

Supporting Information

Thickness-dependent Morphological Behavior of Dendritic (PS)₂-*b*-PLA Copolymer Thin Films on SiO₂ Substrate

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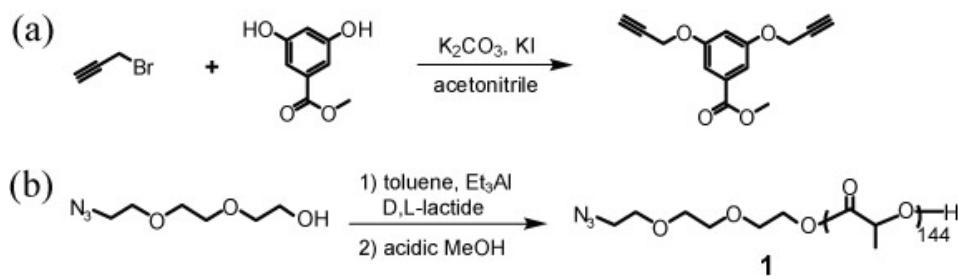
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Materials. 2,2'-Bipyridine ($\geq 99\%$), copper(I) bromide (99.999%), *N,N,N',N'',N'''-*pentamethyldiethylenetriamine (PMDETA, 99%), propargyl bromide solution (80 wt. % in toluene), propargyl alcohol (99%), 4-(dimethylamino)pyridine (DMAP, 99%), methyl 3,5-dihydroxybenzoate (97%), tri(ethylene glycol) (99%), sodium azide (99.99+%), *sec*-butyllithium (*sec*-BuLi, 1.4 M solution in cyclohexane), methanolic HCl (1.25 M in methanol), and triethyl aluminum (1.0 M solution in hexanes) were purchased from Sigma-Aldrich. *D,L*-Lactide (Aldrich) was purified by recrystallization from toluene and then dried under reduced pressure at room temperature. ¹H NMR spectroscopy was used to confirm its purity, and the purified *D,L*-lactide was then stored under argon in a glove box. Tetrahydrofuran, toluene and cyclohexane (from Burdick & Jackson Co.) were dried with deep red 1,1-diphenylethylene (97%, Aldrich)/*n*-butyllithium (2.5 M solution in hexanes, Aldrich), and degassed several times before distillation into a flame-dried Schlenk flask by a high vacuum technique. Styrene (Aldrich, $\geq 99\%$) was dried and purified by stirring over CaH₂ (Acros) for 24 h, and followed by distillation in the same manner as cyclohexane. Ethylene oxide (Aldrich, 99.5+%) was allowed to stand over *n*-butyllithium at 0 °C, and was degassed several times before distillation into flame-dried graduated ampoule under high vacuum. The purified ethylene oxide was sealed and stored under liquid nitrogen just before use. PMDETA was degassed by several freeze-pump-thaw (FPT) cycles and left in argon just before use.

Methods. ¹H-NMR spectra were recorded at room temperature on Varian 200 and 500 spectrometers, using chloroform-*d* (CDCl₃) as the solvent, and tetramethylsilane (TMS) as the internal reference for chemical shifts. Gel permeation chromatography (GPC) measurements were performed on a waters system equipped with a Waters 510 HPLC pump, a Waters M486 tunable absorbance detector, a Waters M410 differential refractive index detector, and three waters styragel HR columns with a continuous porosity of 10²-10⁴ Å. Monodisperse linear polystyrene standards were used for

calibration. THF (with 2% v/v *N,N*-dimethylacetamide) was used as the mobile phase , and the rate was 1.0 mL/min at 35 °C. The purity of the products was checked by using thin-layer chromatography (TLC; Merck, silica gel 60). SAXS measurements were performed at room temperature on beamline 4C1 at the Pohang Light Source (KOREA), where a W/B4C double multilayer delivered monochromatic X-rays on the samples with a wavelength of 0.1608 nm, and a sample-to-detector distance of 2 m. Grazing incidence small-angle X-ray scattering (GISAXS) measurements were performed at 9A beamline of the Pohang Accelerator Laboratory. A monochromatized X-ray radiation source of wavelength = 0.111 nm and a two dimensional charge-coupled device (2D CCD) detector (MAR-CCD) with a resolution of 79 μm/pixel were used. The sample-to-detector distance was 2650 mm. The incident angle was $\alpha_i = 0.165^\circ$. The critical angle for the total external reflection of the polymer is 0.14 °, and that of the silicon substrate is 0.23 °. The data from GISAXS were calculated under the DWBA using NANOCELL made by Hillhouse group. The evolution of the morphology of each thin film was observed by using atomic force microscopy (AFM), (Digital Instruments, Nanoscope III) in the tapping mode under ambient conditions. Si tips (model TESP) were used. The scan rates were between 0.5 and 1.0 Hz. The free oscillation amplitude (A^0) of the oscillating cantilever was in the range 10~50 nm.

Synthesis. The synthesis of the hydroxyl-terminated polystyrene by anionic polymerization has been described in a previous publication.^{S1} The number-average molecular weight (M_n) was determined to be 6,700 g/mol by a ¹H NMR end group analysis.



Scheme S1. Synthesis of (a) methyl 3,5-bis(prop-2-nyloxy)benzoate and (b) azide-terminated polylactide (**1**).

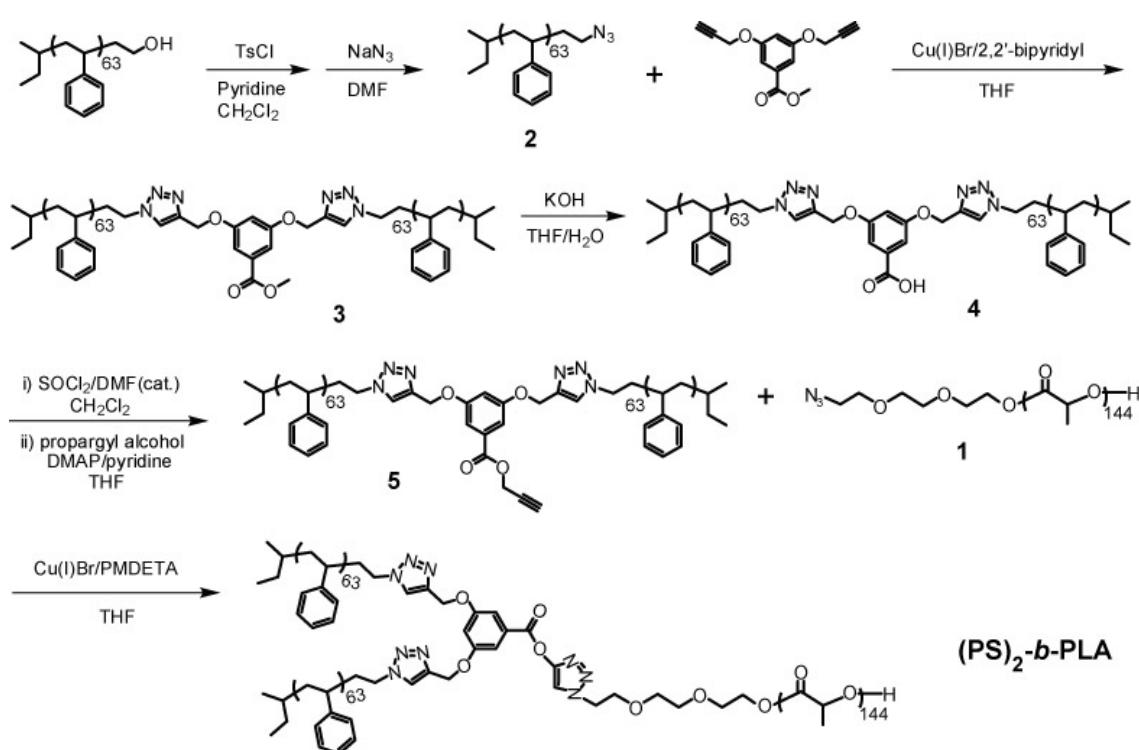
Synthesis of methyl 3,5-bis(prop-2-nyloxy)benzoate. Methyl 3,5-dihydroxybenzoate (2.0 g, 11.9 mmol, 1.0 equiv), K_2CO_3 (4.9 g, 35.7 mmol, 3.0 equiv), and KI (1.98 g, 11.9 mmol, 1.0 equiv) were dissolved in 30 mL of anhydrous acetonitrile. Then, a solution of propargyl bromide (80 wt% in toluene, 3.54 g, 29.8 mmol, 2.5 equiv) was added to the solution. The reaction mixture was stirred at 85 °C for 12 h under nitrogen.

After cooling to room temperature, insoluble solid was filtered off. The solvent was removed using a rotary evaporator. The residue was dissolved in CH₂Cl₂, and then treated with diluted aqueous HCl solution. The organic layer was washed with brine, and concentrated. The crude product was purified by silica-column chromatography (*n*-hexane:CH₂Cl₂ = 1:1), then dried at 30 °C in a vacuum oven for 10 h to yield the product (1.97 g, 68%) as a white solid. TLC (eluent; *n*-hexane:CH₂Cl₂ = 1:1): *R*_f 0.28. ¹H NMR (200 MHz, CDCl₃): δ 7.29 (d, 2H), 6.81 (t, 1H), 4.71 (d, 4H), 3.91 (s, 3H), 2.54 (t, 2H).

Azide-terminated polylactide (1). In a glove box, to a solution of tri(ethylene glycol) monoazide (175.6 mg, 1.0 mmol, 1.0 equiv) in anhydrous toluene (100 mL) was added 1.0 M Et₃Al in hexane solution (0.5 mL, 0.5 mmol, 0.5 equiv) by a syringe at room temperature. The solution was stirred for 16 h, and D,L-lactide (13 g, 90 mmol, 90 equiv) was then added to the reaction mixture. The reaction vessel was placed in an oil bath at 90 °C for 3 h. After cooling to room temperature, the reaction was terminated with 1.0 M acidic methanol (7.0 mL, 7.0 mmol, 7.0 equiv). After pouring excess of methanol into the mixture solution, the resulting precipitate was purified several times by dissolution/precipitation with CH₂Cl₂/*n*-hexane. The collected solid was then dried at 40 °C in a vacuum oven for 10 h to yield azide-terminated polylactide (**1**) (7.1 g, 55%) as a white solid. M_w/M_n (GPC) = 1.06. M_{n(NMR)} = 10,500 g/mol. ¹H NMR (500 MHz, CDCl₃): δ 5.29-5.07 (br, 144H, OOCCH(CH₃)O, repeating unit of PLA), 4.36 (m, 1H, OOCCH(CH₃)OH, end group of PLA), 4.29 (m, 2H, N₃CH₂CH₂OCH₂CH₂OCH₂CH₂OOCCH(CH₃)O of initiator), 3.74-3.61 (m, 8H, N₃CH₂CH₂OCH₂CH₂OCH₂CH₂OOCCH(CH₃)O of initiator), 3.39 (t, 2H, N₃CH₂CH₂OCH₂CH₂OCH₂CH₂OOCCH(CH₃)O of initiator), 2.70 (d, 1H, -OOCCH(CH₃)OH, end group of PLA), 1.77-1.38 (br, 450H, -OOCCH(CH₃)O, repeating unit of PLA).

Azide-terminated polystyrene (2). Hydroxy-terminated polystyrene (1.0 equiv) and 4-toluenesulfonyl chloride (10 equiv) were dissolved in anhydrous CH₂Cl₂. Then, pyridine (10 equiv) was added to the solution. The reaction mixture was allowed to stir for 24 h at room temperature. The crude product was collected, and purified several times by dissolution/precipitation with CH₂Cl₂/methanol, and then dried at 70 °C in a vacuum oven for 9 h to yield the tosylated intermediate as a white solid (18.1 g, 95%). M_w/M_n (GPC) = 1.02. ¹H NMR (200 MHz, CDCl₃) δ 7.60 (Ar-H of tosyl group), 7.28-6.36 (br, Ar-H of PS), 3.83-3.45 (br, Ts-OCH₂CH₂), 2.61-1.70 (br, CH of PS backbone and Ts-OCH₂CH₂), 2.42 (s, Ar-CH₃ of tosyl group), 1.70-1.31 (br, CH₂ of PS backbone), 1.30-0.53 (br, PS-CH(phenyl)CH₂CH(CH₂CH₃)CH₃). Next, the obtained tosylated

intermediate (1.0 equiv) and NaN_3 (50 equiv) were dissolved in DMF. The reaction mixture was then allowed to stir at 90 °C for 24 h under nitrogen environment. After removing DMF using a rotary evaporator, the residue was redissolved in CH_2Cl_2 . The organic solution was washed several times by deionized water, and concentrated. The crude product was collected, and purified several times by dissolution/precipitation with CH_2Cl_2 /methanol, and then dried at 80 °C in a vacuum oven for 10 h to yield azide-terminated polystyrene (**2**) as a white solid (16.1 g, 90%). M_w/M_n (GPC) = 1.02. ^1H NMR (200 MHz, CDCl_3) δ 7.28-6.36 (br, Ar-H of PS), 3.12-2.69 (br, $\text{N}_3\text{CH}_2\text{CH}_2$), 2.61-1.70 (br, CH of PS backbone and $\text{N}_3\text{CH}_2\text{CH}_2$), 1.70-1.31 (br, CH_2 of PS backbone), 1.30-0.53 (br, PS-CH(phenyl) $\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_3$).



Scheme S2. Synthetic procedure of $(\text{PS})_2$ -*b*-PLA.

Ester-functionalized dibranched polystyrene (3). In a glove box, azide-terminated polystyrene (**2**) (2.3 equiv), methyl 3,5-bis(prop-2-ynyoxy)benzoate (1.0 equiv), 2,2'-bipyridine (10 equiv) and Cu(I)Br (5.0 equiv) were dissolved in deoxygenated anhydrous THF. The reaction mixture was allowed to stir at 50 °C for 24 h. The solvent was removed using a rotary evaporator. The residue was redissolved in CH_2Cl_2 , and was then washed three times with brine. The crude product was purified by silica-column chromatography (from *n*-hexane: CH_2Cl_2 = 1:4 to CH_2Cl_2 :EtOAc = 4:1), and then dried at 30 °C in a vacuum oven for 30 h to yield the product as a white solid (7.8 g, 96%).

M_w/M_n (GPC) = 1.02. ^1H NMR (200 MHz, CDCl_3) δ 7.28-6.36 (br, Ar-**H** of PS), 5.10 (triazole-CCH₂O), 3.94 (br, NCH₂CH₂), 3.90 (s, Ar-COOCH₃), 2.61-1.70 (br, **CH** of PS backbone), 1.70-1.31 (br, CH₂ of PS backbone), 1.31-0.58 (br, PS-CH(phenyl)CH₂CH(CH₂CH₃)CH₃).

Acid-functionalized dibranched polystyrene (4). Compound (**3**) (1.0 equiv) and KOH (100 equiv) were dissolved in THF/H₂O, and the reaction mixture was allowed to stir at 95 °C for 5 days. After removal of THF using a rotary evaporator, the residue was redissolved in CH₂Cl₂. The organic solution was treated with diluted aqueous HCl, and washed with brine. By pouring excess of methanol into the organic solution, the collected solid was dried at 100 °C in a vacuum oven for 10 h to yield 4.5 g (93%) of a white solid. M_w/M_n (GPC) = 1.02. ^1H NMR (200 MHz, CDCl_3) δ 7.28-6.36 (br, Ar-**H** of PS), 5.10 (triazole-CCH₂O), 3.94 (br, NCH₂CH₂), 2.61-1.70 (br, **CH** of PS backbone), 1.70-1.31 (br, CH₂ of PS backbone), 1.31-0.58 (br, PS-CH(phenyl)CH₂CH(CH₂CH₃)CH₃).

Alkyne-functionalized dibranched polystyrene (5). Compound (**4**) (1.0 equiv) was dissolved in anhydrous CH₂Cl₂, and thionyl chloride (50 equiv) was then added dropwise. The reaction mixture was allowed to stir for 12 h at room temperature. After removal of the solvent, a yellowish solid (acid chloride-terminated intermediate) was obtained. As another reactant solution, propargyl alcohol (150 equiv), DMAP (50 equiv), and pyridine (150 equiv) were dissolved in anhydrous THF and cooled in an ice-water bath. To this solution, the obtained acid chloride intermediate in anhydrous THF was slowly added. The reaction mixture was stirred in the cooling bath for 1 h, and at room temperature for another 24 h. After removal of the solvent, the crude product was purified by flash silica-column chromatography (CH₂Cl₂:EtOAc = 19:1), then dried at 30 °C in a vacuum oven for 8 h to yield 1.70 g (85%) as a white solid. M_w/M_n (GPC) = 1.02. ^1H NMR (500 MHz, CDCl_3): δ 7.28-6.36 (br, Ar-**H** of PS), 5.10 (triazole-CCH₂O), 4.89 (s, CH≡CCH₂O), 3.95 (br, NCH₂CH₂), 2.47 (s, CH≡CCH₂O), 2.43-1.70 (br, **CH** of PS backbone), 1.70-1.31 (br, CH₂ of PS backbone), 1.31-0.58 (br, PS-CH(phenyl)CH₂CH(CH₂CH₃)CH₃).

(PS)₂-*b*-PLA. In a glove box, compound (**5**) (1.3 g, 0.0956 mmol, 1.15 equiv), (**1**) (0.87 g, 0.0831 mmol, 1.0 equiv), CuBr (238 mg, 1.66 mmol, 20 equiv), and PMDETA (288 mg, 1.66 mmol, 20 equiv) were dissolved in deoxygenated anhydrous THF. The reaction mixture was allowed to stir for 3 h at room temperature. The solvent was removed using a rotary evaporator, and the residue was purified by flash silica-column chromatography (from CH₂Cl₂ to CH₂Cl₂:EtOAc = 1:1). The crude product was collected several times by dissolution/precipitation with CH₂Cl₂/*n*-hexane, and then

dried at 110 °C in a vacuum oven for 24 h to give **(PS)₂-*b*-PLA** (1.6 g, 80%) as a white solid. M_w/M_n (GPC) = 1.05. ¹H NMR (500 MHz, CDCl₃): δ 7.85 (s, H-triazole), 7.28-6.36 (br, Ar-H of PS), 5.44 (s, triazole-CCH₂OOC-Ar), 5.29-5.08 (br, OOCCH(CH₃)O, repeating unit of PLA), 5.07 (triazole-CCH₂O-Ar), 4.52 (s, NCH₂CH₂OCH₂CH₂OCH₂CH₂O), 4.36 (m, OOCCH(CH₃)OH, end group of PLA), 4.27 (s, NCH₂CH₂OCH₂CH₂OCH₂CH₂OOCCH(CH₃)O), 3.93 (br, NCH₂CH₂), 3.86 (s, NCH₂CH₂OCH₂CH₂OCH₂CH₂O), 3.62 (s, NCH₂CH₂OCH₂CH₂OCH₂CH₂OOCCH(CH₃)O), 3.56 (s, NCH₂CH₂OCH₂CH₂OCH₂CH₂OOCCH(CH₃)O), 2.69 (d, OOCCH(CH₃)OH, end group of PLA), 2.31-1.19 (br, OOCCH(CH₃)O repeating unit of PLA and CHCH₂ of PS backbone), 1.18-0.49 (br, PS-CH(phenyl)CH₂CH(CH₂CH₃)CH₃).

Preparation of thin films with different thicknesses. Solutions of (PS)₂-*b*-PLA in chlorobenzene (Aldrich) were used to prepare thin films on Si(100) with an amorphous native oxide layer and hexamethyldisilazane (HMDS) by spin-coating. We varied the concentration of (PS)₂-*b*-PLA solutions from 1 to 7 wt% and spin rate from 1500 to 4000 rpm to control the thickness of BCP films. The BCP films placed on the substrates were annealed at 130 °C for 3 days in the vacuum after drying at room temperature for 24 h in the vacuum. Table 1 shows the thicknesses of thin films controlled by concentration of solution and RPM (resolutions per minute) of spin-coating. The thicknesses of BCP films were checked with an ellipsometry. Thickness was measured after drying the film at room temperature for 24 h in the vacuum.

Reference

(S1) J. Song, H.-Y. Kim and B.-K. Cho, *Bull. Korean Chem. Soc.*, 2007, **28**, 1771.

Table 1. Preparation conditions of thin films.

Concentration (wt%)	Spin-coating rate (rpm)	Thickness (nm)
2	3000	68
2	1500	96
3	2000	114
5	4000	168
5	2000	224
7	2000	328

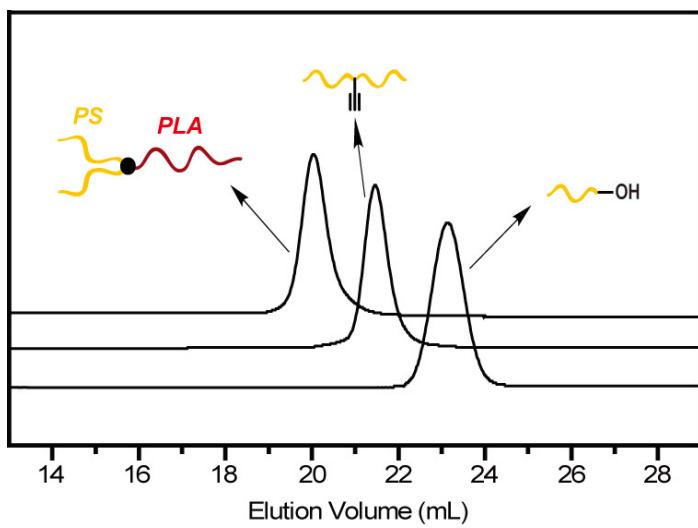


Fig. S1 GPC elugrams of hydroxyl polystyrene, dibranched polystyrene, and $(PS)_2-b$ -PLA.

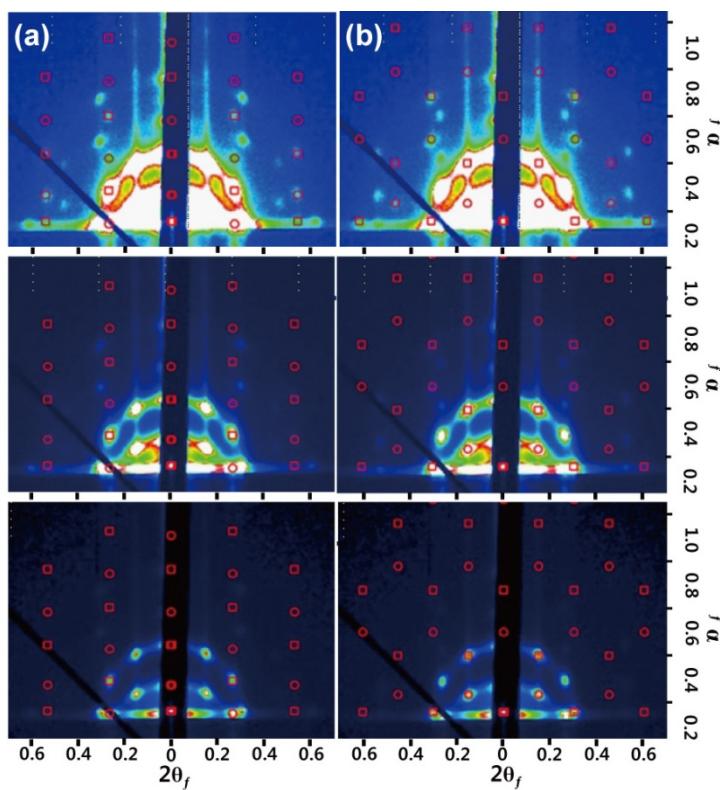


Fig. S2. 2-D GISAXS pattern and fitting result of the 328 nm thick film with different contrasts at $\alpha_i = 0.165$. (a) Left and (b) right images correspond to the “(10)-on” and “(01)-on” orientations, respectively. Open squares and circles represent the scattering spots from the reflected and transmitted X-ray beams, respectively.

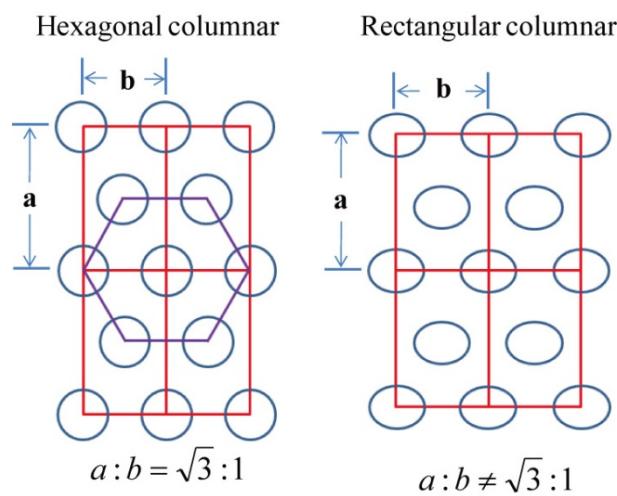


Fig. S3. Structural comparison of hexagonal and base-centered rectangular columnar structures.