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Compatibilization of Immiscible Polymer Blends by Gradient Copolymers

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Novel strategies for blend compatibilization by addition of gradient copolymers have been examined. While block copolymers have a sharp boundary at which the co-monomer composition changes, gradient copolymers possess a gradual change in co-monomer composition either along the entire chain length or a significant part of it. Such a copolymer structure can be obtained by controlled radical polymerization techniques, including nitroxide-mediated controlled radical polymerization (NM-CRP), where polymer chains grow in a controlled manner with increasing conversion. Gradient copolymers of styrene (S)/methyl methacrylate and S/n-butyl methacrylate have been synthesized via NM-CRP added at low levels in blends of polystyrene (PS)/poly(methyl methacrylate) or PS/poly(n-butyl methacrylate). The effects of gradient copolymer characteristics including molecular weight, copolymer composition, and the distribution of co-monomers along the compatibilization capability, which is determined by elimination or suppression of the dispersed-phase coarsening during melt-state annealing, have been investigated. In particular, complete compatibilization can be achieved in the PS/poly(methyl methacrylate) blend if the appropriate architecture is chosen for the S/methyl methacrylate gradient copolymer. In addition, gradient copolymers of S/4-hydroxystyrene (hS) have been synthesized via NM-CRP of S/4-acetoxystyrene (AS) followed by hydrolysis of AS units, and added to immiscible PS/polycaprolactone (PCL) blends during melt processing. Elimination of the dispersed phase PCL phase coarsening during static melt-state annealing is achieved with addition of a variety of S/hS gradient copolymers, due to the formation of hydrogen bonds between PCL and hS repeat units. Thus, this study demonstrates that blend compatibilization can be achieved either in the presence or absence of attractive interactions between a homopolymer and a gradient copolymer repeat unit.