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Congruent Lamellar-to-Disorder Phase Transitions in Diblock Copolymer-Homopolymer Ternary Blends

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— Symmetric ternary blends of AB diblock copolymers and the corresponding A and B homopolymers are predicted to be characterized by a multicritical Lifshitz point within mean-field theory. Previous studies have shown that fluctuations destroy the predicted Lifshitz point and lead to a bicontinuous microemulsion (BμE) channel, which separates the lamellar and 2-phase regions in the ternary phase prism. Here, we establish the existence of a line of congruent first-order lamellar-to-disorder transitions when appropriate amounts of poly(cyclohexylethylene) (C) and poly(ethylene) (E) homopolymers are mixed with the corresponding symmetric CE diblock copolymer. We present complimentary optical transmission, small-angle X-ray scattering, transmission electron microscopy (TEM), and rheological results obtained using two experimental protocols: (1) fixing the CE volume fraction and varying the C/E ratio, and (2) setting the C/E ratio at the condition of congruency and varying CE volume fraction from 0 to 1. These results establish a quantitative and facile method for identifying the detailed phase behavior in the vicinity of the BμE, and provide fresh insight into the nature of such mixtures near the nominal Lifshitz conditions. Surprisingly, well-ordered lamellae are revealed by TEM at compositions within 1% of the BμE channel, suggesting a remarkably close approach to the predicted, mean-field unbinding transition. Moreover, the width of the BμE narrows to about 1% under congruent conditions.

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