPS spectra of bulk P2VP were also obtained by (m) spin-coating of P2VP at 300 nm thickness and (n) spin-coating of P2VP and residual solvent removal process. The raw data is in black open scatters. The fitted curves are in red and the base line is in black, which mostly are hidden by the deconvoluted peaks in blue).
J. XPS spectra of Si 2p for P2VP (37.5k) adsorbed layers

**Figure S8.** XPS spectra of Si 2p for p2vp homopolymer (37.5 k) adsorbed layers described in Figure S6 and Table S2 in Section J. Black open scatters are raw data, red line is fitted curve, black line is base line, and blue is deconvoluted peaks. Black arrows indicate the peaks originated from native oxide.

P2VP adsorbed layers were created by (a) spin-coating of films and washing the non-adsorbed polymers with chloroform, (b) spin-coating, residual solvent removal and washing with solvent (c) spin-coating, thermal annealing and washing with solvent, (d) spin-coating, residual solvent removal, thermal annealing, and washing with solvent.

P2VP adsorbed layers were also created by the film transfer of P2VP monolayer formed at air/water interface at different pressures. (e) 2 mN/m, (f) 5 mN/m, (g) 10 mN/m, and (h) 15 mN/m. (i), (j), (k),
and (l) are the samples which underwent additional thermal annealing after the transfer at (e), (f), (g) and (h), respectively.

For comparison, XPS spectra of bulk P2VP were also obtained by (m) spin-coating of P2VP at 300 nm thickness and (n) spin-coating of P2VP and residual solvent removal process. The raw data is in black open scatters. The fitted curves are in red and the base line is in black, which mostly are hidden by the deconvoluted peaks in blue).
Table S2. Detailed descriptions for samples used for XPS analysis in Figure S6, S7, and S8. The XPS spectra given in the Figure 1c in the manuscripts are sample a, c, e, f, g, h, and m in this table.
L. PS-b-PMMA (64-35k) thin film without SCAL

Figure S9. (a) SEM images of PS-b-PMMA (64-35k) with 25 nm thickness on a bare Si wafer, thermally annealed at 190 °C for 24 hours. (b) ToF-SIMS depth profile of PS-b-PMMA (64-35k) of panel a. Purple color-shaded area represents Si wafer. (c) Schematic illustration of the formation of PS-b-PMMA (64-35k) of panel a and b.
M. GISAXS 1D profile of PS-b-P2VP (44-18.5k) SCALs

Figure S10. GISAXS 1D profile details of PS-b-P2VP (44-18.5k) SCALs (upper row) and SCAL-induced self-assembly of PS-b-PMMA (64-35k) (lower row) in Figure 3e. Surface pressure of SCALs are (a) 1, (b) 5, (c) 10, (d) 15, (e) 20, and (f) 30 mN/m, respectively.
N. Topographic data for PS-\textit{b}-P2VP (44-18.5k) SCALs

![AFM height images and topographic profiles](image)

**Figure S1.** AFM height images of PS-\textit{b}-P2VP (44-18.5k) SCALs in Figure 3a, and its topographic profiles at red lines in the images.
O. Contact angle data for PS-b-P2VP (44-18.5k) SCALs

Figure S12. Water contact angles on the PS-b-P2VP (44-18.5k) SCAL at (left) 10 mN/m, (center) 15 mN/m, and (right) 20 mN/m.
Figure S13. SEM image of PS-\textit{b}-PMMA (35-37k) film spin-coated on a Si wafer at 23 nm thickness, and thermally annealed at 190 °C for 24 hours.
Q. Micelle size for PS-b-PMMA (35-37k)

Figure S1.4. AFM height images of SCAL-induced self-assembly of PS-b-PMMA (35-37k) on the PS-b-P2VP (44-18.5k) SCALs (σ = 2 mN/m). The diameter of the micelle-like structures of PS-b-PMMA (35-37k) is approximately 60 nm.
R. Trench patterns from SCAL-induced self-assembly on strand-forming SCALS

Figure S15. (a) Schematic illustration of the formation of SCAL-induced self-assembly of asymmetric BCPs on the strand-forming SCALS when less polymer was spin-coated with insufficient thickness. (b) SEM image of strand-forming SCAL: PS-b-P2VP (30-8.5k). (c) SEM image and (d) AFM height image of SCAL-induced self-assembly of PS-b-PMMA (64-35k) at 18 nm where only trench pattern is formed (See inset of panel b) (e) The height profile of the white line in AFM height image of the panel d.
S. AFM height images of SCAL-induced self-assembly on strand-forming SCALs

**Figure S16.** AFM height images of SCAL-induced self-assembly of PS-\(b\)-PMMA (64-35k) showing (a) dotted-line pattern, (b) dash-line pattern, and (c) anisotropic cluster pattern on corresponding strand-forming SCALs of PS-\(b\)-P2VP (30-12.5k), PS-\(b\)-P2VP (44-18.5k), and PS-\(b\)-P2VP (79-36.5k), respectively. Each AFM height image in panel a, b, and c is matched with the AFM phase image in the panel h, i, and j of Figure 6, respectively.
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