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Melt Miscibility in Block Copolymers Containing Polyethylene and Substituted Polynorbornenes. WILLIAM MULHEARN, RICHARD REGISTER, Princeton Univ — Very few polymer species exist with a sufficiently weak repulsive interaction against polyethylene (PE), characterized by a low Flory parameter χ or interaction energy density X, to be useful for preparing PE-containing block copolymers with disordered melts at high molecular weights. Most suitably miscible polymers are chemically similar to PE, such as copolymers of ethylene with a minority content of an α-olefin, and so are only marginally useful for property modification due to similar physical properties like the glass transition temperature (T_g). However, the family of polymers consisting of substituted norbornenes prepared via ring-opening metathesis polymerization (ROMP) and subsequent hydrogenation is unique in that many of its members exhibit very low X against PE (comparable with the interaction energy between poly(ethylene-*alt*-propylene) and PE), and some of these also exhibit high T_g. The miscibility between PE and a substituted, hydrogenated ROMP polynobornene, or between two dissimilar hydrogenated polynorbornenes, is a strong function of the substituent appended to the norbornene monomer. The mixing thermodynamics of this polymer series are irregular, in that the interaction energies do not follow $X = (\delta_1 - \delta_2)^2$ where δ is the solubility parameter. However, other systematic trends do apply and we develop a set of mixing rules to quantitatively describe the experimental miscibility behavior. We also investigate statistical copolymerization of two norbornene monomers as a means to continuously tune miscibility with a homopolymer of a third monomer.

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