Melt-Miscibility in Block Copolymers Containing Polyethylene and Substituted Polynorbornene Blocks

WILLIAM MULHEARN, RICHARD REGISTER, Princeton Univ — Block copolymers containing a crystallizable block, such as polyethylene (PE), and a high-\(T_g\) amorphous block are potentially interesting materials since the rigid glassy block can mitigate the poor yield strength of the PE crystals. However, chemical incompatibility between blocks, quantified by the Flory interaction parameter \(\chi\) or the interaction energy density \(X\), drives microphase separation at low temperatures or high chain lengths. To prepare a high molecular weight PE-containing block copolymer that is easy to process (i.e. with a disordered low-viscosity melt) it is necessary to select amorphous blocks that have low mixing energies with PE. The only suitable polymers currently known are chemically similar to PE and therefore have similarly low glass transition temperatures. We investigate a series of both low- and high-\(T_g\) polymers based on substituted norbornene monomers, polymerized via ring-opening metathesis polymerization (ROMP). Several ROMP polymers of this type exhibit high \(T_g\) and low interaction energy against PE. For example, hydrogenated poly(cyclohexyl norbornene) has \(T_g = 88\) °C and has interaction energy density \(X_{hPCyN-PE} \approx 0.8\) MPa, comparable to the interaction energy density between PE and hydrogenated polyisoprene. The miscibility of an amorphous block can be further tuned by statistical copolymerization of norbornene units with aromatic side-groups (high Hildebrand solubility parameter) and norbornene units with aliphatic side-groups (low Hildebrand solubility parameter).