

# Photo-induced ATRP of MMA without ligands in ionic liquid

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**Abstract** Fe-mediated photo-induced atom transfer radical polymerization (ATRP) of methyl methacrylate was studied with chlorophyll A as photoredox catalyst in the absence of ligands. This is the first report on photo-induced and FeBr<sub>3</sub>-mediated ATRP. A low-cost and environmentally friendly ATRP is provided in this system. A good linear semi-logarithmic plot of polymerization kinetics is the first-order time conversion, and narrow molecular weight distributions explain the well-controlled behavior. The measured number average molecular weight,  $M_{n, GPC}$  (determined by gel permeation chromatography), is increased with monomer conversion, and it is in good agreement with the theoretical values ( $M_{n, th}$ ). The effect of FeBr<sub>3</sub> is studied with respect to the polymerization. The values of the resultant PMMA increased with reduced FeBr<sub>3</sub> concentration. In this system, the effect of periodic light/off process has been investigated through chain growth instantly turned on and off in response to the visible light. The polymerization was controllable even though the concentration of Fe-based catalyst was dropped to 4 ppm. The chain-end group having a functionality in the synthesized poly(methyl methacrylate) was characterized by nuclear magnetic resonance spectrometry (<sup>1</sup>H NMR). However, chain extension experiments show reserved chain-end functionality in the

synthesized polymers and further confirm the “living” feature of the Fe-mediated photo-induced atom transfer radical polymerization.

**Keywords** Photo-induced · MMA · Living radical polymerization · Ionic liquid · Chlorophyll A

## Introduction

Polymers with well-defined architectures are increasingly desired in wide range of applications. The adventure of living radical polymerization (LRP) technique provides a facile route to the synthesis of polymers with predetermined molecular weight, a narrow polydispersity, and high-end group purity [1]. Out of three most common LRP methods namely nitroxide-mediated polymerization (NMP) [2], atom transfer radical polymerization (ATRP) [3], and reversible addition–fragmentation polymerization (RAFT) [4], ATRP is the most applicable technique because of its wide variety of monomers polymerized through ATRP. ATRP, also known as metal-mediated radical polymerization, controls the polymerization through a reversible termination mechanism of the growing polymer radicals. The fast and dynamic equilibrium is established between the dormant species and active species. The pioneering work has been conducted by Sawamoto’s group [5] and Matyjaszewski’s group [6].

Significant efforts have been dedicated to the development of the so-called “green chemistry” techniques in the field of polymer synthesis. The catalyst concentration has been reduced to ppm level in the polymerization systems, such as activator regenerated by electron transfer ATRP (ARGET-ATRP) [7], initiators for continuous activator regeneration ATRP (ICAR-ATRP) [8], single-electron

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