Crystal Thickening in Strongly Segregated Crystalline-Amorphous Diblock Copolymers

ADAM B. BURNS, RICHARD A. REGISTER, Princeton University — In semicrystalline-amorphous diblock copolymers the phase behavior and structure are determined by the complex interplay between crystallization and block incompatibility. If the segregation strength is sufficiently high in the melt, crystallization can be confined by the amorphous domains. Strongly segregated, lamellar diblocks containing semicrystalline hydrogenated polynorbornene (hPN) have been studied. Wide-angle x-ray scattering patterns of flow-aligned specimens indicate that the crystal stems lie generally parallel to the domain interfaces. This arrangement avoids incommensurability between the crystal thickness and the domain periodicity. Small-angle x-ray scattering reveals that, although the amorphous block is rubbery when hPN crystallizes, the orientation of the lamellar microdomains is maintained upon crystallization, confirming that the crystals are confined to the hPN microdomains. While the microdomain morphology remains intact, there is a measurable increase in the domain periodicity upon crystallization caused by crystal growth normal to the domain interface. Differential scanning calorimetry is used to show that the confined crystals thicken towards an equilibrium crystal thickness (melting point) when annealed near the melting point. Unlike the homopolymer, where the equilibrium structure is the extended chain crystal, one end of the hPN block (i.e., the block junction) must remain anchored to the microdomain interface, and the concomitant chain stretching at the interface limits the crystal thickness. Furthermore, the limiting crystal thickness increases with increasing molecular weight.

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