Tuning the Structure-Directing Block in Crystalline-Crystalline Diblock Copolymers

SHENG LI, SASHA MYERS, RICHARD REGISTER, Princeton University — Crystalline-crystalline block copolymers containing two or more chemically distinct crystallizable blocks are fascinating because their solid-state structures can be set either by block incompatibility or by crystallization of one or more blocks, depending on macromolecular design and processing history. 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 previous work (Macromolecules 2008, 41, 6773), we showed that for diblock molecular weights of 50 kg/mol and above, the hPN block always crystallized first and set the solid-state microstructure. In the present work, we exploit the difference in molecular weight dependence of the melting/freezing points of LPE vs. hPN to create materials where LPE is the structure-directing (templating) block. In 20 kg/mol diblocks, LPE block crystallizes first, even when LPE is the minority component, and restricts hPN to crystallize between the LPE lamellae. In hPN-rich diblocks, LPE crystallization triggers hPN crystallization and the two blocks crystallize at almost the same rate. During cooling to room temperature, hPN transitions from a rotationally disordered pseudohexagonal phase to a monoclinic structure.

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