Solid-State Structure and Crystallization in Double-Crystalline Diblock Copolymers

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Double-crystalline diblock copolymers of linear polyethylene (LPE) and hydrogenated polynorbornene (hPN) were synthesized, and their crystallization behavior and morphology were examined using two-dimensional simultaneous time-resolved synchrotron small-angle and wide-angle X-ray scattering. In symmetric hPN/LPE diblocks with molecular weights above 50 kg/mol, the hPN block has previously been shown to crystallize first and set the solid-state microstructure. By adjusting total molecular weight, the order of block crystallization may be reversed, even while holding the block length ratio fixed. At a diblock molecular weight of 20 kg/mol, LPE is found to crystallize first, even when LPE is the minority component, and restricts hPN to crystallize between the LPE lamellae. Furthermore, in both the high and low molecular weight diblock copolymers, the second-to-crystallize block always orients its crystals orthogonally to the first-to-crystallize block.