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Phase Behavior of Hydrogenated Derivatives of Linear ABC Block-Random Copolymers of Styrene and Isoprene BRYAN BECKING-HAM, RICHARD REGISTER, Princeton University — The capacity to synthesize block-random copolymers, block copolymers with one or more random copolymer blocks, allows for continuous tuning of the inter-block average segmental interaction parameter, χ , through the composition of the random copolymer without changes to system chemistry. By lithium-initiated anionic polymerization in a mixture of cyclohexane and triethylamine, we synthesized an asymmetric near-monodisperse linear ABC block-random copolymer of styrene and isoprene: S_{30} - I_{12} - SrI_{12} , where SrI denotes a random copolymer block with 50 wt. % styrene, and block molecular weights are 30-12-12 kg/mol. Upon complete hydrogenation, the VCH-hI-VCHrhI triblock exhibits microphase separation into a well-ordered two-domain lamellar structure with an order-disorder transition between 180-185 °C via small-angle x-ray scattering. This two-domain lamellar structure is confirmed using electron density modeling of the SAXS peak intensity and domain spacing arguments. A three-domain lamellar structure is expected in the diene-selective hydrogenated derivative, S-hI-SrhI, due to increased χ between the middle and end blocks. Additional S-I-SrI and S-SrI-I triblock copolymers are being synthesized and the effects of block sequence, end block molecular weight, and hydrogenation (S vs. VCH) on phase behavior are being explored.

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