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A novel initiating system for controlled radical polymerization of methyl methacrylate

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Abstract—The polymerization of methyl methacrylate (MMA) in bulk is initiated with $FeCl_3 \cdot 6H_2O$ or $FeCl_3/PPh_3$ at 90 °C without the addition any conventional radical initiator to the polymerization system. Although the elucidation of the detailed mechanism of the initiation needs further investigation, it is likely that redox-type reactions are involved in the generation of initiating species. Once the initiating radicals are produced, the polymerization proceeds *via* reverse atom-transfer radical polymerization (RATRP). It was found that the polymerization is controlled up to a molecular weight of 12 900 at 92% conversion for the system using $FeCl_3 \cdot 6H_2O$ / PPh_3. The chain extension experiment was carried out to confirm the controlled manner of the polymerization system. In both polymerization systems, polydispersity index and the initiator efficiency were found to be <1.4 and 0.6–0.9, respectively.

Keywords: Reverse atom transfer radical polymerization; methyl methacrylate; Fe(III) salts.

1. INTRODUCTION

Recently, controlled/'living' radical polymerizations have been utilized for the synthesis of well-defined, narrow polydispersity polymers [1–5]. Among them atom-transfer radical polymerization (ATRP), as a multicomponent process, consists of the monomer, an initiator, generally alkyl halides, a transition metal species complexed with suitable ligands (M_t^n/L_x) as a catalyst [6]. The radicals are produced from an alkyl halide via a reversible redox reaction catalyzed by a transition metal complex. This process includes the reversible activation and deactivation of growing radicals. Thus, a very low instantaneous concentration of propagating radicals produced suppresses the termination reactions, enabling the formation of polymer with narrow polydispersity and the molecular weight of the control.

A variety of transition metals (Cu(I), Ru(II), Ni(II), Rh(I) and Fe(II) in lower oxidation state) complexes have been used as ATRP catalysts [6]. Fe(II)-based ATRP

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