

CRYSTALLIZABLE BLOCK COPOLYMERS: DIRECTING CRYSTALLIZATION VIA POLYMER ARCHITECTURE

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Covalently connecting two or more long, homogeneous monomer sequences (such as polyethylene and polystyrene) defines the architecture of the class of materials collectively termed “block copolymers”. Designing two or more self-organizing mechanisms into a single material—such as crystallization of one block and repulsion between unlike blocks—yields both morphological richness and kinetic complexity. In crystallizable block copolymers, the final structure and properties can be governed by nanophase separation in the melt, block crystallization, or a combination of the two dictated by the processing history. This seminar will describe a multipronged approach to control the structure of polymer crystals, and the kinetics of their formation, through molecular design of the block copolymer. A strongly-segregated block copolymer melt can template crystallization on its own length scale, tailoring the continuity of the crystallizable domains and hence physical properties—for example, such materials are optically transparent even when crystallized, as no micron-scale crystalline structures can form. Dividing the crystallizable material into discrete domains, such as cylinders or spheres, mandates that crystallization proceed by homogeneous nucleation, making the crystallization kinetics remarkably sensitive to microdomain connectivity. However, even when the block copolymer forms a homogeneous, low-viscosity melt, the block copolymer architecture can still exert substantial control over the crystal structure. We are currently investigating crystalline-amorphous block copolymers derived from ring-opening metathesis polymerization, which permits the synthesis of a crystallizable block free from chain defects. For highly-crystalline homopolymers, the crystal thickness is determined by the crystallization history of the material, and often a broad distribution of crystal thicknesses is obtained. But by attaching an amorphous block of predetermined length to the crystallizable chain, we can induce the crystallizable block to fold a precise number of times, thus precisely tuning the crystal thickness (and hence melting point) thermodynamically.