

Photo-induced single-electron transfer living radical polymerization (SET-LRP) of MMA in the presence of ZnO

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Abstract In this study, the photo-induced single-electron transfer living radical polymerization (SET-LRP) of methyl methacrylate (MMA) was successfully performed in *N,N*-dimethylformamide (DMF) with ethyl α -bromoisobutyrate (EBiB)/Fe(0)/tetramethylethylenediamine (TMEDA)/[ZnO] as the initiating system. ZnO was used as the inorganic photoinitiator. The living nature of the photo-induced SET-LRP of MMA was confirmed by kinetic studies in the presence or absence of air. The plot of $\ln([M]_0/[M])$ versus polymerization reaction time was linear, and the molecular weight distribution (MWD) of the resulting PMMA was narrow. The effects of the amounts of Fe(0)/TMEDA, EBiB, ZnO, and light intensity on the photo-induced SET-LRP of MMA were investigated. The conversion increased with increasing the amounts of Fe(0)/TMEDA, EBiB, and ZnO. Increasing the light intensity resulted in a higher polymerization reaction rate. The catalyst and ZnO played important roles in the photo-induced SET-LRP of MMA. The polymerization proceeded in

an uncontrollable fashion when the molar ratio of Fe(0)/TMEDA was 0:0.1, and no reaction took place in the absence of ZnO. In comparison with other SET-LRP of MMA in bulk or conventional solvents, the photo-induced SET-LRP of MMA proceeded periodically when the light was turned on or off under the mild experimental conditions. The polymerization did not take place when the light was turned off. However, the polymerization was very fast when the light was turned on. The chemical structure of resulting PMMA was characterized by ¹H NMR. The living characteristics were demonstrated by chain extension experiment.

Keywords Irradiation · Photo-induced SET-LRP · Methyl methacrylate · Living polymerization · Kinetics

Introduction

As a promising method, single-electron transfer living radical polymerization (SET-LRP) has received much scientific attention in recent years since its emergence in 2006 [1]. Compared with other living radical polymerization methods, SET-LRP has many advantages, for example, lower concentration of catalyst and ease of its removal, mild reaction temperature even in the presence of air, and ultra-fast polymerization rate. In a typical SET-LRP system, Cu(0) was employed as catalyst. Cu(0) was disproportionated to generate Cu(I)X and Cu(II)X₂ in aprotic and protic solvents in the presence of an N-containing ligand. By using an activated alkyl halide or dormant polymer chain ends as an initiator, all of the chains can start growing at the same time [1]. A dynamic equilibrium between active propagating radicals and dormant chains is established. Thus, a low concentration of propagating radicals is ensured and the probability of termination is reduced.

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