



Photoinduced atom transfer radical polymerization of methyl methacrylate with conducting polymer nanostructures as photocatalyst

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Received: 30 October 2018 / Accepted: 5 January 2019 / Published online: 10 January 2019
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Abstract

Light-mediated control/living radical polymerization (CLRP) provides a convenient method to synthesize polymers with controlled molecular weight and narrow molecular weight distribution. However, high-energy wavelengths (such as UV light) and blue light are needed to initiate the polymerization, leading to unwanted side reactions. To overcome these defects, the use of long-wavelength light for light-mediated CLRP is highly desirable. In this work, photoinduced atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) was successfully carried out for the synthesis of polyMMA (PMMA) with predictable molecular weights ($M_{n,GPC}$) and narrow molecular weight distribution (M_w/M_n). This was achieved using one-dimensional nanopoly(diphenyl butadiyne) (nanoPDPB) as photocatalyst, which activated the dormant alkyl bromides initiator to reversibly produce propagating radicals at ambient temperature. Initiation and termination of polymerization were regulated by periods of light. The polymerization of MMA was accomplished by the radicals generated in the redox reaction of nanoPDPB with EBP. Both ¹H nuclear magnetic resonance (¹H NMR) spectroscopy and chain-end extension polymerization show highly preserved bromine chain-end functionality in the synthesized PMMA. nanoPDPB displays remarkable photophysical properties in the visible light region. The polymerization of MMA followed the first-order kinetics and the evolution of the $M_{n,GPC}$ versus monomer conversion and M_w/M_n demonstrated the well-controlled polymerization process. The living character of heterogeneous photomediated ATRP with nanoPDPB as photocatalyst was successfully confirmed.

Keywords Poly(diphenyl butadiyne) · Atom transfer radical polymerization · Living radical polymerization · Photocatalyst · Control/living radical polymerization

Introduction

The advent of living free-radical polymerizations has provided the unprecedented ability to prepare the polymers with complex molecular compositions and three-dimensional architectures, such as polymer brushes of poly(acrylonitrile-*g*-*N,N'*-dimethylaminoethyl methacrylate) [1], methyl methacrylate [2], and cellulose nanocrystals [3]. Living free-radical polymerizations, such as atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP), and reversible addition-fragmentation chain transfer (RAFT) polymerizations, have been utilized in a variety of

controlled polymers with predictable molar mass ($M_{n,GPC}$), narrow molecular weight distribution (M_w/M_n), and functional chain ends [4]. Among them, ATRP is the most rapidly developing area of living free-radical polymerization, which was reported by two independent research groups in 1995 [5, 6]. ATRP has a wide range of applications including the synthesis of nanocomposite hydrogels [7], self-healing hydrogels [8], ethyl acrylate [9], and *N*-chlorosulfonamide polystyrene [10].

The general mechanism of ATRP process is to establish reversible redox equilibrium between growing and dormant polymer chains, holding on a low-level concentration of radicals to suppress side reactions. Microwave- [11], ultrasound- [12], light- [13], and electrochemically-mediated ATRP [14] are new research areas with strong interest for ATRP. Among external stimuli, light offers multiple advantages such as low cost, environmentally friendly, tunability, and both spatial and temporal control [15].

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