236d Synthesis and Novel Application of Gradient Copolymers: Compatibilization of Immiscible Polymer Blends

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Compatibilization of immiscible polymer blends, which can lead to synergistic material properties, is a major academic and technological challenge. Optimal properties often rely on an average dispersed-phase diameter less than several microns; hence, stabilization of the dispersed-phase domain size against coarsening, a definition of compatibilization, is key to processing immiscible blends. Many compatibilization strategies have been tested, most involving a reduction in interfacial tension and/or steric hindrance against coarsening. These strategies include the addition of pre-made block, tapered block, graft, and random copolymers during melt processing. The use of added block/graft copolymers has led to compatibilization in small-scale studies but has not been commercialized, due in part to the very low critical micelle concentration (cmc) that prevents sufficient copolymer from reaching interfacial regions during melt processing. Random copolymer addition leads to encapsulation of the dispersed phase and thus does not lead to compatibilization even in small-scale studies. Nitroxide-mediated controlled radical polymerization (NM-CRP) and atom-transfer radical polymerization have led a new class of polymer called gradient copolymers that possess a gradual change in composition along the chain length. Theory predicts that gradient copolymers dispersed in homopolymer have much higher cmcs and exhibit broader interfacial coverage than block copolymers of the same composition, suggesting that gradient copolymers may be effective blend compatibilizers. Here we demonstrate that compatibilization of immiscible blends can be achieved via addition of gradient copolymer during melt processing, providing for a new technological application of copolymers made by controlled radical polymerization. By comparing several blend systems in terms of the evolution of the number-average dispersed phase diameter, Dn, of the melt mixed samples after static annealing, we show that coarsening can be eliminated upon addition of several weight percent gradient copolymer during melt mixing of the blend. Systems described here include polymer A/polymer B/A-B copolymer (polystyrene (PS)/poly(methyl methacrylate) (PMMA)/styrene (S)-methyl methacrylate (MMA) copolymer) and polymer A/polymer B/A-C copolymer (PS/polycaprolactone (PCL)/S-hydroxystyrene (SOH) copolymer). Thus, this study demonstrates that compatibilization can be achieved in either the presence or the absence of attractive enthalpic interactions between a homopolymer and a gradient copolymer repeat unit (PCL can undergo hydrogen bonding interactions with hydroxystyrene units on the copolymer).