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**Regular and Irregular Mixing in Hydrocarbon Block Copolymers**

RICHARD REGISTER, BRYAN BECKINGHAM, Princeton University — Since hydrocarbon polymers interact through relatively simple (dispersive) interactions, one might expect them to be described by simple models of mixing energetics, such as regular mixing. However, the pioneering work of Graessley on saturated hydrocarbon polymer blends showed that while regular mixing is obeyed in some cases, both positive and negative deviations (in the magnitude of the mixing enthalpy) from regular mixing are observed in other cases. Here, we describe the mixing energetics for two series of hydrocarbon polymers wherein the interaction strengths may be continuously tuned, and which can be readily incorporated into block copolymers. Random copolymers of styrene and medium-vinyl isoprene, in which either the isoprene or both the isoprene and styrene units have been saturated, obey regular mixing over the entire composition range and for both hydrogenated derivatives. Well-defined block copolymers with arbitrarily small interblock interaction strengths can be constructed from these units, permitting the interdomain spacing to be made arbitrarily large while holding the order-disorder transition temperature constant. However, block copolymers of hydrogenated polybutadiene with such random copolymers show very strong positive deviations from regular mixing when the styrene aromaticity is preserved, and sizable negative deviations when the styrene units are saturated to vinylcyclohexane. Both of these cases can be quantitatively described by a ternary mixing model.

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