Abstract

This thesis reports the synthesis and characterizations of tailor made polyacrylates with varying chain lengths (i.e., poly (ethyl acrylate) and poly (hexyl acrylate)) and their nanocomposites via atom transfer radical polymerization (ATRP), a recent development in the field of controlled radical polymerization methodologies. ATRP of acrylates has been performed using different reaction parameters viz., ligand, catalyst, initiator, solvent and temperature. The polymerization proceeds through first order kinetics and molecular weights increase linearly with conversion, close to the targeted molecular weights. The living nature of the end group has been confirmed by MALDI-TOF mass spectrometry as well as by chain extension experiment. Use of nanoclay as additive in the ATRP of acrylates has been found to have a beneficial effect in enhancing the polymerization rate without losing control. Fourier Transform Infrared Spectroscopy (FTIR) and Dynamic Mechanical Thermal Analysis (DMTA) reveal that there is an interaction between the hydroxyl groups of clay and carbonyl moiety of the dormant species, thereby activating the C-Br bond next to the ester carbonyl bond, hence generating higher concentration of active radicals. Interestingly, the resulting nanocomposite has exfoliated clay particles, as evident from Wide Angle X-ray diffraction (WAXD) and Transmission Electron Microscopy (TEM) studies. A comprehensive structure-property analysis has been carried out by means of dynamic mechanical, rheological and thermal properties of the as-prepared *in situ* polymer–clay nanocomposites. Hybrid nanoarchitecture of tailor-made poly (ethyl acrylate) (PEA)/clay has also been prepared by surface initiated atom transfer radical polymerization (SI-ATRP), by tethering ATRP initiator on to clay via transesterification reaction, followed by polymerization from it. PEA chains with controlled polymerization and narrow polydispersities have been forced to be grown from within the clay gallery (intergallery) as well as from the outer surface (extragallery) of the clay platelets, thereby promoting extensive exfoliation of clay tactoids. Finally, a series of well-defined triblock copolymers, i.e., poly (methyl methacrylate)-*b*-poly (hexyl acrylate)-*b*-poly (methyl methacrylate) (PMMA-*b*-PHA-*b*-PMMA) has been synthesized by ATRP and their morphology, dynamic mechanical and tensile properties are thoroughly investigated. Eventually, the as-prepared block copolymers offer to be an effective stabilizer for preparing gold nanoparticle aggregates (with core diameter of 10-15 nm), the shape and size of which can be modulated by tuning the block copolymer compositions.

Keywords: Controlled radical polymerization, Atom transfer radical polymerization, Poly (ethyl acrylate), Poly (hexyl acrylate), Nanoclay, In-situ nanocomposite, Physico-mechanical properties, Block copolymer, Thermoplastic elastomer, Gold nanoparticle