

MAR12-2011-000820

Abstract for an Invited Paper
for the MAR12 Meeting of
the American Physical Society

Crystallization and Microphase Separation in Chiral Block Copolymers

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Block copolymers composed of chiral entities, denoted as chiral block copolymers (BCP*s), were designed to fabricate helical architectures from self-assembly. A helical phase (denoted H*) was discovered in the self-assembly of poly(styrene)-*b*-poly(L-lactide) (PS-PLLA) BCPs*. To examine the phase behavior of the PS-PLLA, self-assembled superstructures resulting from the competition between crystallization and microphase separation of the PS-PLLA in solution were examined. A kinetically controlled process by changing non-solvent addition rate was utilized to control the BCP* self-assembly. Single-crystal lozenge lamellae were obtained by the slow self-assembly (i.e., slow non-solvent addition rate) of PS-PLLA whereas amorphous helical ribbon superstructures were obtained from the fast self-assembly (i.e., fast non-solvent addition rate). As a result, the formation of helical architectures from the self-assembly of the PS-PLLA reflects the impact of chirality on microphase separation, but the chiral effect might be overwhelmed by crystallization. Consequently, various crystalline PS-PLLA nanostructures in bulk were obtained by controlling the crystallization temperature of PLLA ($T_{c, PLLA}$) at which crystalline helices and crystalline cylinders occur while $T_{c, PLLA} < T_{g, PS}$ (the glass transition temperature of PS) and $T_{c, PLLA} \geq T_{g, PS}$, respectively. Anisotropic arrangement of the PLLA crystallites grown within the microdomains was identified. The formation of this exclusive crystalline growth is attributed to the spatial confinement effect for crystallization. While $T_{c, PLLA} < T_{g, PS}$, winding crystals with specific crystallographic orientation within the helical microdomains can be found. By contrast, while $T_{c, PLLA} \geq T_{g, PS}$, the preferential growth may modulate the curvature of microdomains by shifting the molecular chains to access the fast path for crystalline growth due to the increase in chain mobility. As a result, a spring-like behavior of the helical nanostructure can be driven by crystallization so as to dictate the transformation of helices and to result in crystalline cylinders.