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Solid-State Structure and Crystallization in Double-Crystalline Diblock Copolymers SHENG LI, SASHA MYERS, RICHARD REGISTER, Princeton University — Crystalline-crystalline block copolymers, containing two or more chemically distinct crystallizable blocks, can potentially exhibit a rich array of complex solid-state structures. 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. Previously, we showed that in symmetric diblock copolymers of hPN and LPE, with molecular weights above 50 kg/mol, the hPN block crystallizes first and sets the solid-state microstructure. In the present work, we extend these studies to lower molecular weights, and more importantly, we examine the structural relationship between the crystals formed by the two blocks under different conditions of confinement. When the diblock molecular weight is reduced to 20 kg/mol, the LPE block crystallizes 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.

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