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OP-2. Mechanistic aspect of Fe(III)/2,2'-bipyridine catalyzed ATRP and reverse ATRP of n-alkyl (meth)acrylates

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ABSTRACT: Well-defined polymers of n-alkyl (meth)acrylates with narrow molecular weight distribution have been synthesized by atom transfer radical polymerization (ATRP) and reverse ATRP in N, N-dimethylformamide (DMF) using the (CBr₄)/Fe(III)/2,2'-bipyridine (bpy) initiation system in the presence of 2,2'-azobisisobutyronitrile (AIBN) as the source of reducing agent. Effects of various Fe(III) species on both normal and reverse ATRP systems have been reviewed and probable reaction mechanisms are proposed to explain the observed results. The rates of polymerization for both the systems exhibit first-order kinetics with respect to the monomer. From the kinetic studies and molecular weight data, it reveals the controlled nature of polymerization for n-alkyl (meth)acrylates. The effect of various reaction parameters on number average molecular weight (Mₙ) and molecular weight distribution (Mₘ/Mₙ) have been investigated for both normal and reverse ATRP systems. The resulting poly(n-alkyl (meth)acrylate) obtained by reverse ATRP shows the best control of molecular weights and its distribution as compared to normal ATRP system. The cocrystallization behavior of comb-like poly(n-alkyl (meth)acrylate) and its blends with corresponding fatty acids were explored by differential scanning calorimetry (DSC) and X-ray diffraction (XRD) studies. The DSC curves for blended samples show the characteristic melting endotherms of corresponding crystallites and the existence of hexagonally packed crystalline lattice is confirmed by XRD studies. Thermal degradation of the polymers and its blends proceeds in a one-step reaction.

Key words: atom transfer radical polymerization; n-alkyl(meth)acrylates; kinetics; polydispersity; comb-like polymers; cocrystallization