Abstract

Poly(2-ethylhexyl acrylate) (PEHA) is an important polymer which has branched long alkyl chain, low T_g and very good film formation property. This thesis reports the preparation of tailor-made poly(2-ethylhexyl acrylate) (PEHA), its block and graft copolymers via atom transfer radical polymerization (ATRP). The effect of different additives on polymerization kinetics of ATRP of EHA was studied. Addition of small amount of acetone enhanced the polymerization rate and importantly it maintains good control over molecular weight and poly dispersity index (PDI) of the polymer. The rate of the polymerization was further increased, when nanoclay was added into the polymerization system. The poly(2-ethylhexyl acrylate)/clay nanocomposite was characterized by GPC, FT-IR, ^{1}H NMR, TGA, WAXD and TEM analyses. Atom transfer radical copolymerization (ATRcP) of EHA and glycidyl methacrylate (GMA) was also successfully carried out in toluene. The reactivity ratios of the two monomers were calculated using different models. The oxirane ring of GMA was not opened during ATRcP as evidenced by ^{1}H NMR analysis. Surface initiated ATRP (SI-ATRP) of EHA was carried out from modified nanoclay surface. The SI-ATRP of EHA led to PEHA/clay nanocomposite and on block copolymerization with MMA led to block copolymer/clay nanocomposites. These nanocomposites were characterized by GPC, ^{1}H NMR, DSC, TGA and TEM analyses. A series of AB and ABA type di- and tri- block copolymers of EHA with MMA were prepared via ATRP based on macroinitiator approach. Structural characterization of these block copolymers was carried out by ^{1}H NMR analysis. Tensile properties of these block copolymers were evaluated by using UTM. It was observed that tensile properties of these block copolymers were reinforced with PMMA contents. DSC thermograms of the block copolymers showed two distinct T_gs which correspond to a soft PEHA phase and a hard PMMA phase. ^{1}H NMR and DSC analyses confirmed the successful block copolymerization. Morphological study of the block copolymers using SAXS and AFM analyses supported nano-phase separated morphology for both block copolymers but a more ordered morphology and a smaller domain size for the tri-block copolymers. Atom transfer radical graft copolymerization (ATRgP) of EHA was successfully carried out on chlorinated polypropylene (CPP) to prepare brush like graft copolymer. Mechanical and dynamic mechanical properties were evaluated by using UTM and DMA analyses. The stress-strain plot of grafted CPP as well as its tension set data indicates the characteristics of a typical thermoplastic elastomer (TPE). The grafted copolymers had brush like structure where brush length can be tuned by using different reaction parameters. A single pot synthetic route was developed to prepare tailor-made PEHA /or PMMA grafted EPDM via reverse ATRP (RATRP). Gelation and formation of homopolymer of grafted monomers were absent during graft copolymerization on EPDM. The grafted EPDMs showed high surface energy and its oil resistance property was also improved. The grafted EPDMs were characterized by FT-IR, ^{1}H NMR, TGA, DMA, SEM, TEM, and AFM analyses.

KEY WORDS: atom transfer radical polymerization (ATRP), reverse ATRP (RATRP), poly(2-ethylhexyl acrylate) (PEHA), graft copolymer, block copolymer, thermoplastic elastomer (TPE), nanocomposite