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Effects of B Segment Polydispersity on ABA Triblock Copolymer Phase Behavior MAHESH MAHANTHAPPA, JOAN SCHROEDER, ANDREW SCHMITT, ADAM SCHMITT, KYUHYUN IM, University of Wisconsin-Madison — Advanced polymerization techniques enable the synthesis of a variety of polymeric materials with well-defined chain architectures, compositions, and tunable molecular weights and molecular weight distributions. The inherent chain length polydispersity of polymers derived from these syntheses affects their ultimate materials properties and applications. Relying on tandem ring-opening metathesis polymerization with chain transfer (ROMP-CT) and atom transfer radical polymerization (ATRP), we have synthesized a series of poly(styrene-*b*-1,4-butadiene-*b*-styrene) triblock copolymers in which the polybutadiene blocks are polydisperse ($M_w/M_n = 1.7-2.0$) and the polystyrene end blocks are monodisperse ($M_w/M_n = 1.05-1.30$). We systematically explore the role of block polydispersity, a molecular chain length heterogeneity, on the melt-phase self-assembly behavior of these block copolymers. Using a combination of temperature-dependent X-ray scattering and transmission electron microscopy, we demonstrate that monodispersity is not a necessary condition for molecular self-assembly into well-defined supramolecular morphologies. The origins of these effects are discussed and a preliminary experimental phase portrait for this system is presented.

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