

Competition between liquid crystallinity and block copolymer self-assembly in core-shell rod-coil block copolymers†

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Core-shell type of architecture revealed the subtle competition between liquid-crystalline ordering and block copolymer (BCP) self-assembly in a rod-coil BCP system.

Block copolymer (BCP) self-assembly offers a simple and controllable means to obtain nanostructures with typical orders on the scale of ~5–100 nm.¹ Liquid crystals (LCs) are one class of soft materials that undergo self-organization at 1–10 nm.² Incorporating LCs as one of the blocks in a BCP results in LCBCPs that possess both structural hierarchy and functionality.³ One unique type of LCBCP is the rod-coil BCP (RCBCP), in which one block adopts a rigid rod-like conformation.⁴ Several factors affect the thermodynamic behavior of these systems, including χ (Flory–Huggins parameter), N (degree of polymerization), f (volume fraction of each block), the order parameter of the macromolecular mesogen, and the area per junction of the rod (A^{rod}) and the coil (A^{coil}).⁴ Novel self-assembling behaviors with complex phase structures different from the coil-coil systems have been observed.⁴ In general, at symmetric volume fractions, lamellar morphology is prevalent. At asymmetric volume fractions, morphologies with highly curved interfaces such as sphere (S) or gyroid (G) have only been observed in low molecular mass rod-coil systems.^{4c,5} As the molecular weight of the rod increases, the rigid rod becomes incompatible with the curved inter-material dividing surface (IMDS) dictated by S or G phases; there thus exists competition between liquid crystallinity of the rods and BCP self-assembly. Most of the reported work showed that liquid crystallinity dominated the phase behavior and the S or G phase was often degenerated into structures with planar IMDS such as zig-zag, arrow-head, mushroom, perforated lamellae, etc.^{4a-d} This is because the interaction between the rods is relatively strong and LC ordering dominates the ordering process. Thus, we hypothesize that in a RCBCP system with relatively weak LC interactions, BCP self-assembly could dominate the overall phase structure.

In order to test this hypothesis, we designed a core-shell RCBCP using mesogen-jacketed LC polymers (MJLCP). Side-attaching LC

mesogens directly along the polymer backbone leads to MJLCP systems within which the strong interactions between the mesogens and backbone force the backbone to adopt an extended chain conformation and the polymer chains arrange in the form of macromolecular columns.⁶ Further linking MJLCPs with coil chains leads to MJ-RCBCPs. Compared to other types of rod-forming macromolecules such as polypeptides,⁷ LC/conjugated oligomers,⁸ and poly(hexyl isocyanate) (PHIC) and its derivatives,^{4a} using MJLCP as the rod to form RCBCP is advantageous because the length, diameter and the surface chemistry of the macromolecular rods can be readily controlled.⁹ The molecular weight of the rod dictates the rod length, and the mesogen structure determines the rod diameter and surface chemistry. By using relatively long soft tails in the molecular design, a core-shell rod can be obtained with an aromatic core and an aliphatic shell. (Scheme 1a). Herein we report that, in this system, the shell decouples the strong rod-rod interactions and influences the competition between liquid crystallinity of the rods and BCP self-assembly, which in turn, leads to a variety of new hierarchical structures. The unique role of the shell in the RCBCP structure formation is two fold: first, in the symmetric BCPs, both BCP self-assembly and LC ordering dictate planar IMDS. In this case, the shell enhances the LC ordering and novel columnar-hexagonal-in-lamellar (Φ_{H} -in-L) hierarchical nanostructure was observed. Second, in the asymmetric BCPs, since BCP self-assembly and LC ordering dictate different types of IMDS (curved vs. planar), the shell decreased rod-rod interaction and BCP self-assembly became the dominant factor. Consequently, LC symmetry breaks (from Φ_{H} to Φ_{N}) to compromise with the stronger BCP self-assembly process.

Poly[styrene-*block*-(3,5-bis((4'-(4'-tetradecanoylbenzoyl)oxy)benzoyl)oxy)styrene)] (PS-*b*-PTBOS) where the mesogen is a bent-core LC (BCLC), was chosen as the model RCBCP system (Scheme 1b, see ESI† for the detailed experimental procedure).⁹ BCLCs exhibit unique phase structures and possess excellent electro-optical properties.¹⁰ In the present case, the five-ring mesogen ensures a rigid core of the rod with a relatively large diameter while the 14-C tails of the mesogen render a relatively thick “shell”.

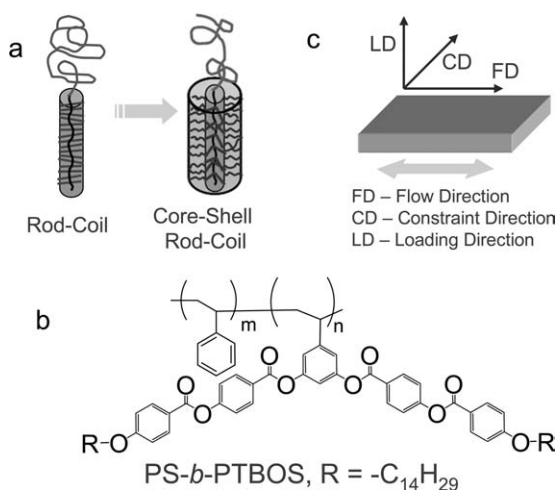
A series of BCPs have been synthesized using atomic transfer radical polymerization, representing the symmetric, PS-rich and PTBOS-rich BCPs. On the basis of differential scanning calorimetry and polarized light microscopy experiments, all these samples show LC behavior with the isotropization temperature of ~240 °C (see ESI†). Small-angle X-ray scattering and wide-angle X-ray diffraction (SAXS, WAXD) experiments were conducted on the sheared BCP samples, and Scheme 1c shows the shear geometry consisting of the flow direction (FD), constraint direction (CD), and load direction (LD). For the symmetric BCPs, (*i.e.* PS₂₀₂-*b*-PTBOS₃₅ $f^{\text{PTBOS}} \sim 0.58$),

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Scheme 1 Core-shell rod-coil BCPs. (a) Rod-coil vs. core-shell rod-coil. The aliphatic shell can be readily obtained by tuning the chemical structure of the soft tails of the LCs. (b) Chemical structure of PS-*b*-PTBOS, the long tail (14 carbon) renders a relatively thick shell for the PTBOS rod. (c) Schematic representation of the shear geometry.

four orders of scattering arcs are evident along the equator of the 2-D SAXS pattern when X-ray was along the CD (Fig. 1a).¹¹ These scattering arcs possess a ratio of 1 : 2 : 3 : 4 and the *d*-spacing corresponding to the first scattering peak is ~27.4 nm, indicating a lamellar phase, consistent with the TEM observation (Fig. 1e).

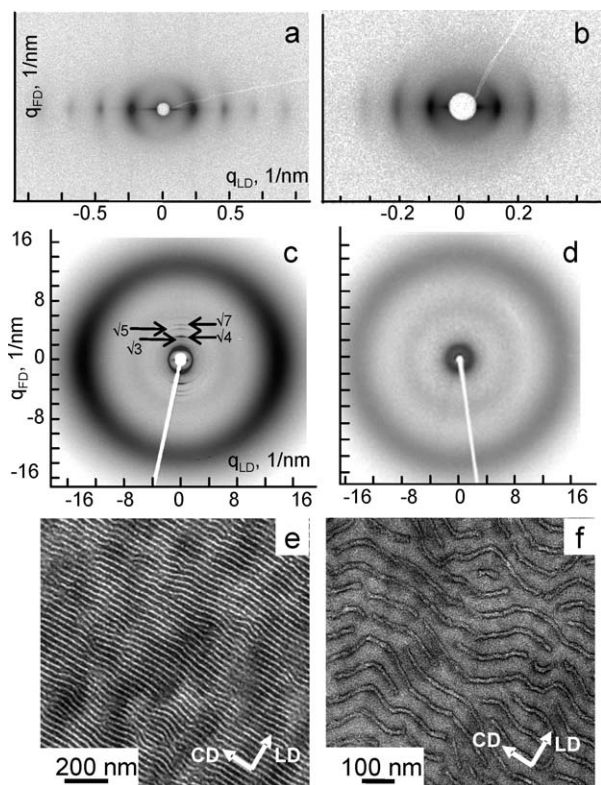


Fig. 1 SAXS, WAXD patterns and TEM images of PS₂₀₂-*b*-PTBOS₃₅ (a, c, e), PS₅₆₇-*b*-PTBOS₂₄ (b, d, f). Similar X-ray patterns and morphologies were obtained both in the CD/LD and FD/LD planes.

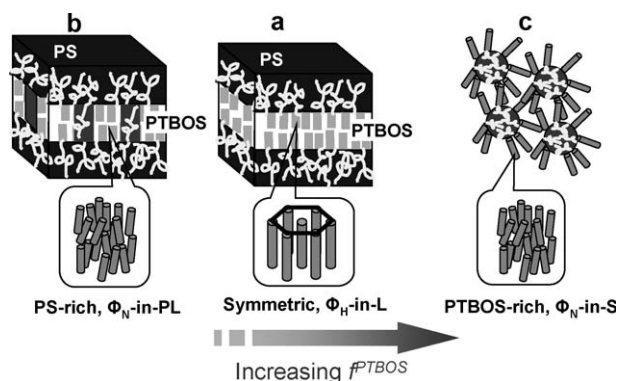


Fig. 2 Three different hierarchical structures (a) Φ_H -in-L in PS₂₀₂-*b*-PTBOS₃₅, (b) Φ_N -in-PL in PS₅₆₇-*b*-PTBOS₂₄, and (c) Φ_N -in-S in PS₁₆₀-*b*-PTBOS₁₂₆. LC symmetry breaking in (b) and (c) is due to BCP self-assembly. Shell is not shown in the cartoon to avoid ambiguity.

The dark layers are PS stained with RuO₄. WAXD (Fig. 1c) showed (CD zone) six orders of diffraction arcs along the meridian direction with a ratio of 1 : $\sqrt{3}$: $\sqrt{4}$: $\sqrt{5}$: $\sqrt{7}$, indicating a Φ_H structure with a *d*-spacing of ~3.6 nm: the BC-MJLCPs form the columns which pack into a 2-D hexagonal lattice. Therefore, a columnar-hexagonal-in-lamellar (Φ_H -in-L) hierarchical structure was formed (Fig. 2a). In our previous study on similar RCBCP systems where short mesogen tail length was used, the hierarchical structure was columnar-nematic-in-lamellar (Φ_N -in-L).^{4,12} We attribute the change of LC symmetry to the increased size of the “soft” tails which apparently serve as a “buffer” layer among the rigid cores of the rods and lead to hexagonal symmetry formation. To our knowledge, this is the first observation of the Φ_H -in-L in macromolecular systems.

Two types of asymmetric PS-*b*-PTBOS samples were designed to study the competition between liquid crystallinity and BCP self-assembly. PS₅₆₇-*b*-PTBOS₂₄ possesses an $f^{PTBOS} \sim 0.25$ and it represents a PS-rich RCBCP. Fig. 1b shows the 2-D SAXS pattern when the X-ray was along CD. Three orders of scattering can be clearly seen along the equatorial direction. The *q* values of these scattering peaks possess a 1 : 2 : 3 ratio, indicating a lamellar BCP structure with a *d*-spacing of ~52.7 nm. Fig. 1f shows the TEM micrograph of the CD/LD plane of PS₅₆₇-*b*-PTBOS₂₄. Bright broken lamellae can be clearly seen. The bright strips are PTBOS domains and they are perforated by PS chains. Observing perforated layer (PL) structure in coil-rich RCBCP is not surprising since the macromolecular rods are more compatible with the planar interface.^{4,12} Of interest is the dramatic change of the WAXD pattern as compared to that of the symmetric BCP: in the low angle region, higher order peaks completely disappeared and the LC structural order reduced from Φ_H to Φ_N phase (Fig. 1d); the hierarchical structure is thus columnar-nematic-in-perforated layer (Φ_N -in-PL, Fig. 2b). This LC symmetry breaking is possibly because in PL structures, the coil chains stretch and perforate the rod layer, there thus exists lateral repulsion of the coil chains as shown in Fig. 3a(i). Because the rods and the coils are covalently linked, this lateral repulsion of the coil chains further renders a splaying stress field on the LC rods, which forces the rod to bend thereby reducing the LC order. In order to confirm this, we hypothesize that if splaying stress field is the reason for LC symmetry breaking, by blending with small amount of PS oligomers, this stress could be partially released and the original

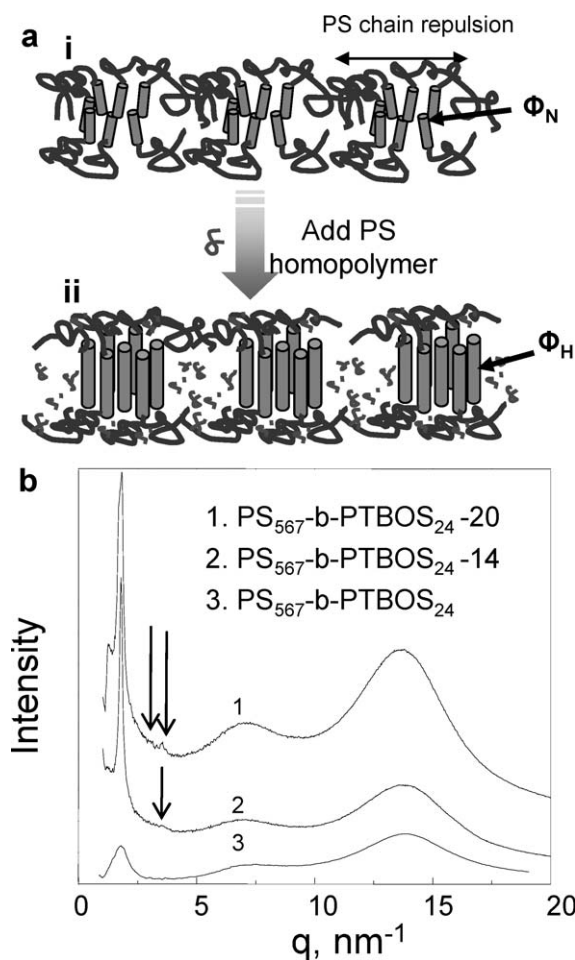


Fig. 3 (a). Schematic representation of the stress releasing process in the Φ_N -in-PL hierarchical structure before (i) and after (ii) blending with low molecular weight PS. Shell is not shown in the cartoon to avoid ambiguity. (b) WAXD patterns show that the LC ordering was dramatically enhanced in the blend samples with 20 and 14% PTBOS (1, 2) compared to the pure BCP (3).

Φ_H could be recovered (Fig. 3a(ii)) (as the low molecular weight PS acts as a diluent in the system). To this end, two blend samples were prepared and the PTBOS volume fractions were controlled to be 20 and 14%, respectively (PS₅₆₇-b-PTBOS₂₄-20 and PS₅₆₇-b-PTBOS₂₄-14). As shown in Fig. 3b, compared to the WAXD pattern of pure BCP PS₅₆₇-b-PTBOS₂₄, the diffraction peaks of the blends became much sharper and the higher order reflections can be clearly seen. The LC order was thus dramatically increased upon blending, confirming that the Φ_H LC symmetry was restored. This clearly supports our hypothesis on the stress-induced LC symmetry breaking. In the conventional rod-coil systems, similar phenomenon was not observed because the rod-rod interaction is much stronger and it overcomes the stress induced by the coil-coil repulsion.

The soft shell of the rods also dramatically influences the assembled structure in PTBOS-rich BCPs. Fig. 4 shows a TEM, 2-D SAXS pattern (lower inset) and 2-D WAXD (upper inset) pattern of a sheared PS₁₆₀-b-PTBOS₁₂₆ ($f^{\text{PTBOS}} = 0.86$) film. A diffuse ring-like scattering is evident from the SAXS pattern, indicating the lack of any orientation in the sample. Dark spherical PS domains are evident in a bright PTBOS background from the TEM image.

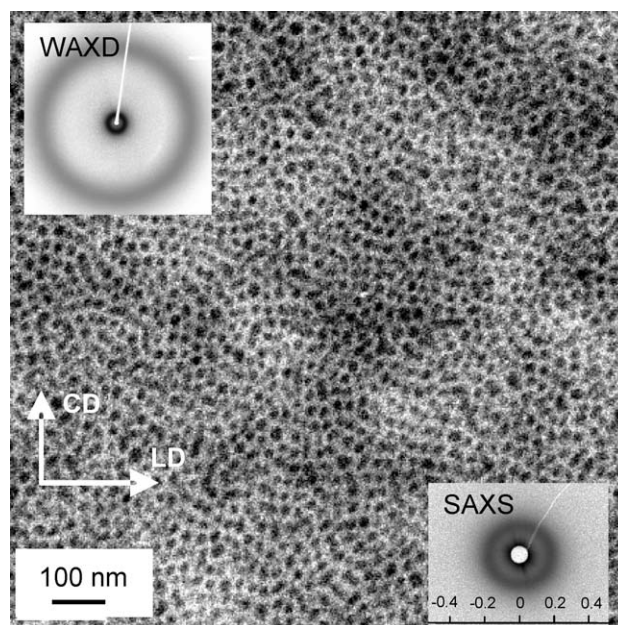


Fig. 4 TEM micrograph of PS₁₆₀-b-PTBOS₁₂₆ indicating a Φ_N -in-S hierarchical structure. Upper and lower insets show the WAXD and SAXS patterns of the same sample.

This indicates that PS forms spherical domains in the PTBOS matrix. In most reported rod-rich RCBP systems, strong LC ordering leads to different smectic structures with a planar IMDS. In the present case, again the core-shell design of the system decreases the LC interaction among the rods, which enables the BCP self-assembly to dominate LC ordering in the hierarchical structure formation; S phase with curved IMDS was thus formed. The WAXD pattern of this sample shows that the LC order was reduced and instead of Φ_H , Φ_N phase was formed. The hierarchical structure is Φ_N -in-S (Fig. 2c). This clearly indicates that the curved IMDS reduces the order of LC and the LC symmetry breaking is because of the incompatibility of the translational symmetry of LC and the curved IMDS.

In summary, by designing a novel core-shell RCBP, the LC ordering of the rods was decreased and the subtle competition between liquid crystallinity and BCP self-assembly was revealed. Contrary to the conventional rod-coil systems where LC ordering always dictates the phase structure, in the core-shell rod-coil system, BCP self-assembly could be the dominant factor in RCBP structure formation. Novel Φ_H -in-L, Φ_N -in-PL, Φ_N -in-S structures were observed in the symmetric, coil-rich and rod-rich BCPs, respectively. The Φ_H symmetry was broken in the asymmetric BCPs, due to the lateral chain repulsion in the perforated layers in the coil-rich sample, and the curved IMDS in the S BCP structure in the rod-rich sample. The unique core-shell RCBP also opens a new avenue for the hierarchical structure design of soft matter.

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