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The Influence of Polydispersity on the Thermodynamics of Diblock Copolymers NATHANIEL LYND, MARC HILLMYER, University of Minnesota, Department of Chemistry — The effects of the molecular weight distribution on the thermodynamics of diblock copolymers have been predicted to affect order-disorder transitions (ODT), order-order transitions and the equilibrium morphology adopted.^{1,2} We prepared several sets of Poly[(ethylene-*alt*-propylene)-*b*-(D,L-lactide)] diblock copolymers with controlled molecular weights, compositions and polydispersities (PDIs). Rheology and small angle x-ray scattering were used to evaluate the effects of PDI on the lamellar domain spacing, the ODT, and the resultant morphology. For symmetrical samples, the lamellar domain spacing increased with increasing PDI. The degree of segregation at the ODT $((\chi N)_{ODT})$ was dependent upon the volume fraction of the polydisperse component (f_{PLA}) . Interestingly, for $f_{PLA} = 0.33 \ (\chi N)_{ODT}$ decreased with increasing PDI but for $f_{PLA} =$ $0.64 (\chi N)_{ODT}$ increased with increasing PDI. We also demonstrated that an increase in PDI at constant f_{PLA} results in a change in equilibrium morphology. Monte Carlo simulations addressing the effects of fluctuations on the ODT of polydisperse diblock copolymer melts were also performed. .(1) Sides, S.W.; Frederickson, G.H. J. Chem. Phys. 2004, 121,4974. (2) Burger, C.; Ruland, W.; Semenov, A.N. Macromolecules 1990, 23, 3339.

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