Electronic Supplementary Material (ESI) for Soft Matter

Supporting Information

Successive Order-Order Transitions of the Hierarchical Morphology of a Dendron-jacketed Block Copolymer via Subsequent Stretching Alignment and Self-assembly

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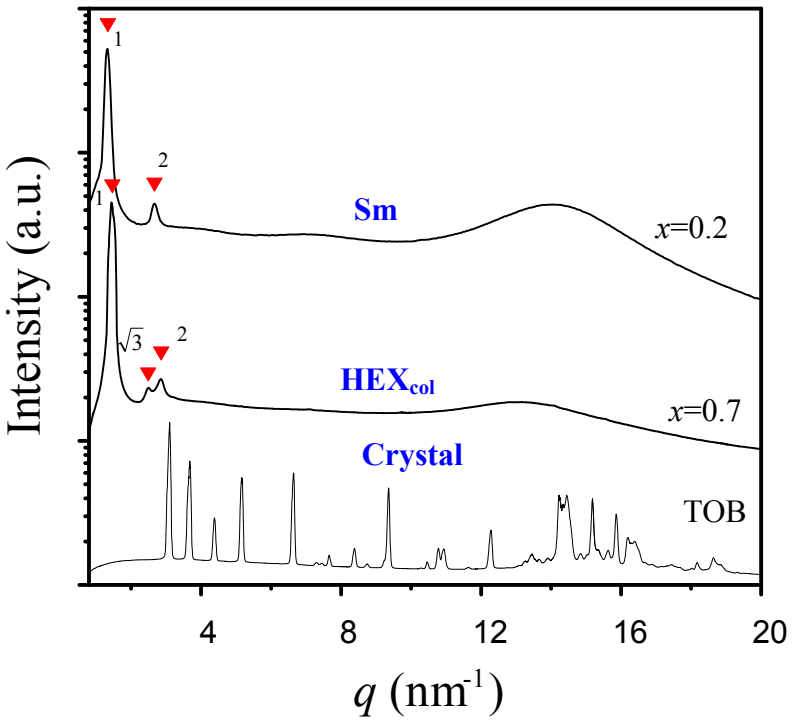

Figure S1. WAXS profiles of PS-*b*-P4VP(TOB)$_x$. Note that with x = 0.7 and 0.2, there is no observable reflections from pure TOB crystals, indicating that TOB can disperse in the supramolecular complex well up to x = 0.7.

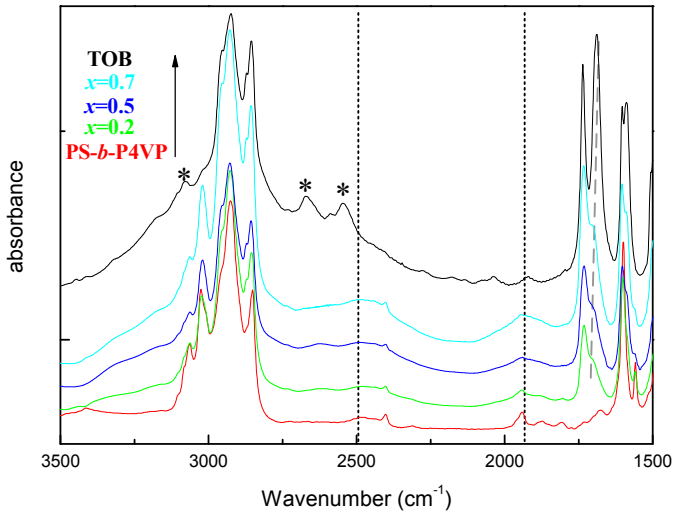

Figure S2 FT-IR spectra for the TOB, PS-*b*-P4VP(TOB)$_x$, and PS-*b*-P4VP, respectively.

The FT-IR spectra of the pure TOB, PS-*b*-P4VP and PS-*b*-P4VP(TOB)$_x$ are shown in Figure S2. For pure TOB, the stretching modes of the hydroxyl groups involving the hydrogen-bonded dimers and Fermi resonances are evidenced by the 3100, 2670, and 2545 cm^{-1} bands (marked by asterisks). The absence of the TOB dimer bands together with the appearance of two new broad bands near the 2500 and 1940 cm^{-1} (marked by dotted lines), in the spectra of PS-*b*-P4VP(TOB)$_x$ with different TOB contents, are attributed to the O-H stretching band and its Fermi resonances of well dispersed TOB hydrogen-bonding with P4VP. The shift of the carbonyl band of TOB at 1687 cm^{-1} to 1704 cm^{-1} (as marked by the broken line) furthermore supports the formation of hydrogen bonding between carboxylic acids of TOB and pyridines of P4VP blocks in PS-*b*-P4VP(TOB)$_x$.

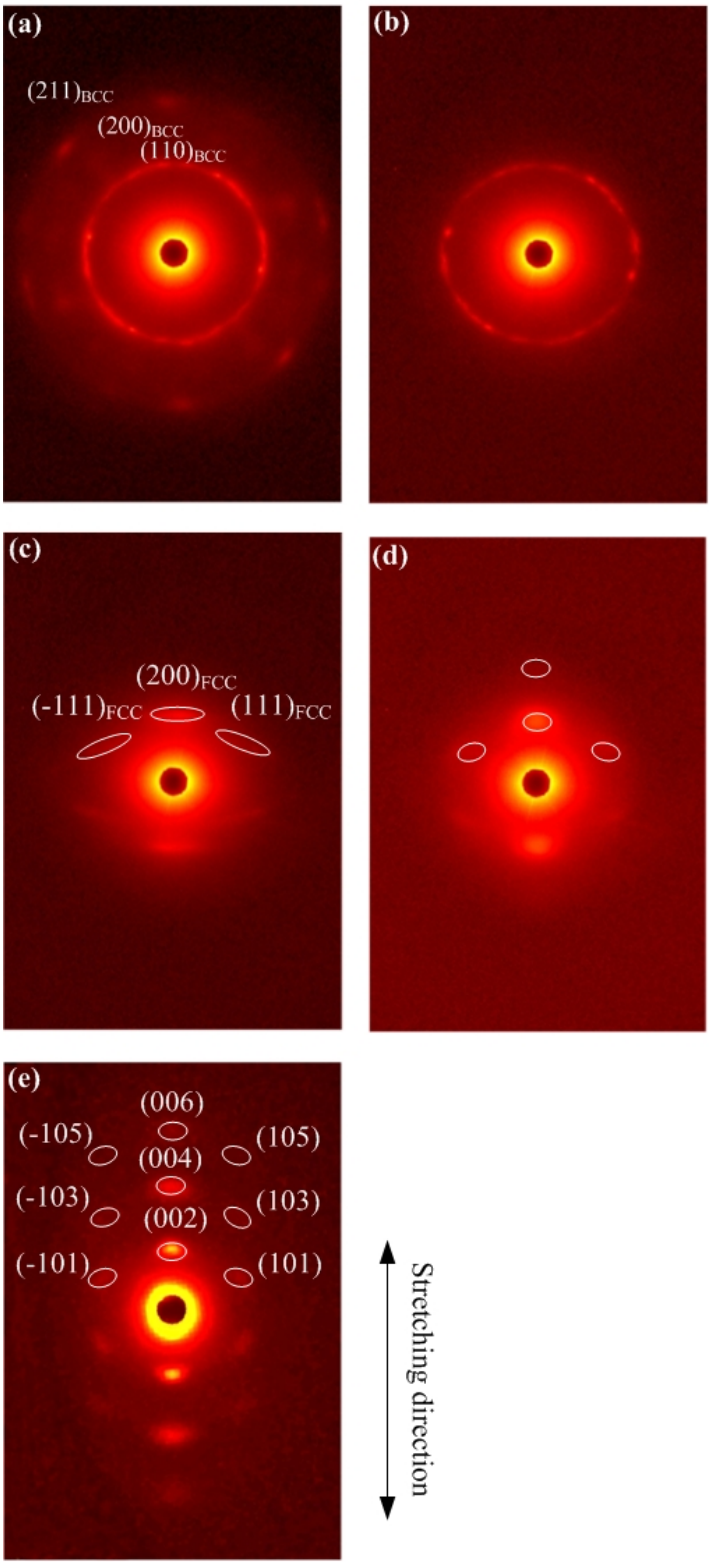

Figure S3 Detailed evolution of 2D SAXS patterns in situ obtained for the solvent-cast film of PS-*b*-P4VP(TOB)$_{0.7}$ subject to subsequent thermal stretching and annealing: at room temperature before stretching (a), at 120 ^{o}C under low stretched ratio of ~1.2 (b), at 120 ^{o}C under higher stretched ratio of ~2 (c), cooled down to 85 ^{o}C following by releasing stress (d), at 85 ^{o}C for long annealing time of more than 6 hours (e). The arrow in (e) indicates the stretching direction.

Details of the columnar LC structure.

In the text, Figure 2f exhibits three sharp arc-like reflections along the equatorial direction with a peak position ratio 1: $3^{1/2}$: 2, revealing a corresponding local LC phase transformation (from the oriented smecitc layers) to HEX_{col} columns of $P4VP(TOB)_{0.7}$. These columnar domains are highly oriented in the direction perpendicular to the stretching. Moreover, the 2D WAXS pattern (inset of Figure 2f) displays a diffuse halo at q = 13 nm^{-1} (d = 0.48 nm) with an emphasis on the four-lobe pattern (Figure S4 shown below). This corresponds to oriented TOB molecules, with the fan-like molecular plane (including π-π stacking and the three coplanar aliphatic chains) forming a preferred inclined angle 55° with the column axis; spread of the orientation is, however, significant (± ~20°) as shown in Figure S4.

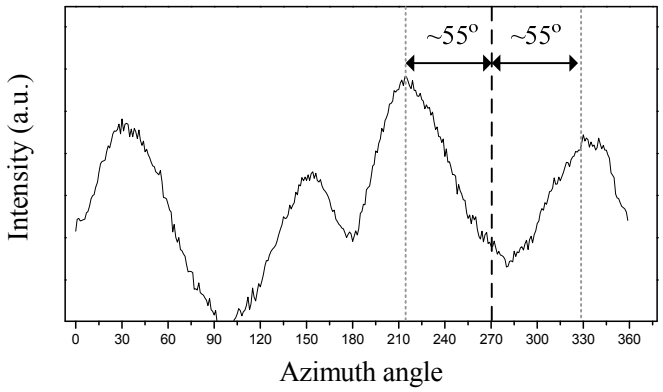

Figure S4 Azimuthal scan for the intensity profile of the four-lobe reflection pattern observed (q = 13 nm^{-1}) in the inset of Figure 2f.

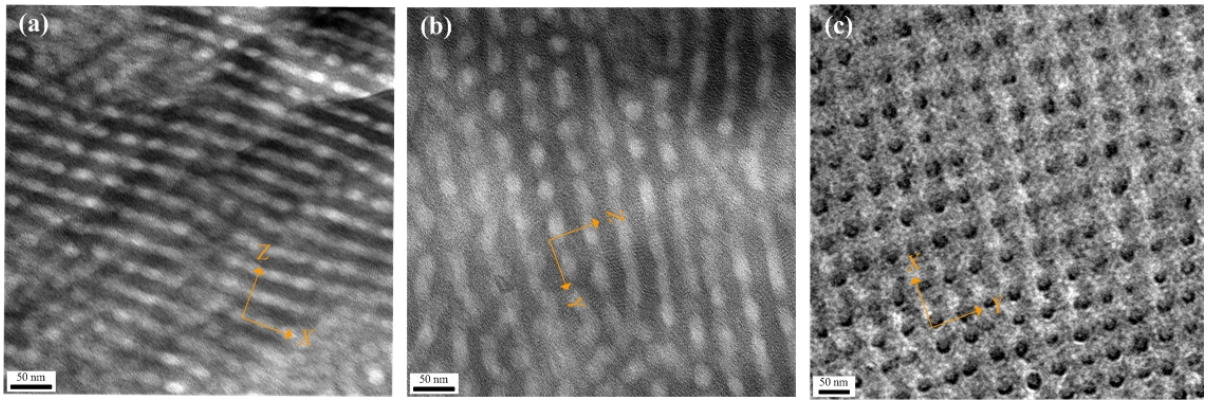

Figure S5 TEM images of microtomed sections (with iodine-stained P4VP domains in black) cut along the *XZ* plane (a), YZ plane (b) and the *XY* plane (c), for constructing the 3D representation in Figure 4 for the HEX_{col}-*within*-TPL structure of PS-*b*-$P4VP(TOB)_{0.7}$.

Reference

S1. Kihara, H.; Kato, T.; Uryu, T.; Fréchet, J. M. J. *Chem. Mater.* **1996**, 8, 961-968.