

ABSTRACT

Fluoropolymers have interesting properties like excellent resistance to chemicals, oils and fuels, high thermal stability and high hydrophobicity. Poly(2,2,3,3,4,4,4-heptafluorobutyl acrylate) (PHFBA) is an interesting polymer with long fluoroalkyl side chain, low T_g and good film formation property. This thesis reports the preparation of tailor-made PHFBA, its random and block copolymers via reversible addition-fragmentation chain transfer (RAFT) polymerization in solution. The rate of polymerization decreased with increase in chain transfer agent (CTA) to thermal initiator ratio. ^1H NMR and MALDI-TOF-MS analyses showed the presence of RAFT end group in the tailor-made PHFBA. It was successfully used as the macro-RAFT agent for the synthesis of block copolymer. TGA analysis showed higher thermal stability of PHFBA prepared by RAFT polymerization than the same prepared by conventional free radical polymerization (FRP). Reactivity ratios for the copolymerization of HFBA and butyl acrylate (BA) were determined by different models. The study showed that the reactivity ratio of HFBA was lower than BA. The mean sequence length calculation showed lower incorporation of HFBA than BA in the copolymer. TGA analysis showed the increase in thermal stability with increasing HFBA content in the copolymer. Poly[poly(ethylene glycol) methyl ether methacrylate] (PPEGMA) was prepared via RAFT polymerization and this was used as macro-RAFT agent for polymerization of HFBA. The resultant block copolymer (BCP), PPEGMA-*b*-PHFBA showed amphiphilic characteristic and formed spherical micelles, as evidenced by TEM analysis. This amphiphilic BCP (Am-BCP) was used in the surfactant free miniemulsion polymerization of styrene, in which Am-BCP acted as surfactant as well as RAFT agent i.e. as surf-RAFT agent. The TEM analysis of the polystyrene latex showed core-shell morphology of which the core was made of polystyrene and shell was of Am-BCP. A series of AB type diblock copolymers of PMMA with HFBA were prepared via RAFT polymerization based on macro-RAFT approach. DSC thermogram of the block copolymer (BCP) showed two distinct T_g s corresponding to soft PHFBA phase and hard PMMA phase. TEM and AFM analyses showed the nano-phase separated morphology in BCP. The lamellar stacking of the BCP was confirmed by SEM, TEM and XRD analyses. The aggregation behavior of the BCP was investigated by TEM analysis in the mixed solvent of THF/methyl ethyl ketone (MEK). The change in solution morphology of the BCP was observed with increasing ratio of MEK in the solution. Importantly, a new dithiocarbamate based RAFT agent was synthesized and was successfully used for the controlled radical polymerization of HFBA. The linear kinetic plot and narrow dispersity (\mathcal{D}) of the synthesized polymers indicated the controlled nature of the polymerization reaction. The presence of RAFT end group in PHFBA was analyzed by UV-Vis spectroscopy and was confirmed by chain extension reaction using the polymer as macro-RAFT agent. Thus this new RAFT agent was found to be very effective for low activated monomer, like HFBA.

KEYWORDS: Reversible addition-fragmentation chain transfer (RAFT), fluoroacrylate, poly(2,2,3,3,4,4,4-heptafluorobutyl acrylate) (PHFBA), macro-RAFT, amphiphilic block copolymer, random copolymer, block copolymer, surf-RAFT.