Electronic Supplementary Information

Discovery of hierarchical superstructures in block copolymers by integrating different liquid crystalline interactions

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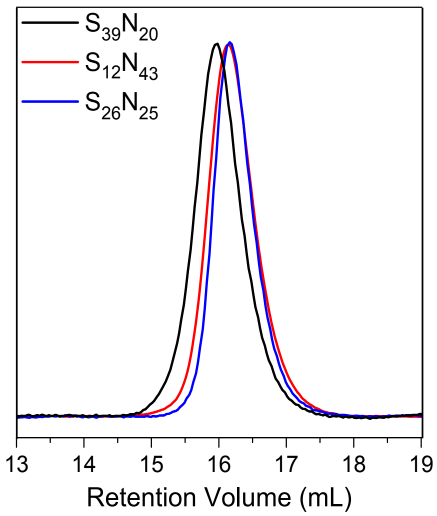

Fig. S1. GPC curves of the S-N copolymers. A series of mono-modal peaks with narrow distributions (PDI<1.05) at different retention volumes indicate the successful synthesis of the diblock copolymers. The detailed chemical characterizations are summarized in the main text Table 1.

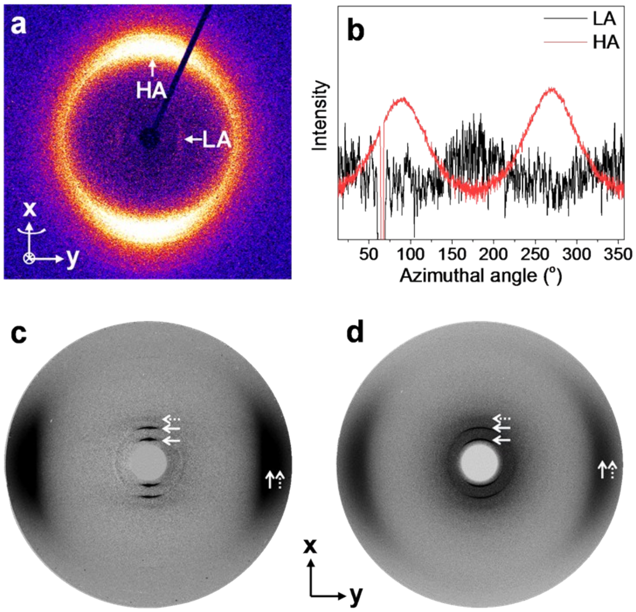

Fig. S2 2D-WAXD measurements of the N homopolymer and the S-N diblock copolymers $S_{26}N_{25}$ and $S_{12}N_{43}$. (a) 2D WAXD fiber pattern of the N homopolymer and (b) the azimuthal scans of LA (low angle) and HA (high angle) regions in (a). The fiber is drawn along the x direction as indicated in (a). The scattering on the equator in LA region originates from the short range positional order of the N phase along the director, and the scattering in the meridian in HA region represents the lateral packing of mesogenic groups. (c-d) 2D WAXD patterns of sheared $S_{26}N_{25}$ and $S_{12}N_{43}$ samples in the shear gradient direction (normal to the x-y plane) at 110 ^{o}C and 90 ^{o}C, respectively. The shear is along the y direction. The reflections ascribed to the S and N phases are marked by arrows.

In Fig. S2c, two reflections at q = 2.68 nm^{-1}, 4.02 nm^{-1} (marked by solid arrows) from the S layers and a weak scattering at q = 5.13 nm^{-1} which is not the higher order reflection of the S layers (marked by a dashed arrow) are observed. In Fig. S2d, two reflections at q = 2.76 nm^{-1}, 4.11 nm^{-1} from the S layers are marked by solid arrows; a weak scattering at q = 5.22 nm^{-1}, which is not the higher order reflection of the S layers, is marked by a dashed arrow. The weak scattering arises from the short range positional order of the N phase, which position agrees with that of the N homopolymer shown in (a). The reflections from the S layers in the S-N block copolymers are consistent with those in the S homopolymer with a similar d-spacing around 4.5 nm.[1] The scatterings originating from the lateral packing of the mesogens in the S and N blocks are merged together. Based on the geometric relationship, it can be deduced that the mesogens of the S and N blocks are parallel with each other and along with the normal of the S layers.

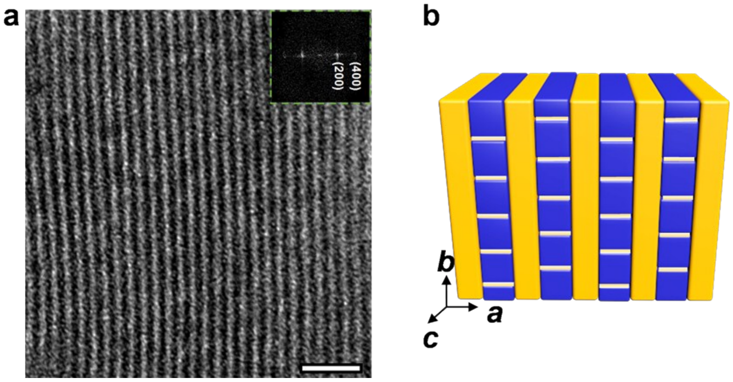

Fig. S3 (a) BF TEM image in the a-c projection of **Lo** structure as illustrated in the model (b). If the structure viewed in the a-c projection, only regular dark S and light grey N strips could be identified, which is similar with the feature of Lam structure. The interdigitated pattern described in the main text corresponds to the a-b projection of **Lo** as demonstrated in (b).

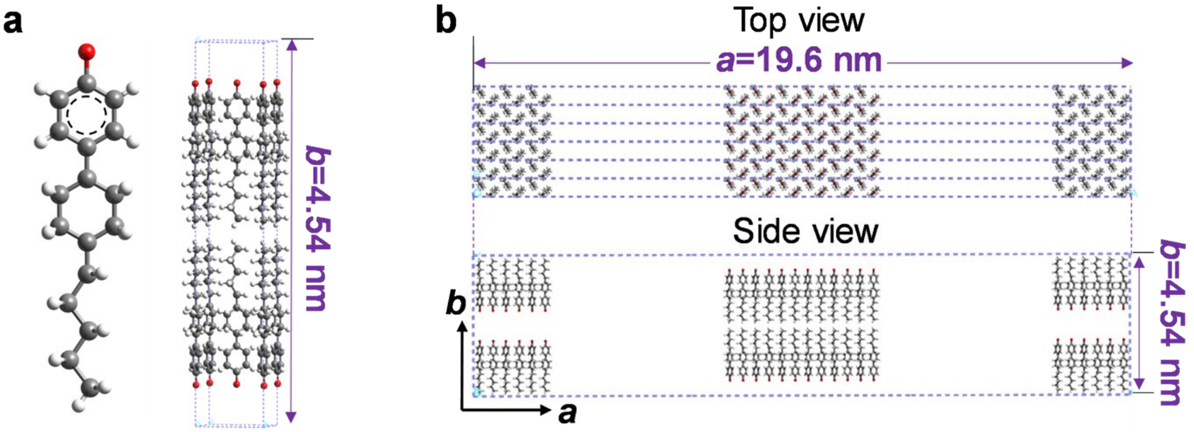

Fig. S4 Simulated **Lo** superlattice of $S_{26}N_{25}$ in Cerius^2. (a) The smectic motif used in construction of the superlattice. The smectic layer is built from the smectic mesogens in which oxygen, carbon, and hydrogen atoms are in red, grey, and white, respectively. (b) The model of **Lo** of $S_{26}N_{25}$.

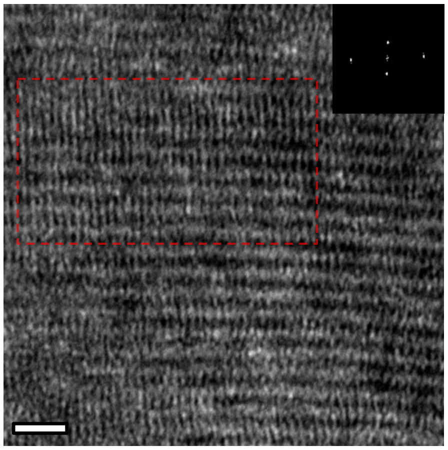

Fig. S5 Side view TEM image (normal to the (100)) of the superstructure of $S_{12}N_{43}$ and the FFT pattern in the selected area. According to the FFT pattern, the average distance between the neighboring cylinders is ~12 nm and the thickness of the S layer is 4.6 nm, in agreement with the results deduced from the SAXS results. The normal of the S layers is along the axis of cylinders. In the image, the S layers organize along parallel lines across neighboring cylinders which are perpendicular to the cylinders without offset. The scale bar represents 30 nm.

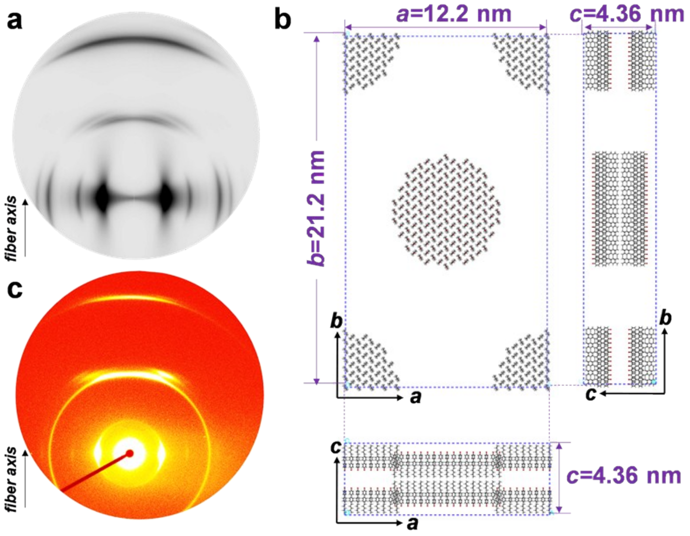

Fig. S6 Experimental and simulated SAXS fiber patterns of $S_{12}N_{43}$ at 90 °C. (a) Simulated fiber pattern of $S_{12}N_{43}$ and the corresponding model (b) in the simulation of the superlattice, where each cylinder is in a diameter of 6.4 nm, consistent with the value from the SAXS and TEM experiments. (c) 2D SAXS experimental fiber patterns of $S_{12}N_{43}$ at 90 °C. As discussed in the main text (Fig. 5b), the simulated pattern matches the reflections observed in the experiments.

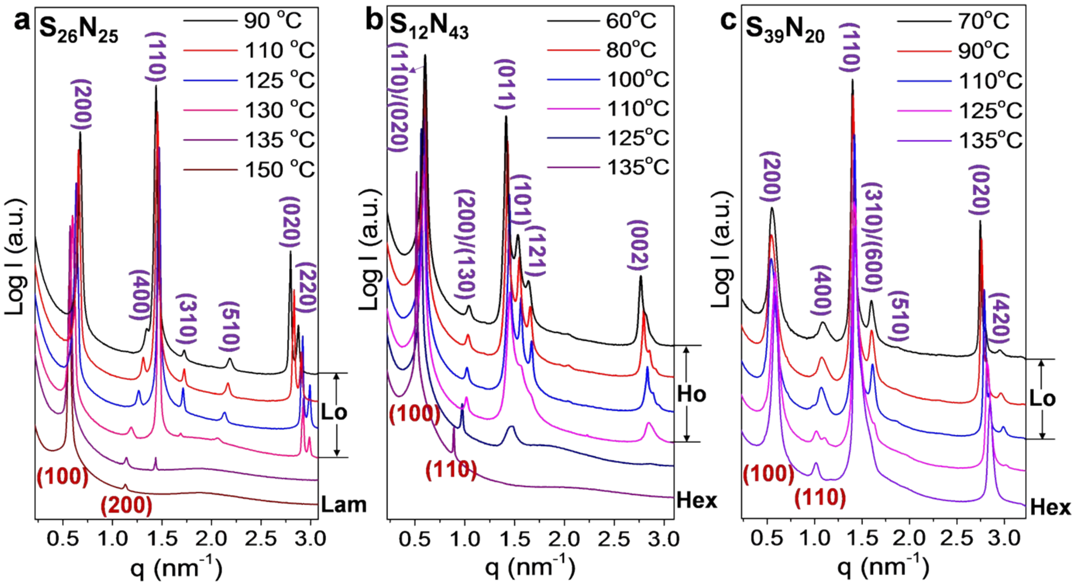

Fig. S7 The SAXS profiles of $S_{26}N_{25}$ (a), $S_{12}N_{43}$ (b) and $S_{39}N_{20}$ (c) during the cooling process. All the samples exhibit OOTs during the cooling process which are reversible compared to the heating process.

Two S-coil diblock copolymers which are composed of the same S block and a coil block of poly(oxybutylene) (B), $S_{50}B_{145}$ and $S_{50}B_{129}$, were obtained by sequential anionic polymerization as reported previously.[2] The subscript numbers represent the mean (nominal) number of repeat units of the S and B component blocks, respectively. The structural characterizations are shown in Figs. S8-9.

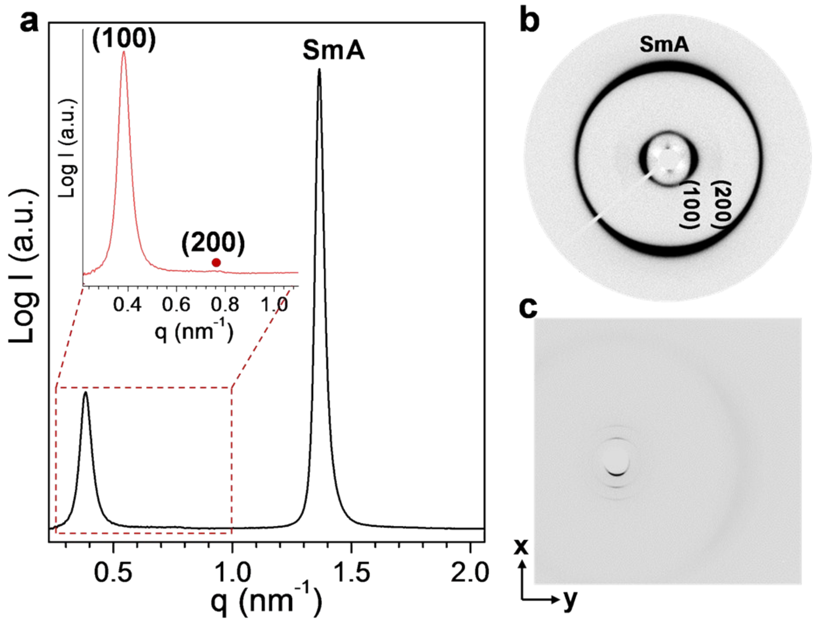

Fig. S8 Self-assembled structure of $S_{50}B_{145}$. (a) 1D SAXS profile of $S_{50}B_{145}$, 2D SAXS pattern (b) and 2D WAXD pattern (c) of the sheared sample in the shear gradient direction (normal to the x-y plane). The shear is along the y direction. No sign of superstructure can be detected.

The volume fraction of B block in $S_{50}B_{145}$ is 0.36 (based on the density of each block).[1] The nano-phase separated structure is illustrated in the SAXS patterns in Fig. S8, in which a pure lamellar structure with reflections at a ratio of 1:2 (q_{100} = 0.38 nm^{-1}) in low scattering angle and the characteristic reflection of SmA (q_{SmA} = 1.36 nm^{-1})[1] are observed. In Fig. S8c, three orders of reflections from the S layers are observed in the meridian. On the equator, scatterings from the mesogen lateral packing of the S phase can be identified. No any satellite reflections can be observed, suggesting the absence of superstructure in this sample.

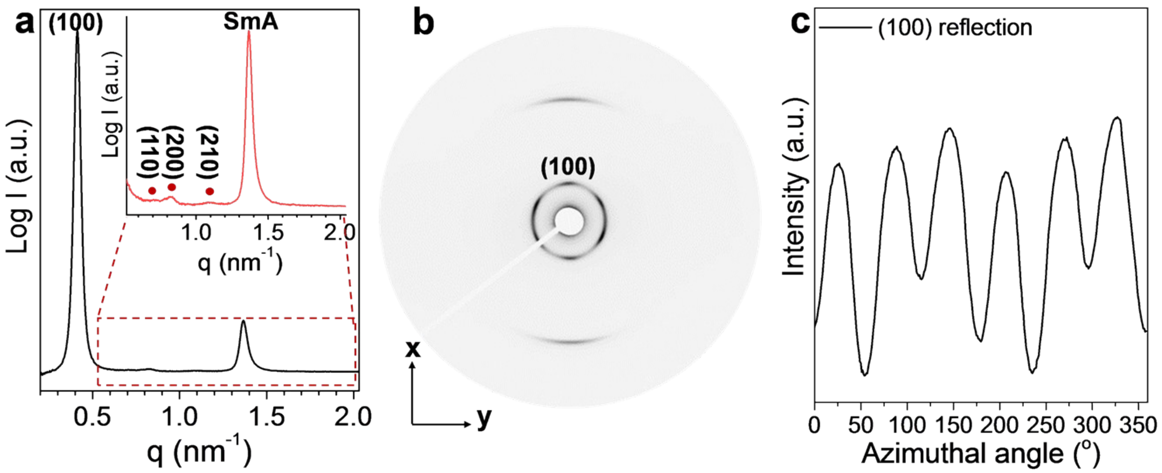

Fig. S9 Self-assembled structure of S$_{50}$B$_{129}$. (a) 1D SAXS profile of S$_{50}$B$_{129}$, (b) the 2D SAXS pattern of the sheared sample in the shear gradient direction (normal to the x-y plane). The shear is along the y direction. (c) The azimuthal scan profile of the (100) reflection. No sign of superstructure can be detected.

Fig. S9 exhibits the SAXS results of the S$_{50}$B$_{129}$ sample, in which the volume fraction of the B block is 0.33. The sample forms a pure Hex cylindrical structure as demonstrated in SAXS profiles (Fig. S9a), which exhibits a series of reflections with a q ratio of 1: $\sqrt{3}$: 2: $\sqrt{7}$ ($q_{100} = 0.41$ nm^{-1}). Six distinguishable arcs are observed in the 2D SAXS pattern (Fig. S9b), as further clarified in its azimuthal scan (Fig. S9c). The characteristic reflection of S (q_{SmA} = 1.36 nm^{-1}) is also indicated in the profile. In this simple Hex nano-phase separated structure, cylinders composed of the B blocks are dispersed in a matrix composed of the S blocks. No sign of forming superstructure can be detected.

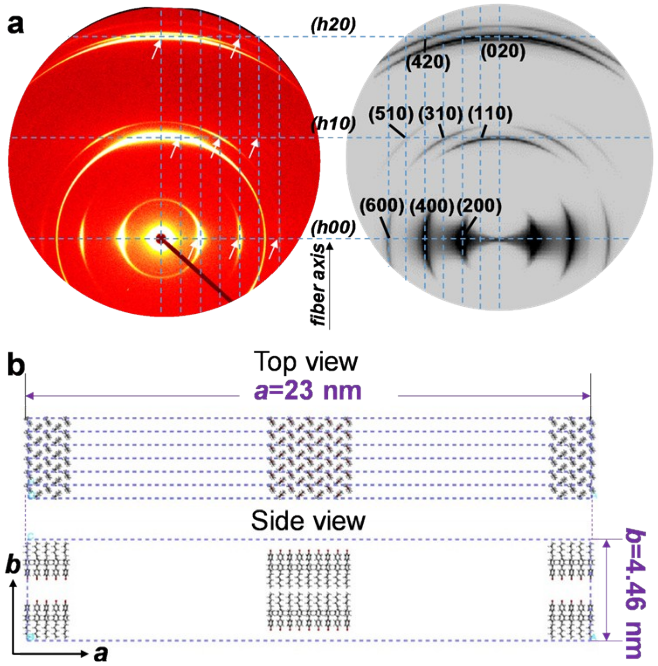

Fig. S10 Experimental and simulated SAXS fiber patterns of $S_{39}N_{20}$ at 110 ^{o}C. (a) Experimental 2D SAXS fiber pattern (the left) and its simulated pattern (the right) of $S_{39}N_{20}$ at 110 ^{o}C. The simulation is generated by Cerius^{2} based on the reconstructed superlattice model shown in (b). The superlattice is indexed in the simulated diffraction pattern while the corresponding reflections in the experimental diffraction pattern are marked by arrows. The simulated pattern fits the observed reflections in the experiment, indicating the correct identification of **Lo** phase.

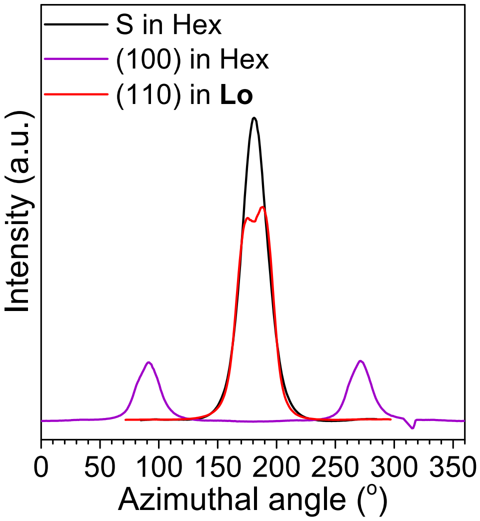

Fig. S11 Azimuthal scans of the (100) reflection, the primary scattering of the S layers in Hex, and the (110) reflection in Lo of $S_{39}N_{20}$ sample. The (110) reflection in **Lo** shows obvious split. In contrast, no apparent split of the first order reflection of the S layers in Hex in off-meridian direction is observed in its azimuthal scan. Comparison of its azimuthal scan with that of the (100) reflection from the Hex nano-phase separated structure suggests the coincidence of the normal of the S layers with the axis of cylinders.

Table S1. X-ray diffraction results of Lo in $S_{26}N_{25}$ at 110 °C

q /nm^{-1}	$d_{Obs.}$/nm	$d_{Cal.}$/nm[a]	***hkl***
0.640	9.8	9.80	200
1.279	4.9	4.9	400
1.383	4.5	4.42	110
1.651	3.8	3.73	310
2.086	3.0	2.96	510
2.687	2.3	2.27	020
2.762	2.3	2.21	220

[a] d-spacings of the (hkl) reflections are calculated in accordance to a centered-orthorhombic unit cell with the parameter a = 19.6 nm, b = 4.54 nm by using: $d_{Cal.}=[(h/a)^2+(k/b)^2+(l/c)^2]^{-1/2}$.

Table S2. X-ray diffraction results of Ho in $S_{12}N_{43}$ at 90 ^{o}C

q /nm^{-1}	**d_{Obs}./nm**	**$d_{Cal.}$/nm[a]**	***hkl***
0.594	10.6	10.57	110
			020
1.030	6.1	6.10	200
			130
1.440	4.4	4.27	011
1.556	4.0	4.10	101
1.597	3.9	4.01	150
		4.00	240
		3.99	310
1.663	3.8	3.82	121
2.813	2.2	2.18	002

[a] d-spacings of the (hkl) reflections are calculated in accordance to a pseudo-hexagonal superlattice unit cell with the parameter a = 12.2 nm, b = 21.2 nm, c = 4.36 nm. d_{Cal}. is calculated using: d_{Cal}.$=[(h/a)^2+(k/b)^2+(l/c)^2]^{-1/2}$.

Table S3. X-ray diffraction results of Lo in $S_{39}N_{20}$ at 110 °C

q /nm^{-1}	$d_{Obs.}$/nm	$d_{Cal.}$/nm[a]	*hkl*
0.545	11.5	11.5	200
1.079	5.8	5.75	400
1.407	4.5	4.37	110
1.601	3.9	3.85 3.82	310 600
1.876	3.3	3.2	510
2.760	2.3	2.23	020
2.964	2.1	2.08	420

[a] *d*-spacings of the (*hkl*) reflections are calculated in accordance to a centered-orthorhombic unit cell with the parameter a = 23.0 nm, b = 4.46 nm by using: $d_{Cal.}=[(h/a)^2+(k/b)^2+(l/c)^2]^{-1/2}$.

REFERENCES:

(1) Y. Liu, W. Wei and H. M. Xiong, *Polymer*, 2013, **54**, 6572-6579.

(2) Y. Liu, W. Wei and H. M. Xiong, *Polym. Chem.*, 2015, **6**, 583-590.