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# Supporting information

# Perpendicular Orientation of Sub-10 nm Channels in Polystyrene-*b*-poly(4-hydroxyl styrene)/PEG Oligomers Blend Thin Films

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## Experimental Section

### Materials

Toluene and tetrahydrofuran (THF) (NacalaiTesque Inc., Extra Pure) were used as a solvent withoutfurther purification. In order to remove a stabilizer and inhibitors in monomers, granular activated alumina (Kanto Chemical Inc.) wasadded into styrene (Nacalai) and4-*tert*-butoxy styrene (Wako Chemical, Inc.) respectively.Poly(ethyleneglycol) mono-methyl ether (PEG, *M*n = 550) was purchasedfrom (Aldrich Chemical Company). Styrene monomer was further distilled under reduced pressurebefore polymerization. Silicon wafer (<0.02 Ω cm, 0.5mm in thickness) was obtained from the NilacoCorporation. The wafer was washed with distilled water beforeuse. The wafer was fully dried in air for 48 h.

### Sample Preparation

A block copolymer polystyrene-*b*-poly(4-*tert*-butoxystyrene) (PS-*b*-PBS) was synthesized bysequential anionic polymerization. The*tert*-butoxy groups in the block copolymer were fully hydrolyzed by trifluoroacetic acid in toluenesolution. The obtained PS-*b*-poly(4-hydroxyl styrene) (PS-*b*-PHS) with 17.7% volume fraction of PS was dissolved intoluene and THF solution. Subsequently, PEG was blended in the solutions until total volume fractionof PS in polymers equaled to 75vol%. The solutions were vigorously stirred at room temperature for 24 h. Total concentration of the polymer solution was 12 wt%. Thin films on the silicon wafer were obtained

byspin coating at 3000rpm for 30 sec of the solutions at room temperature without further thermal annealing. The thin films were exposed to THF vapor (THF solvent annealing) for given time in an annealingchamber. After solvent annealing, the sample was taken out from the chamber and was set on the stageused for GISAXS measurement.

**Characterization**

The micro-phase separated structures were observed using small angle X-ray scattering (SAXS) andgrazing incidence smallangleX-ray scattering (GISAXS). SAXS and GISAXS measurements were conducted at BL6A, BL9C and BL15A in Photon Factory of KEK,Tsukuba in Japan and BL40B2 and BL03XUin SPring-8, Hyogo in Japan. In BL9C, an imaging plate(FUJI BAS2500) was used as a detector which was set at a position of 110 cm apart from sample position. In BL6A, BL03XU, and BL40B2,the charge-coupled device with an image intensifier (II-CCD, Hamamatsu Photonics Co., Ltd.) wasused as a detector that was set at a position of 250 ~300 cm apart from sample position. Thewavelength $\lambda$ of X-rays was 0.15 (PF) and 0.10 (SPring-8) nm in the stations. Collagen (chickentendon) was used as a standard specimen to calibrate the SAXS detectors. The grazing angle $\alpha_i$ of X-raybetween X-ray and sample surface was in a range of 0.16 ~ 0.21º which is smaller than the criticalangle (~0.22º for $\lambda = 0.15$ nm) of the interface between the block copolymer and the substrate,but bigger than that ofthe block copolymer surface (~0.15º for $\lambda = 0.15$ nm).

The surface topography of thin films on a siliconwafer was imaged by AFM (Vecco, Nanoscope IV) inthe tapping modewith a silicon cantilever (NCH-10T) at a scan rate of 0.8-1.1 Hz at ambient conditions.The thickness measurement was conducted using AFM (Seiko Instruments Inc. NPX200/Nanopics 2100).The films were partly scratched by a steel needle and the height difference was evaluated by AFM as for film thickness.

Proton nuclear magnetic resonance ($^1$HNMR) spectra were recorded on a Bruker 200M NMRinstrument with tetramethylsilane (TMS) as the internal standard, usingd-toluene as the solvent at room temperature.

XPS measurements were performed on an ESCALAB250 spectrometer (Thermo Electron Corporation) equippedwith a monochromatic Al K$\alpha$ X-ray source.

For the TEM observation from cross-section view, the thin films afterTHF vapor annealing were prepared onto a 100 micro meter thick Kapton film.The samples are previously embedded in epoxy resin (Quetol-812, Nissin EM).After curing, the sample is microtomed using an Ultracut N microtome,Reichert-Nissei. Diamond knives, DIATOME) were used forboth the trimming and cutting process. The sample was trimmed and cut at room temperature. From the ultra-microtoming process, ca. 200 nm thick slices are obtainedand placed over carbon coated copper grids (grid 75/300 mesh Cu, Veco). Thethin sections were picked up onto the copper grids and stained in $RuO_4$ vaporfor ca. 10 min. TEM (H-800, HITACHI Co.) was performed with electron beamenergy of 100 keV.As for through view, the sample was removed (peeled off) from the siliconwafer by immersed into waterfor long time after confirming the perpendicular orientation of thecylindrical morphology by GISAXS.

The thin film was floated in water. Asmall piece of the floating thin film was scoop up by a carbon coated coppergrids for TEM observation as the sample surface was parallel to the gridsurface, i.e., the cylinder axis was parallel to the electron beamdirection. The thin film was not stained with any heavy metals. TEM (JEOLJEM-2500z) was operated with 200keV electron beam.

**ParacrystallineDistortion Theory**

We performed model calculationof the SAXS profiles (in-plane GISAXS profiles) for hyxagonally packed cylindricalmicrodomain based on Hosemann'sparacrystal theory[63,66,68]. According to the theory, scattering intensity $I(\boldsymbol{q})$ for microphase-separated block copolymers can be formulated as

$$I(\boldsymbol{q}) = \langle |f^2(\boldsymbol{q})| \rangle - |\langle f(\boldsymbol{q}) \rangle|^2 + |\langle f(\boldsymbol{q}) \rangle|^2 Z(\boldsymbol{q})$$

where$f(q)$ and $Z(q)$ denote the scattering amplitude due to the intraparticle interference and the scattering intensity due to the interparticle interference (structure factor), respectively. Hereafter, $f(q)$ and $Z(q)$ are referred to as the particle and the lattice factor, respectively. In above equation, $\langle x \rangle$ is the average of the quantity of $x$, $f(q)$ for a cylindrical particle with radius r and length L can be expressed as follows;

$$f(\boldsymbol{q}) = 2\pi r^2 L \frac{J_1(qr\sin\beta)}{qr\sin\beta} \frac{\sin\left(\frac{qL}{2}\cos\beta\right)}{\frac{qL}{2}\cos\beta} \exp\left[-\frac{1}{2}q^2\sigma^2\sin^2\beta\right]$$

where$\sigma$ is a parameter characterizing the interface thickness of the cylinders along there radii (here we assumed$\sigma = 0$ for simplicity) and $\beta$ is an angle between cylinder axis and scattering vector.

Here it is assumed that the distribution of the radius $r$ of the cylindrical particle follows a Gaussian distribution $P(r)$:

$$P(r) \sim exp\left[-\frac{(r-\bar{r})^2}{2\sigma_r^2}\right]$$

where$\bar{r}$ and $\sigma_r$ are the mean radius and a standard deviation of $r$ from $\bar{r}$, respectively. Then $\langle f(q) \rangle$ is given by

$$\langle f(\boldsymbol{q}) \rangle = \frac{\int_0^\infty P(r)\, f(\boldsymbol{q}) dr}{\int_0^\infty P(r)\, dr}$$

For a paracrystalline lattice consisting of cylinders, the structure factor $Z(q)$ can be determined from the Fourier transform of a complete set of lattice points. In a paracrystal with distortion of the second kind, the position of the lattice points can be only be described with a positional distribution function of the crystal lattice is given by the convolution product of the lattice points along three axes, and the distribution function is a Gaussian, $Z(\boldsymbol{q})$ can be expressed by the following equation:

$$Z(\boldsymbol{q}) = \prod_{k=1}^{3} Z_k(\boldsymbol{q})$$

The $k$-th lattice factor $Z_k(\boldsymbol{q})$ is given by

$$Z_k(\boldsymbol{q}) = 1 + \frac{F_k(\boldsymbol{q})}{1 - F_k(\boldsymbol{q})} + \frac{F_k^*(\boldsymbol{q})}{1 - F_k^*(\boldsymbol{q})}$$

where

$$F_k(\boldsymbol{q}) = |F_k(\boldsymbol{q})|\exp(-i\boldsymbol{q} \cdot \boldsymbol{a}_k)$$

and

$$|F_k(\boldsymbol{q})| = \exp\left[-\frac{1}{2} g_k^2 q^2 \boldsymbol{a}_k^2\right]$$

Here, $g_k$ are paracrystal distortion factor (Hosemann's $g$-factor) defined by

$$g_k^2 = \Delta^2 \boldsymbol{a}_k / \boldsymbol{a}_k^2$$

where $\boldsymbol{a}_k$ and $\Delta \boldsymbol{a}_k$ are the fundamental vector of the $k$-th axis and its displacement, respectively. In the present study, isotropic displacement is assumed.We adjusted the parameters, $g$-factor, radius of the cylinders, a standard deviation of the $r$ from $\bar{r}$, and domain spacing for the fitting.

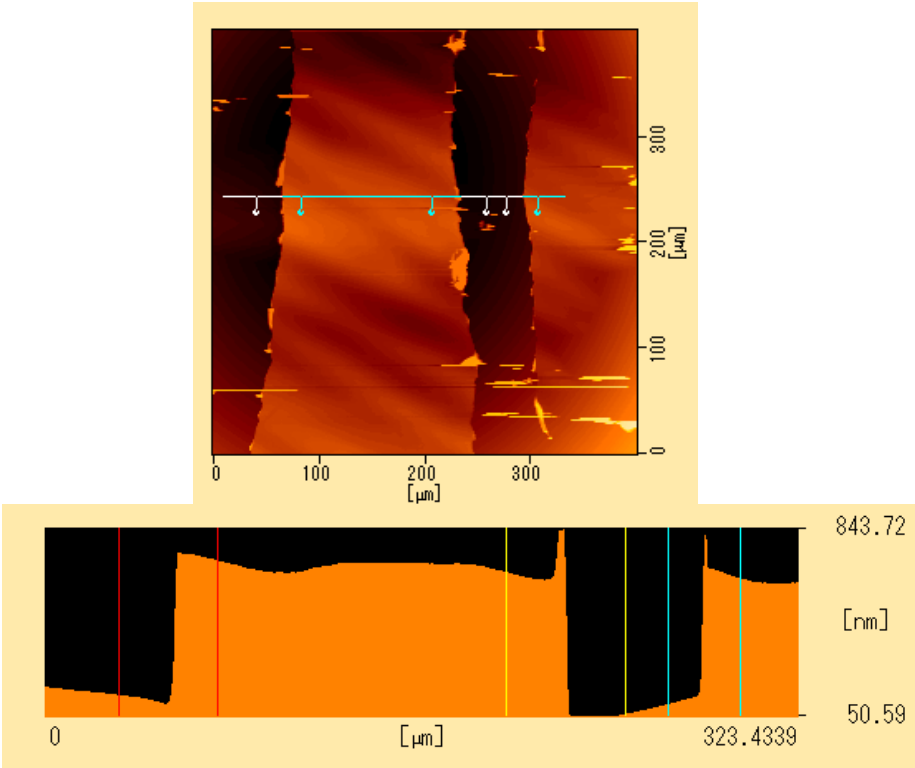


**Figure S1** Thickness measurementof the thin films spin cast from about 10 wt% solution, which were partly scratched by a steel needle and the height difference was evaluated by AFM as for film thickness.

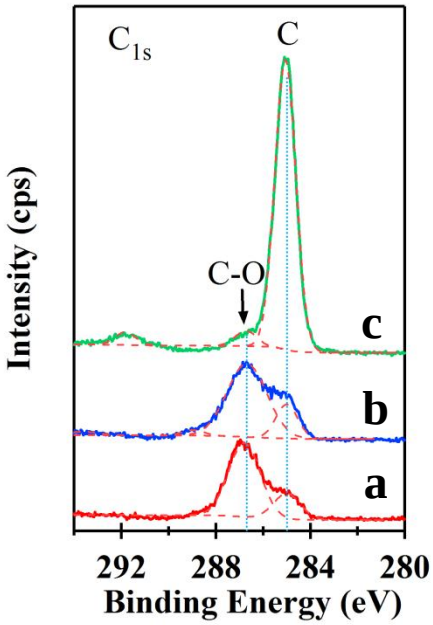


**Figure S2** XPS C 1s core-level spectra for the thin films (a) after spin cast, (b) after THF annealing and (c) after removal of PEG

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**Table S1** Parameters of Cylinders and Channels from AFM, TEM and GISAXS

| | AFM | | TEM | | GISAXS | |
|---|---|---|---|---|---|---|
| | Diameter [a] | *d* [b] | Diameter [a] | *d* [b] | Diameter [a] | *d* [b] |
| Solvent annealing | 16nm | 26 nm | - | - | 15 nm | 26.7 nm |
| Removal of PEG | 11nm | 27 nm | 10 nm | 28 nm | 9 nm | 26.7 nm |

[a] diameters of cylinders before removal of PEG and diameters of nanochannels after removal of PEG; [b] domain spacing;

**Table S2** Calculated Electron Density (ρ) of Diverse Components in BulkUsed to Calculate Theoretical Scattering Intensity

| | PS | PHS | PEG | air | PHS/PEG |
|---|---|---|---|---|---|
| ρ (mol/cm$^3$) | 0.565 | 0.629 | 0.594 | ~0 | 0.616 |