

Transfer of Chirality in Self-Assembled Chiral Block Copolymers

This report features the works of Rong-Ming Ho and his co-workers published in *J. Am. Chem. Soc.* **134**, 10974 (2012) and *Chem. Commun.* **48**, 3665 (2012).

Block copolymers (BCP), composed of incompatible blocks with a covalent connection, can self-assemble into periodically ordered nanostructures, including lamellae, cylinder, sphere and gyroid phases, depending on the volume fractions of the constituent blocks and the strength of the segmental interactions. In contrast to the conventional phases generated on the self-assembly of BCP, BCP composed of chiral blocks (denoted chiral block copolymers, BCP*) can self-assemble into atypically helical assemblies, indicating that the chirality and helical entity have an inseparable relation. Chirality is, generally, identified as the principal origin for the formation of helical architectures. In a system of BCP*, chiral centers (configurational chirality) in a repeating unit of chiral blocks typically result in helical macromolecular conformations (conformational chirality). When chiral blocks of BCP* agglomerate to form ordered structures, the chirality might break the local mirror symmetry and yield helical nanostructures (phase chirality). Although the transfer of chirality in BCP* is recognized to be an interesting topic, little is known about how a chiral assembly develops from the molecular level to a mesoscale structure.

A laboratory for frontier polymer research led by Prof. Rong-Ming Ho from National Tsing Hua University, Taiwan, is devoted to the investigation of self-assembly BCP*, nanopatterning technologies via integration of top-down and bottom-up methods, and hybridization via block-copolymer templating. Prof. R.-M. Ho and his co-workers utilized synchrotron-based small-angle X-ray scattering (SAXS) at beamline **BL23A1** in NSRRC and a transmission electron microscope (TEM) to identify the formation of a helical (H*)

phase on poly(styrene)-*block*-poly(L-lactide) PS-*b*-PLLA, poly(styrene)-*block*-poly(D-lactide) PS-*b*-PDLA and blending PS-*b*-PLLA and homopolymer PS of small molecular mass.^{1,2} In their study,¹ PLLA and PDLA microdomains appeared as bright helical nanostructures (H* phase) in TEM images (as insertions of Fig. 1(a) and 1(b)), and SAXS profiles shown well-defined reflections at q^* ratios of $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{13}$ in both PS-*b*-PLLA and PS-*b*-PDLA (Fig. 1(a) and 1(b)), characteristic of hexagonally packed helical nanostructures. They found also that the handedness of the H* phase in PS-*b*-PLLA is preferentially left-hand, whereas the handedness of the H* phase in PS-*b*-PDLA is preferentially right-hand; that is, the chiral entity of the chiral polylactide block not only produces a helical conformation but also determines the handedness of that helical conformation (Fig. 2).¹ To investigate systematically the mechanism of chiral transfer across various scales of hierarchical length, they examined the circular dichroism (CD) and fluorescence of the achiral perylene moieties located at the junctions of the BCP* of PS-*b*-PLLA and PS-*b*-PDLA. The evidence of strong CD signals and a bathochromic shift of the fluorescent emission associated with

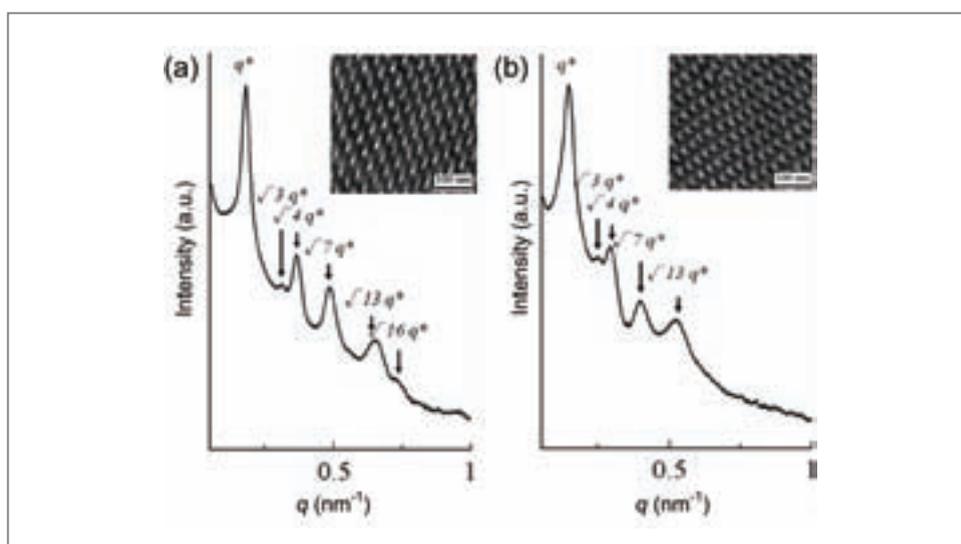


Fig. 1: (a) and (b): One-dimensional SAXS profiles of PS-PLLA and PS-PDLA, respectively; corresponding TEM images also shown in the insets of (a) and (b). This figure is adapted from Ref. 1.

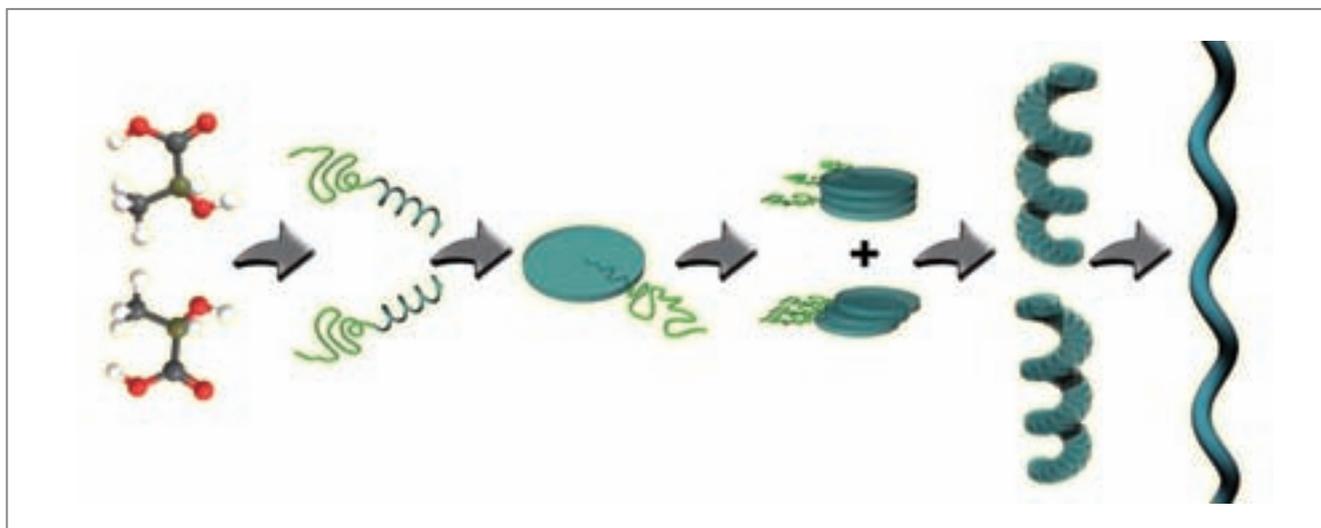


Fig. 2: Schematic illustration of an hypothetical mechanism of transfer of chirality from molecular chirality into phase chirality in the self-assembly of BCP*. This figure is adapted from Ref. 1.

the self-assembly of the PS-*b*-PLLA and PS-*b*-PDLA in toluene was interpreted to indicate a twisting and shifting initiated from the microphase-separated interfaces. This effect of twisting and shifting resulted from a handed intermolecular packing of PLLA and PDLA that ultimately drove the formation of the H* phase.

References

1. R.-M. Ho, M.-C. Li, S.-C. Lin, H.-F. Wang, Y.-D. Lee, H. Hasegawa, and E. L. Thomas, *J. Am. Chem. Soc.* **134**, 10974 (2012).
2. H.-F. Wang, H.-W. Wang, and R.-M. Ho, *Chem. Commun.* **48**, 3665 (2012).

