Block Copolymer Surfactants in Immiscible Homopolymer Blends

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Kwanho Chang

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David C. Morse and Christopher W. Macosko, Advisors

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Abstract

Block copolymers have been often used as emulsifying agents in binary homopolymer blends. We have used both theory and experiment to study the competition between interfacial adsorption and micellization of copolymer in mixtures of copolymer and two immiscible homopolymers.

Self-consistent field theory (SCFT) has been used to characterize the elastic properties of a block copolymer monolayer dividing A- and B-rich homopolymer domains in the context of the Canham-Helfrich theory, and to study the thermodynamics of two phase systems in which one of the coexisting phases contains micelles.

Interfacial tension has been measured between polyisoprene and polydimethylsiloxane in the presence of poly(isoprene-b-dimethylsiloxane) copolymer using a spinning drop tensiometer. In the case of a symmetric block copolymer, we observed a decrease of interfacial tension by three orders of magnitude. Experimental measurements of interfacial tension were compared with the SCFT predictions for a system in which swollen spherical micelles are present in one phase. The predicted dependence of interfacial tension on the block composition f_A agreed well with the experiment results for sufficiently asymmetric copolymers, with $f_A > 0.65$. However, for nearly symmetric copolymers with $0.5 < f_A < 0.6$, interfacial tension was much lower than these predictions. For those nearly symmetric copolymers, the formation of a bicontinuous microemulsion phase has been observed.

Interfacial tension and the cmc have also been measured in a system of polybutadiene and polystyrene with poly(styrene-b-butadiene) block copolymer. The cmc has been de-

termined by both X-ray scattering and transmission electron microscopy. In this system, measured interfacial tension was strongly affected by the slow diffusion of block copolymer.