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Random isotropic structures and possible glass transitions in diblock copolymer melts CHENGZHONG ZHANG, ZHEN-GANG WANG, Chemical Engineering, Caltech — We study the microstructural glass transition in diblock-copolymer melts using a thermodynamic replica approach. Our approach performs an expansion in terms of the natural smallness parameter – the inverse of the scaled degree of polymerization $\bar{N}$, which allows us to systematically study the approach to mean-field behavior as the degree of polymerization increases. We find that in the limit of infinite chain length, both the onset of glassiness and the vitrification transition (Kauzmann temperature) collapse to the mean-field spinodal, suggesting that the spinodal can be regarded as the mean-field signature for glass transitions in this class of microphase-separating system. We also study the order-disorder transitions (ODT) within the same theoretical framework; in particular, we include the leading-order fluctuation corrections due to the cubic interaction in the coarse-grained Hamiltonian, which has been ignored in previous studies on the ODT in block copolymers. We find that the cubic term stabilizes both the ordered (body-centered-cubic) phase and the glassy state relative to the disordered phase. In melts of symmetric copolymers the glass transition always occurs after the order-disorder transition (below the ODT temperature), but for asymmetric copolymers, it is possible for the glass transition to precede the ordering transition.

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