



Photomediated atom transfer radical polymerization of MMA under long-wavelength light irradiation

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Abstract

In this study, a novel photocatalyst, pentarylenebis(dicarboximide) dye: (1,6,13,18-tetra(4-(2,3,3-trimethylbut-2-yl)phenoxy)-*N,N'*-(2,6-diisopropylphenyl)-pentarylene-3,4,15,16-tetracarboxidiimide) (TTPDPT), was first used in metal-free photoinduced atom transfer radical polymerization (ATRP) of methyl methacrylates (MMA). The initiator was methyl α -bromoisobutyrate (MBI) and the light source was mild near-infrared (NIR) light irradiation ($\lambda_{\max} \approx 870$ nm). The TTPDPT-mediated ATRP relies on in situ photoreduction of a MBI through an electron transfer process to generate the desired alkyl radical, which could induce polymerization of the monomer. The photoinduced metal-free ATRP of MMA shows typical characteristics of controlled free radical polymerization, showing the linear evolution of number-average molecular weight ($M_{n,GPC}$) with monomer conversion, where polymers with predetermined degree of polymerization have well-controlled molecular weights and narrow molecular weight distribution (M_w/M_n). The photoinduced metal-free ATRP of MMA can be carried out with just ppm level of TTPDPT. The polymerization initiation and propagation can be operated by the aid of pulsed light sequences while NIR light source was used to promote carbon–carbon bond formation and to produce poly(methyl methacrylate) (PMMA) with M_w/M_n as low as 1.5. The synthesized PMMA was characterized by ¹H nuclear magnetic resonance (¹H NMR). The resultant PMMA contained a bromide end group that can be employed to reinitiate styrene polymerization to produce block copolymers through chain extension experiments.

Keywords Perylene derivatives · Living radical polymerization · Photomediated · Atom transfer radical polymerization · Long-wavelength light

Introduction

Atom transfer radical polymerization (ATRP), discovered in 1995, is an efficient way for living radical polymerization [1–3]. In ATRP, transition metal salts or complexes [4, 5] have been employed to maintain a dynamic equilibrium

between active species and dormant species. One major shortcoming of classical ATRP was due to the use of relatively high catalyst concentration relative to monomer in contaminating the final polymer. Some efficient technologies have been developed to reduce the catalyst concentration [6–8], even ATRPs were performed without catalyst [9–11].

Recently, light-induced polymerization techniques have been a dramatic resurgence of interest in the field of photomediated ATRP due to its easy operation at ambient temperature and atmospheric pressure, and they offered spatial and temporal control over the polymerization [12–14]. In this system, photoinitiator played a key role in the photopolymerization. Many low-molecular weight photoinitiators and their derivatives, for example, benzophenone [15], phenothiazine [16], and phenoxazine [17], have been reported in photomediated ATRP. In addition, some semiconductor nanoparticles and transition metal-based photoredox catalysts, such as ZnO [18], Fe/ZnO [18], TiO₂ [19], and Fe₂O₃ [20], have also been used in photomediated ATRP systems.

Le-Lin Zeng and Wan-Yun Xie are the first authors.

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