Abstract

This thesis reports the preparation of tailor-made poly (meth)acrylates bearing reactive functional groups (like, furfuryl, adamantyl, and amino-adamantyl) via atom transfer radical polymerization (ATRP), the post-polymerization reaction of these specialty functional groups in the tailor-made polymers and the characterization of these specialty polymers as well as of the modified polymers. Tailor-made homo-, coand block copolymers bearing furfuryl functionality were successfully prepared by ATRP. In all cases the polymerization of furfuryl methacrylate (FMA) proceeds through first order kinetics and the resultant polymers had controlled molecular weights and narrow polydispersity index. When the polymers were prepared via conventional radical polymerization, they were severely gelled and were insoluble in any solvent. However, during ATRP the reactive furfuryl group was not affected which was confirmed by the FT-IR and NMR studies. The composition of the random and the ABA triblock copolymers of FMA were determined by ¹HNMR. Interestingly, the 'Click Chemistry' of Diels Alder (DA) reaction and retro-DA reaction was used to carry out the post-polymerization reaction in the tailor-made homo-, co- and block copolymers of FMA. In this case the reactive furfuryl functional group of PFMA acted as a diene and a bismaleimide (BM) was used as dienophile. The self-healing properties of these smart PFMA-BM adducts were characterized by DSC, DMA, FT-IR and SEM analysis. The tailor-made polyacrylates bearing adamantyl and amino-adamantyl functional group were prepared via ATRP using different catalyst systems. ATRP of monomers and initiators bearing adamantyl group enhanced the rate of polymerization in toluene. But the use of amino-adamantyl group in the initiator or in the monomer decreases the rate of ATRP. This is due to the coordination between the $-NH_2$ group in the amino-adamantyl group and the copper catalyst as evidenced by kinetic study, UV and FT-IR analysis. Incorporation of adamantyl or amino-adamantyl functional group tremendously increased the thermal stability and raised the glass transition temperature of the polymer. Interestingly, the post-polymerization reaction between the -NH₂ group of amino-adamantyl functional group and epoxy group in the tailor-made polyglycidyl methacrylate led to a new porous hydrogen bonded crosslinked polymeric material as evidenced by FT-IR and FE-SEM analysis. The functional monomers, initiators and tailor-made polymers prepared in this investigation were characterized by NMR, FT-IR, GPC, MALDI-TOF-MS, DSC, DMA, TGA and SEM analysis.

Keywords: Atom Transfer Radical Polymerization (ATRP), Thermoreversible polymer, Click Chemistry, Self-healing polymer, Diels Alder reaction, PFMA, Adamantane, Amantadine, Thermoplastic elastomer, Smart Polymers.