Supporting Information

Effects of Chiral Interface and Orientation-Dependent Segmental Interactions on Twisting of Self-Assembled Block Copolymers

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Materials. Unless otherwise noted, chemical reagents and solvents were purchased from Aldrich and used without further purification.

Synthesis of PS-PLLA, S-LA-A and S-A-LA. PS-PLLA, S-LA-A and S-A-LA BCPs* were prepared by sequential living polymerization processes according to the methods introduced in our previous report.[1] In briefly, a double-headed initiator was used to prepare hydroxyl-terminated polystyrene (denoted as PS-OH) by bulk atom-transfer radical-polymerization (ATRP) of styrene. The number-average molecular weight (M_n) of PS-OH was determined by Gel-permeation chromatography (GPC) (see Tables S1 and S2). Subsequently, PS-OH was used as a macro-initiator for typical ring-opening polymerization (ROP) of L-lactide or D,L-lactide by using $Sn(Oct)_2$ as catalyst to prepare PS-PLLA-OH (denoted as S-LA-OH) or PS-PLA-OH (denoted as S-A-OH). To assure the complete exchange of residual stannyl ether catalytic end groups to hydroxyl functionality, the as-prepared polymers were dissolved in $CHCl_3$ and dripped into a mixture of methanol and aqueous HCl solution.[2] The number of LA repeating units versus the number of styrene repeating units in S-LA-OH or S-A-OH was determined by ^1H NMR analysis (see Figure S2). Finally, S-LA-A and S-A-LA can be synthesized by using S-LA-OH or S-A-OH as macro-initiator for the ROP of D,L-lactide or L-lactide followed by the same procedure as above. The total number of LA repeating units versus the number of styrene repeating units in the final products can be determined by ^1H NMR analysis and M_n of the third block can be calculated accordingly. The dispersity ($Đ_M$) of BCPs* was determined by GPC (see Figure S2). The single peak in the GPC profile suggests the completion of the exchange of hydroxyl end group of S-LA-OH or S-A-OH (see Figure S1).

Sample Preparation. Self-assembled bulk samples of PS-PLLA, S-LA-A and S-A-LA were prepared by solution casting from solution with 1 wt% BCPs* in CH_2Cl_2. The solution was sealed with aluminum foil having a pin-punched hole. The time required for the solvent to evaporate was controlled to be approximately one week. Subsequently, the cast samples were further dried in vacuum oven over night to

remove residual solvent.

Transmission electron microscopy (TEM). Bright-field TEM images were obtained using a JEOL JEM-2100 LaB_6 transmission electron microscope (at an accelerating voltage of 200 kV). Bulk samples were sectioned at room temperature using a Leica Ultramicrotome (approximately 70 nm in thickness). Then the microsections were collected on copper grids. Staining was accomplished by exposing the samples to the vapor of a 4% aqueous RuO_4 solution for three hours to enhance the mass-thickness contrast under TEM observation.

Small-Angle X-ray Scattering (SAXS). SAXS experiments were conducted at the synchrotron X-ray beamline 23A1 at the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. The wavelength of the X-ray beam was 0.155 nm. A MAR CCD X-ray detector (MAR USA) was used to collect the two-dimensional (2D) SAXS patterns. A one-dimensional (1D) linear profile was obtained by integration of the 2D pattern. The scattering angle of the SAXS pattern was calibrated using silver behenate, with the first-order scattering vector q^* ($q^*= 4\pi\sin\theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength) being 1.076 nm^{-1}.

Table S1. Characterization of PS-PLLA and S-LA-A.

Sample [a]	M_n^{PS} [b] g/mol	M_n^{PLLA} [c] g/mol	M_n^{PLA} [c] g/mol	M_n^{total} g/mol	$Đ_M$ [b]	$f_{PLLA+PLA}^{v}$ [d]
PS-PLLA	27300	17100	--	44400	1.07	34.3 %
$S_{0.63}$-$LA_{0.18}$-$A_{0.19}$	27300	9400	10200	46900	1.08	37.2 %
$S_{0.66}$-$LA_{0.11}$-$A_{0.23}$	27300	5700	11500	44500	1.08	34.5 %
$S_{0.66}$-$LA_{0.06}$-$A_{0.28}$	27300	2800	14400	44500	1.10	34.5 %

[a] The subscript denotes the volume fraction of each block. [b] Measured by GPC versus polystyrene standards. [c] Calculated by ^{1}H NMR analysis.

[d] $f_{PLLA+PLA}^{v} = (M_{n,PLLA+PLA}/1.25)/[(M_{n,\ PLLA+PLA}/1.25)+(M_{n,PS}/1.04)]$.

Table S2. Characterization of S-A-LA.

Sample [a]	M_n^{PS} [b] g/mol	M_n^{PLA} [c] g/mol	M_n^{PLLA} [c] g/mol	M_n^{total} g/mol	$Đ_M$ [b]	$f_{PLLA+PLA}^{v}$ [d]
$S_{0.63}$-$A_{0.17}$-$LA_{0.20}$	27300	9500	10400	47200	1.08	37.5 %
$S_{0.63}$-$A_{0.14}$-$LA_{0.23}$	27300	7400	12000	46700	1.07	37.2 %
$S_{0.63}$-$A_{0.08}$-$LA_{0.29}$	27300	4000	15400	46700	1.07	37.2 %

[a] The subscript denotes the volume fraction of each block. [b] Measured by GPC versus polystyrene standards. [c] Calculated by ^{1}H NMR analysis.

[d] $f_{PLLA+PLA}^{v} = (M_{n,\,PLLA+PLA}/1.25)/[(M_{n,\,PLLA+PLA}/1.25)+ (M_{n,PS}/1.04)]$.

GPC measurements.

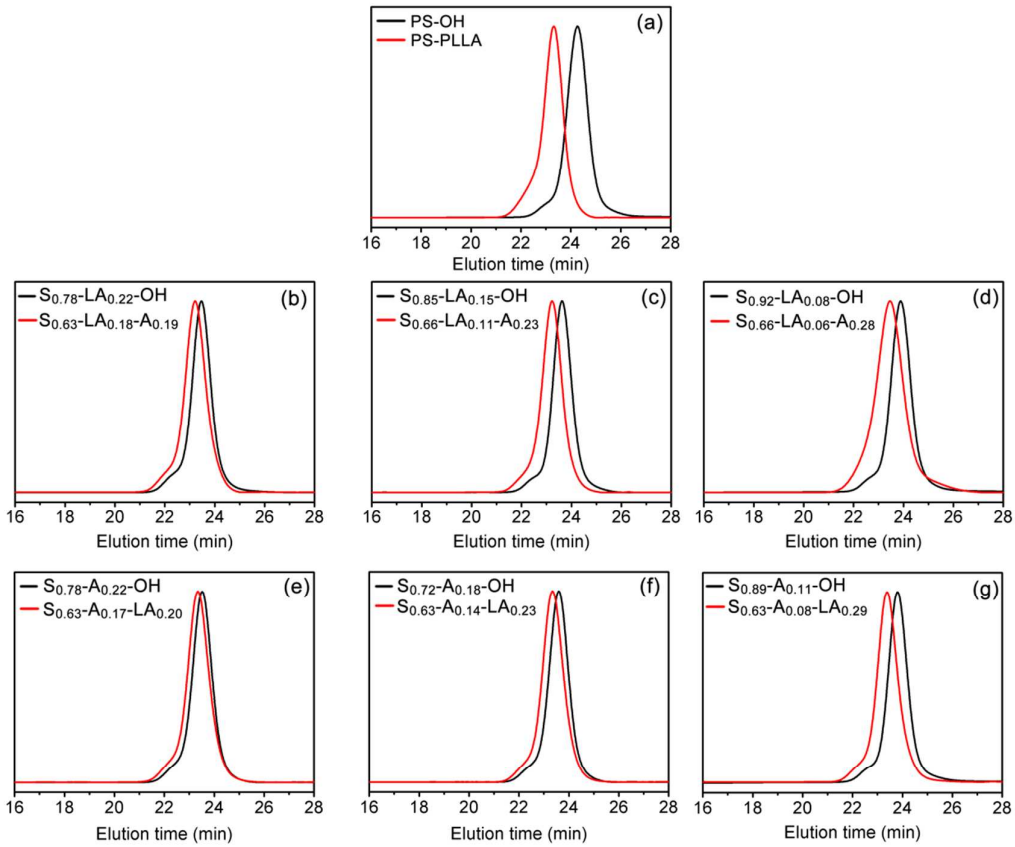

Figure S1. GPC results of PS-OH, PS-PLLA, S-LA-OH, S-A-OH, S-LA-A and S-A-LA.

NMR measurement.

Figure S2 shows the NMR results of PS-PLLA, S-LA-OH, S-A-OH, S-LA-A and S-A-LA. Figure S2a shows the chemical structure of PS-PLLA and the corresponding NMR results. The number of LA repeating units versus the number of styrene repeating units in BCPs can be calculated by the ratio of the peak integration of α and β.

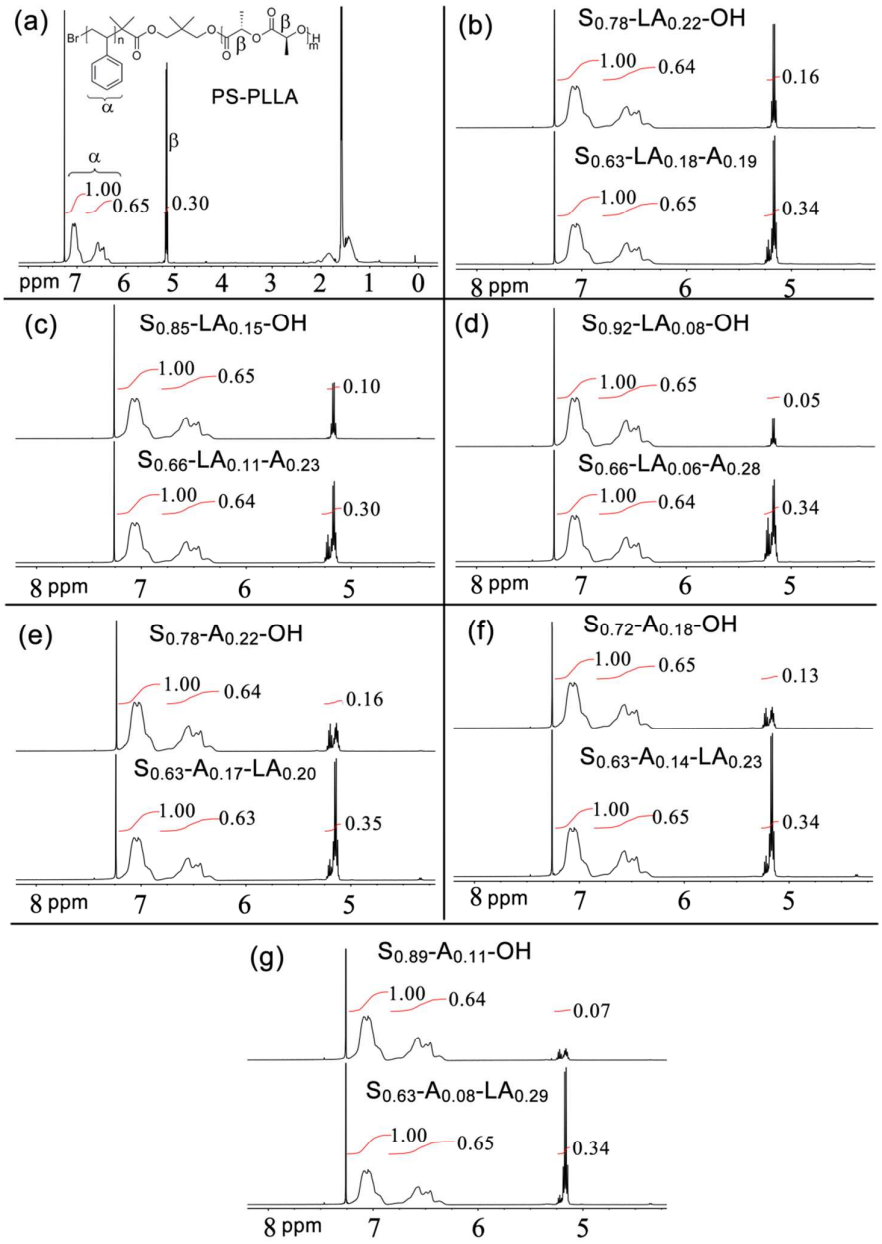

Figure S2. ^{1}H NMR results of PS-OH, PS-PLLA, S-LA-OH, S-A-OH, S-LA-A and S-A-LA.

TEM tilt experiments and 1D SAXS profiles

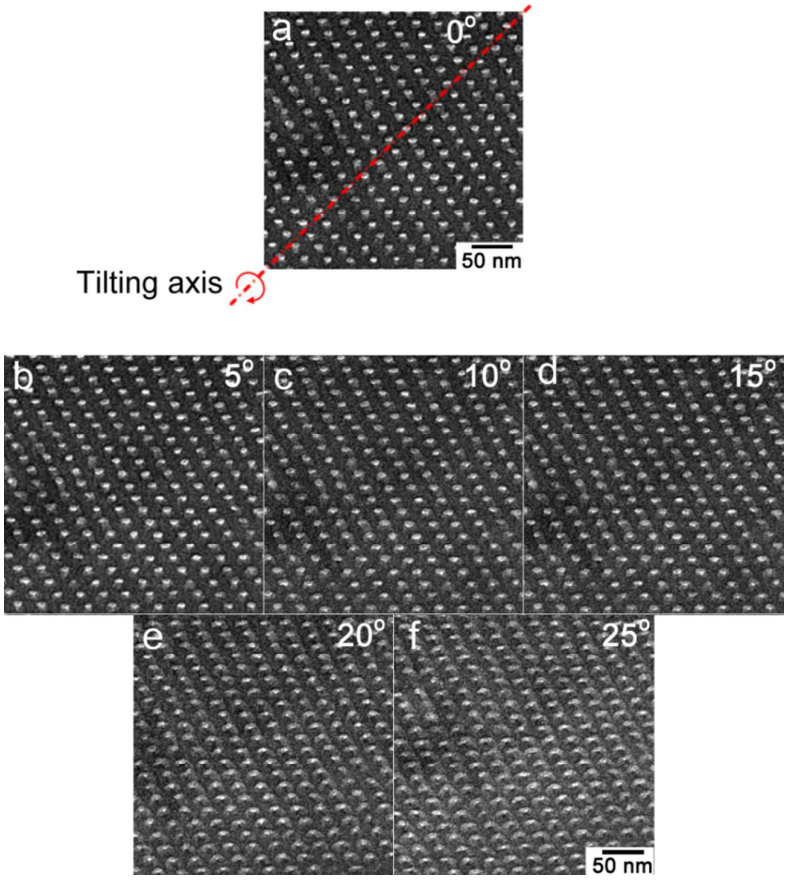

Figure S3. TEM micrographs of self-assembled PS-PLLA at different tilting angles. The corresponding tilting angles are labeled in the images.

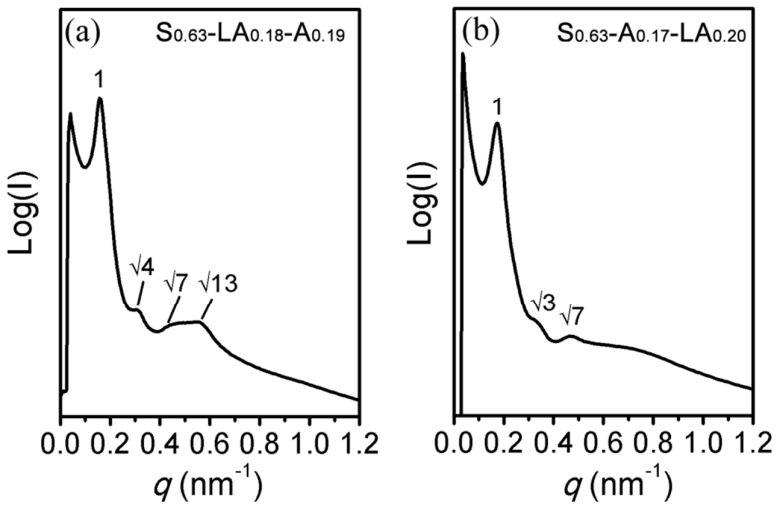

Figure S4. 1D SAXS profiles of self-assembled $S_{0.63}$-$LA_{0.18}$-$A_{0.19}$ (a) and $S_{0.63}$-$A_{0.17}$-$LA_{0.20}$ (b).

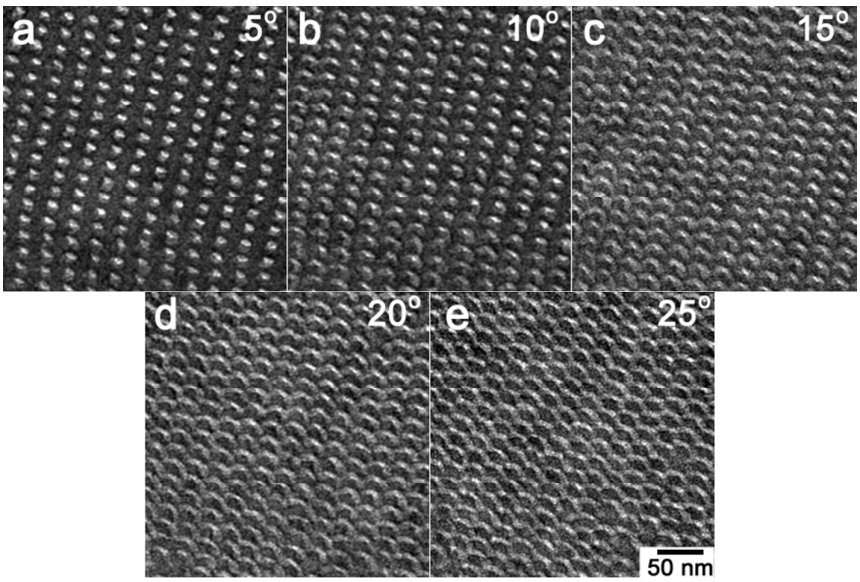

Figure S5. TEM micrographs of self-assembled $S_{0.63}$-$LA_{0.18}$-$A_{0.19}$ at different tilting angles. The corresponding tilting angles are labeled in the images.

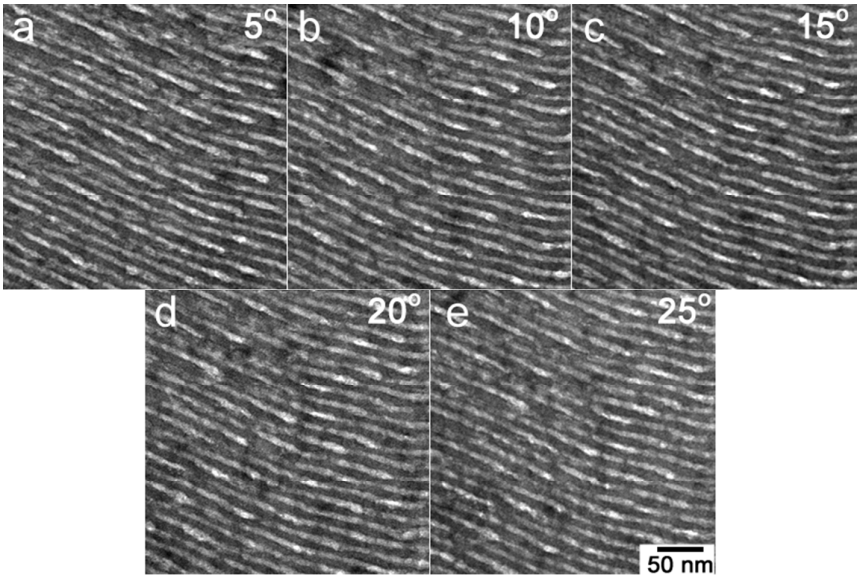

Figure S6. TEM micrographs of self-assembled $S_{0.63}$-$A_{0.17}$-$LA_{0.20}$ at different tilting angles. The corresponding tilting angles are labeled in the images.

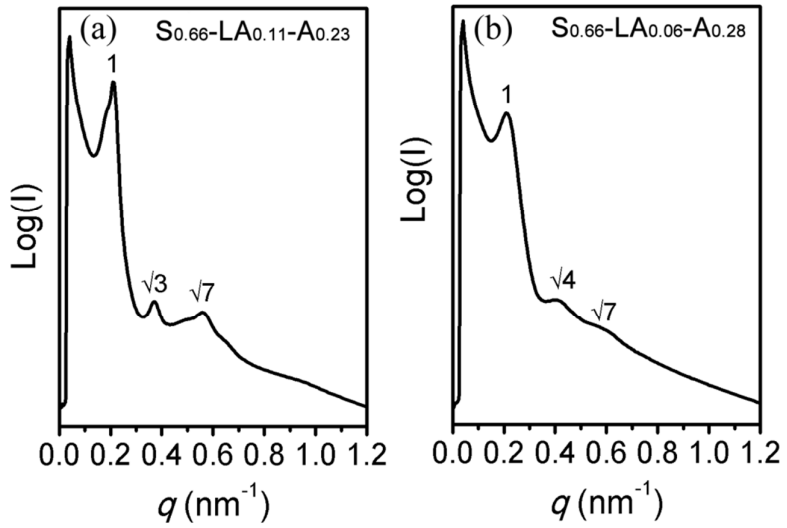

Figure S7. 1D SAXS profiles of self-assembled $S_{0.66}$-$LA_{0.11}$-$A_{0.23}$ (a) and $S_{0.66}$-$LA_{0.06}$-$A_{0.28}$ (b).

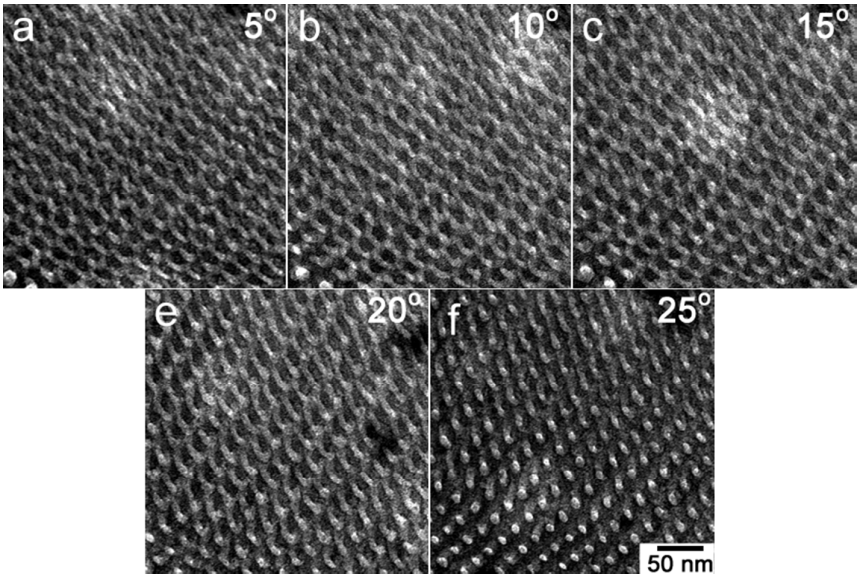

Figure S8. TEM micrographs of self-assembled $S_{0.66}$-$LA_{0.11}$-$A_{0.23}$ at different tilting angles. The corresponding tilting angles are labeled in the images.

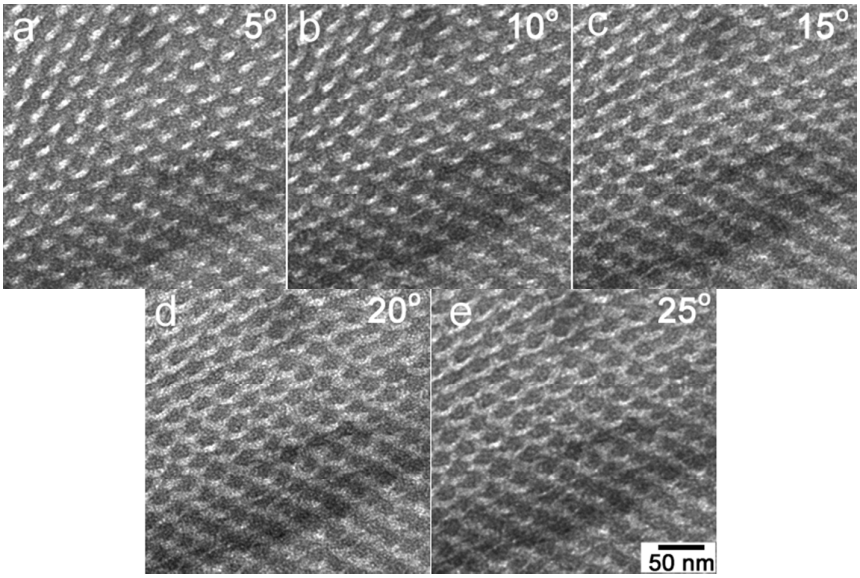

Figure S9. TEM micrographs of self-assembled $S_{0.66}$-$LA_{0.06}$-$A_{0.28}$ at different tilting angles. The corresponding tilting angles are labeled in the images.

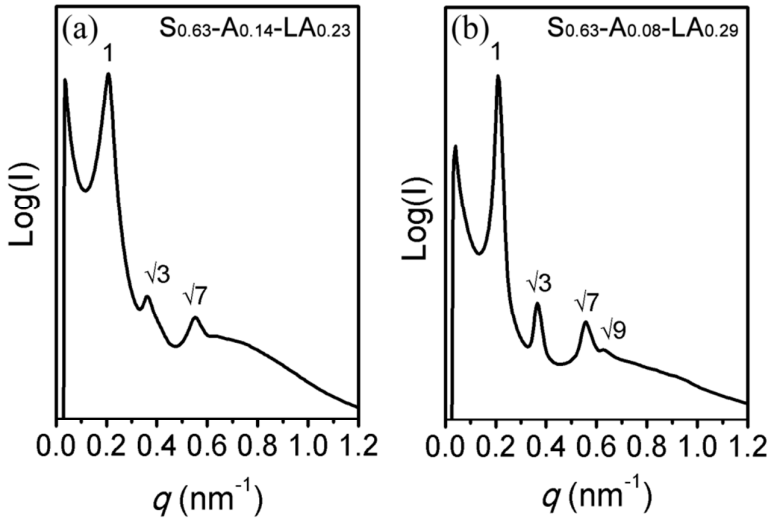

Figure S10. 1D SAXS profiles of self-assembled $S_{0.63}$-$A_{0.14}$-$LA_{0.23}$ (a) and $S_{0.63}$-$A_{0.08}$-$LA_{0.29}$ (b).

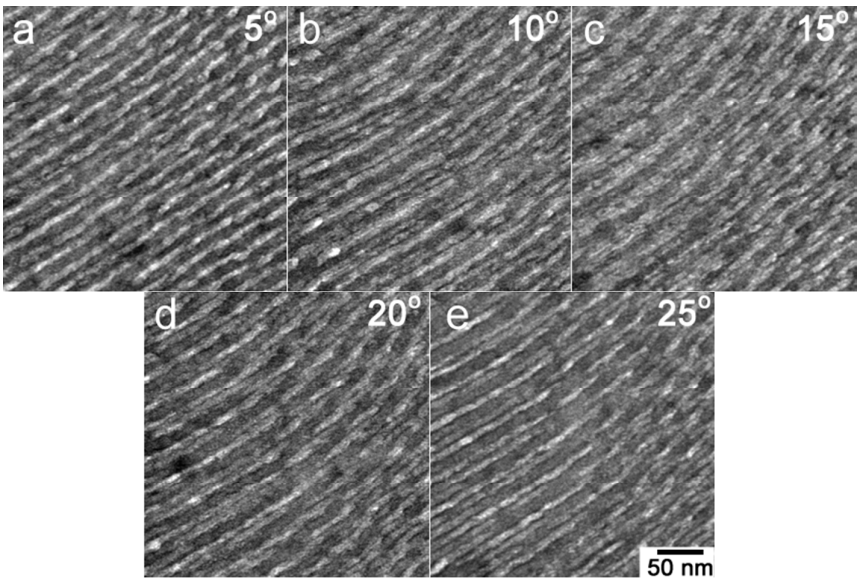

Figure S11. TEM micrographs of self-assembled $S_{0.63}$-$A_{0.14}$-$LA_{0.23}$ at different tilting angles. The corresponding tilting angles are labeled in the images.

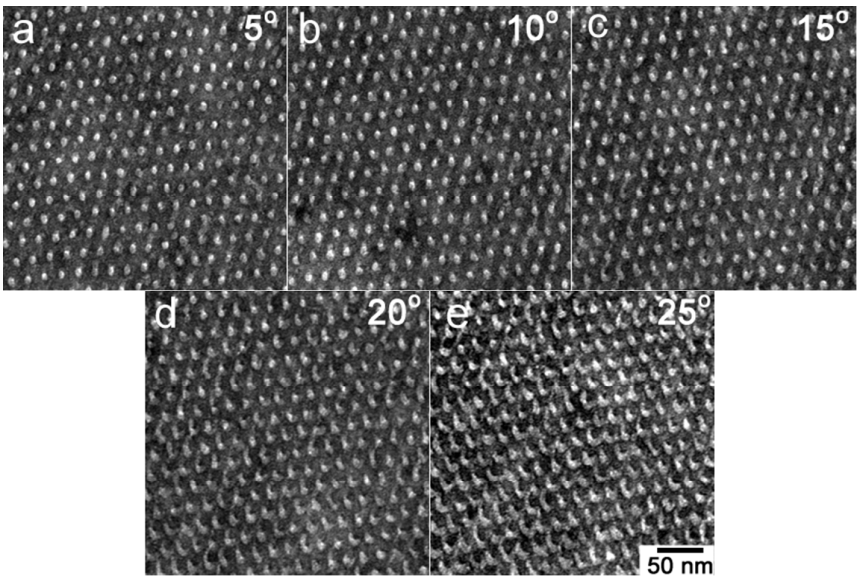

Figure S12. TEM micrographs of self-assembled $S_{0.63}$-$A_{0.08}$-$LA_{0.29}$ at different tilting angles. The corresponding tilting angles are labeled in the images.

References:

(1) Ho, R.-M.; Li, M. C.; Lin, S.-C.; Wang, H.-F.; Lee, Y.-D.; Hasegawa, H.; Thomas, E. L. *J. Am. Chem. Soc.* **2012**, *134*, 10974.

(2) Wiggins, J. S.; Hassan, M. K.; Mauritz, K. A.; Storey, R. F. *Polymer* **2006**, *47*, 1960.