

Photo-induced atom transfer radical polymerization with nanosized α -Fe₂O₃ as photoinitiator

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ABSTRACT: Photo-induced atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) was achieved in poly(ethylene glycol)-400 with nanosized α -Fe₂O₃ as photoinitiator. Well-defined poly(methyl methacrylate) (PMMA) was synthesized in conjunction with ethyl 2-bromoisobutyrate (EBiB) as ATRP initiator and FeCl₃·6H₂O/Triphenylphosphine (PPh₃) as complex catalyst. The photo-induced polymerization of MMA proceeded in a controlled/living fashion. The polymerization followed first-order kinetics. The obtained PMMA had moderately controlled number-average molecular weights in accordance with the theoretical number-average molecular weights, as well as narrow molecular weight distributions (M_w/M_n). In addition, the polymerization could be well controlled by periodic light-on-off processes. The resulting PMMA was characterized by ¹H nuclear magnetic resonance and gel permeation chromatography. The brominated PMMA was used further as macroinitiator in the chain-extension with MMA to verify the living nature of photo-induced ATRP of MMA. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42389.

KEYWORDS: kinetics; photopolymerization; radical polymerization

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INTRODUCTION

Atom transfer radical polymerization (ATRP) is one of the most effective and most widely studied techniques of controlled radical polymerization (CRP) because ATRP can be performed under mild reaction conditions. ATRP is compatible with a great variety of monomers, and it gives polymeric materials with excellent control.^{1–4}

However, conventional ATRP have some disadvantages: toxic catalyst and difficult to remove it from polymer product. To overcome these drawbacks, some new techniques were developed: initiators for continuous activator regeneration atom transfer radical polymerization (ICAR ATRP),^{5–8} activators regenerated by electron transfer in atom transfer radical polymerization (ARGET ATRP)^{9–12} and single-electron transfer living radical polymerization (SET LRP).^{13–16} Recently, photo-induced ATRP have been attractive since the polymerizations were controlled through turning on/off light.^{17–22} In addition, the amount of catalysts is reduced to ppm levels.

Iron-mediated ATRP may be an alternative to the most extensively studied Cu catalyst in ATRP due to the broad avail-

ability and low potential toxicity, low cost, and environmental friendliness.

A number of ligands were used in the iron based ATRP, for example, phosphines,^{23,24} N-heterocyclic carbenes,²⁵ nitrogen-based ligands,^{26–29} carboxylic acids⁸ etc.

Poly (ethylene glycol) (PEG) is easily available, inexpensive, biodegradable and nontoxic, which is particularly attractive in terms of industrial applications as well as the recent demand for environmentally benign processes. There have been some reports about PEG as solvent for living radical polymerization.^{8,30,31} In addition, photopolymerization was carried out to enhance the polymerization rate with PEG as solvent.³²

Some semiconductors have been used as photoinitiator for living radical polymerization of vinyl monomers.³³ Iron oxides are abundantly available, environment-friendly and have been extensively used in many fields. Recently, Fe₂O₃ has been studied as photocatalyst.^{34,35}

In this article, we reported the first example of CRP of methyl methacrylate (MMA) with Fe₂O₃ as photoinitiator. The photo-

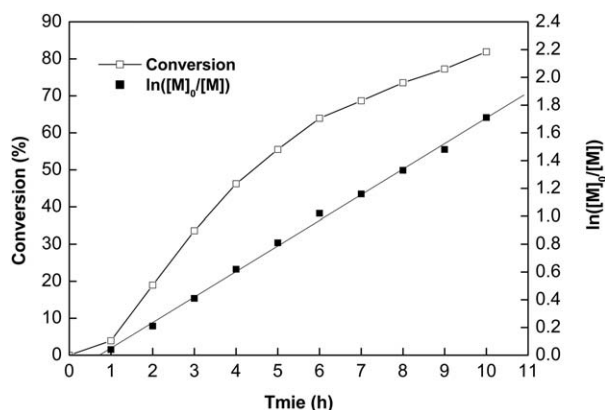


Figure 1. Plots of monomer conversion and $\ln([M]_0/[M])$ versus reaction time t of the photo-induced ATRP of MMA in PEG-400 at 25°C. $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[Fe_2O_3]_0 = 200 : 1 : 0.01 : 0.01 : 1$, $V_{PEG-400} = 20\text{ mL}$.

induced controlled/living radical polymerizations were successfully performed in PEG-400 in conjunction with ethyl 2-bromoisobutyrate (EBiB) as initiator.

EXPERIMENTAL

Materials

MMA was obtained from Tianjin Fuchen Chemical Reagent Factory (China) and was distilled under reduced pressure prior to use. Nanoparticles Fe_2O_3 (with a size of about 14 nm) and EBiB (98%) were obtained from Aladdin (China) and used as received. PEG-400 was obtained from Sinopharm Chemical Reagent (Shanghai, China), and was used as received. Ferric chloride hexahydrate was purchased from Shanghai Qingfeng Chemical Factory (China). Triphenylphosphine (PPh_3) was purchased from Chengdu Best-Reagent (Chengdu, China). Other chemicals were commercially available and used as received.

Polymerization Procedure

The photo-induced ATRP of MMA was performed in a 50-mL three-necked flask equipped with a magnetic stirring bar under dry nitrogen with PEG-400 as solvent. An example for a typical polymerization procedure was MMA (2.0 g, 0.02 mol), EBiB (0.0195 g, 0.0001 mol), $FeCl_3 \cdot 6H_2O$ (0.0003 g, 0.000001 mol), PPh_3 (0.0003 g, 0.000001 mol), Fe_2O_3 (0.016 g, 0.0001 mol), and PEG-400 (20 mL) were introduced into the flask. The molar ratio of $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[Fe_2O_3]_0$ was kept at 200 : 1 : 0.01 : 0.01 : 1. Then the flask was placed in a water bath at 25°C. The flask was irradiated with 100 mW/cm² of UV-light (obtained from a 500 W high-pressure Hg lamp for wavelength ranging between 300 and 450 nm). After polymerization, an excess of methanol was added to the reaction mixture to precipitate the polymers. Then the obtained polymers were dried under vacuum. Monomer conversions were determined gravimetrically.

Characterizations

The molecular weight ($M_{n, GPC}$) and molecular weight distribution (M_w/M_n) of the product polymers were characterized at 35°C with tetrahydrofuran (THF) as an eluent on a Waters 1515 gel permeation chromatography (GPC), consisting of a set of

HT1, HT3, and HT4-styragel columns. The flow rate of THF was set to 1.0 mL/min. A series of standard poly(methyl methacrylate) (PMMA) was used to calibrate the curves. ¹H NMR spectrum was recorded at room temperature on a Bruker ARX 400 NMR spectrometer with tetramethylsilane (TMS) as internal standard. $CDCl_3$ was used as solvent.

RESULTS AND DISCUSSION

The Photo-Induced ATRP of MMA in PEG-400 With Fe_2O_3 as Photoinitiator

The photo-induced ATRP of MMA was investigated using Fe_2O_3 combined with EBiB as ATRP initiator at 25°C with PEG-400 as solvent. The $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[Fe_2O_3]_0$ molar ratio was 200 : 1 : 0.01 : 0.01 : 1.

The relationship between $\ln([M]_0/[M])$ and polymerization reaction time is shown in Figure 1. As can be seen from Figure 1, linear first-order kinetic plots were observed, indicating that a constant number of active species was maintained and the radical termination reaction was negligible throughout the polymerization. However, an induction period of about 42 min was observed for the reaction in Figure 1. At the beginning of polymerization, the concentration of $FeCl_2$ generated from $FeCl_3$ was too low to establish the equilibrium between $Fe(III)$ and $Fe(II)$. Thus, it needed some time to establish the equilibrium. The apparent rate constant (i.e., k_{app} -slope of the kinetic plot of $\ln([M]_0/[M])$ versus reaction time t) was $5.15 \times 10^{-5} \text{ s}^{-1}$.

Figure 2 shows the $M_{n, GPC}$ values and M_w/M_n values of the product polymers synthesized in PEG-400 determined by means of GPC. As shown, the $M_{n, GPC}$ increased linearly with respect to monomer consumption, indicating that the polymerizations proceeded in a controlled/living fashion. However, $M_{n, GPC}$ values were higher than the theoretical values ($M_{n, th}$) calculated according to the equation (1)

$$M_{n, th} = (\Delta[M]_0/[I]_0) \times M_W \times \text{Conv} \quad (1)$$

where $\Delta[M]_0$ is the consumed monomer concentration, $[I]_0$ the initial initiator concentration, and M_W and Conv the molecular weights of monomer and reaction conversion, respectively. The

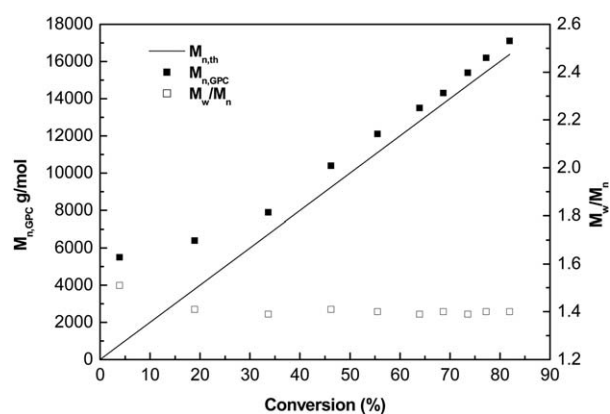


Figure 2. Dependence of $M_{n, GPC}$ and WMDs of the polymers on monomer conversion in the photo-induced ATRP of MMA in PEG-400 at 25°C. $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[Fe_2O_3]_0 = 200 : 1 : 0.01 : 0.01 : 1$, $V_{PEG-400} = 20 \text{ mL}$.

Table I. Effect of Amount of Catalyst on the Photo-Induced ATRP of MMA in PEG-400 with Fe_2O_3 as Photoinitiator^a

Run	$[\text{EBiB}]/[\text{Fe}^{3+}]$	Time (h)	Conv (%)	$M_{n,\text{th}}^c$ (g/mol)	$M_{n,\text{GPC}}^d$ (g/mol)	M_w/M_n^e
1	1 : 0.0001	3	10.5	2100	4100	1.68
2	1 : 0.0005		14.5	2900	4800	1.52
3	1 : 0.001		19.3	3860	5300	1.45
4	1 : 0.005		24.4	4880	6100	1.41
5	1 : 0.01		33.6	6720	7900	1.39
6	1 : 0.05		46.2	9240	11,100	1.39

^aThe experimental conditions: the temperature is 25°C; the volume of PEG-400 is 20 mL.

^b $R = [\text{MMA}]_0/[\text{EBiB}]_0/[\text{PPh}_3]_0/[\text{Fe}_2\text{O}_3]_0 = 200 : 1 : 0.01 : 1$.

^c $M_{n,\text{th}} = ([\text{MMA}]_0/[\text{EBiB}]_0 \times W_{\text{MMA}} \times \text{Conv})$.

^{d,e} $M_{n,\text{GPC}}$: determined by GPC.

difference in $M_{n,\text{GPC}}$ and $M_{n,\text{th}}$ may be due to radical termination at the early stage of photo-induced polymerization, suggesting that relatively slow initiation occurred with respect to propagation. M_w/M_n values of the product polymers was less than 1.5 when the conversion exceeded 20%, which is characteristic of controlled/living polymerizations.

Effect of Amount of Catalyst on the Photo-Induced ATRP of MMA in PEG-400 With Fe_2O_3 As Photoinitiator

One of the advantages of photo-induced ATRP system is that the amount of catalyst is diminished.³⁶ The varied amounts of catalyst were investigated to elucidate the effect of catalyst concentration on the photo-induced ATRP of MMA in PEG-400 with Fe_2O_3 as photoinitiator. The results are presented in Table I.

As can be seen from Table I, when the molar ratio of $[\text{EBiB}]/[\text{Fe}^{3+}]$ was changed from 1 : 0.0001 to 1 : 0.0005, the conversion increased from 10.52% to 16.18%. However, when the molar ratio of $[\text{EBiB}]/[\text{Fe}^{3+}]$ was 1 : 0.0001 and 1 : 0.0005, the M_w/M_n values were 1.68 and 1.52, respectively. It indicated that the polymerization was uncontrollable. The polymerization was controllable when the molar ratio of $[\text{EBiB}]/[\text{Fe}^{3+}]$ was 1 :

0.001. A detailed study was carried out on the molar ratio of $[\text{EBiB}]/[\text{Fe}^{3+}] = 1 : 0.0005$ and 1 : 0.001, and the results are shown in Figures 3 and 4.

As seen in Figure 3, the linear first-order kinetic plots with respect to monomer were displayed, indicating that the amount of the active propagating radicals remained constant throughout the polymerization process in the two cases and that termination reactions were limited. The plots of $M_{n,\text{GPC}}$ values and M_w/M_n values vs monomer conversion are illustrated in Figure 4. The $M_{n,\text{GPC}}$ value increased rapidly at the early stage of the polymerization when the conversion was less than 20%. Then the $M_{n,\text{GPC}}$ value increased linearly with monomer conversion and matched well with the theoretical value in the two cases. The M_w/M_n values decreased with monomer conversion. Unfortunately, the M_w/M_n value was found to be a little higher at the beginning of the polymerization. In the case of $[\text{EBiB}]/[\text{Fe}^{3+}] = 1 : 0.0005$, the M_w/M_n value was below 1.5 when the conversion exceeded 30%. It indicated that the polymerization proceeded in a controlled manner.

Effect of Amount of Fe_2O_3 on the Photo-Induced ATRP of MMA in PEG-400 With Fe_2O_3 as Photoinitiator

Different amounts of Fe_2O_3 were used in the photo-induced ATRP of MMA in order to investigate the effect of amount of

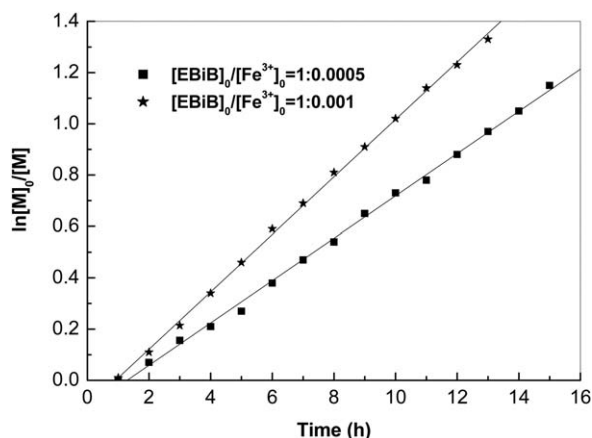


Figure 3. Plots of monomer conversion and $\ln([M]_0/[M])$ versus reaction time t of the photo-induced ATRP of MMA in PEG-400 at 25°C with varied amount of catalyst. $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{PPh}_3]_0/[\text{Fe}_2\text{O}_3]_0 = 200 : 1 : 0.01 : 1$, $V_{\text{PEG-400}} = 20$ mL.

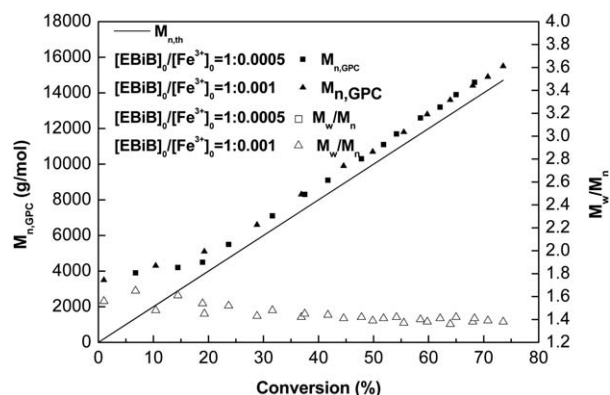


Figure 4. Dependence of $M_{n,\text{GPC}}$ and WMDs of the polymers on monomer conversion in the photo-induced ATRP of MMA in PEG-400 at 25°C with varied amount of catalyst. $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{PPh}_3]_0/[\text{Fe}_2\text{O}_3]_0 = 200 : 1 : 0.01 : 1$, $V_{\text{PEG-400}} = 20$ mL.

Table II. Effect of Amount of Fe_2O_3 on the Photo-induced ATRP of MMA in PEG-400 with Fe_2O_3 as Photoinitiator^a

Run	$[\text{EBiB}]_0/[\text{Fe}_2\text{O}_3]_0$	Time (h)	Conv (%)	$M_{n,\text{th}}^b$ (g/mol)	$M_{n,\text{GPC}}^d$ (g/mol)	M_w/M_n^e
1	1 : 0		0	0	0	0
2	1 : 0.1		9.3	1860	4700	1.53
3	1 : 0.5	4	27.6	5520	6800	1.46
4	1 : 1		46.2	9240	10,400	1.41
5	1 : 2		61.8	12,360	13,600	1.42

^a The experimental conditions: the temperature is 25°C; the volume of PEG-400 is 20 mL.

$R = [\text{MMA}]_0/[\text{EBiB}]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[\text{PPh}_3]_0 = 200 : 1 : 0.01 : 0.01$.

^b $M_{n,\text{th}} = ([\text{MMA}]_0/[\text{EBiB}]_0 \times W_{\text{MMA}} \times \text{Conv})$.

^{d,e} $M_{n,\text{GPC}}$: determined by GPC.

Fe_2O_3 on the photo-induced ATRP of MMA in PEG-400 with Fe_2O_3 as photoinitiator. The initial conditions and results of the polymerizations are listed in Table II.

It can be seen from Table II, no monomer conversion was detected in the absence of Fe_2O_3 . When the molar ratio of $[\text{EBiB}]_0/[\text{Fe}_2\text{O}_3]_0$ was changed from 1 : 0.1 to 1 : 2, the conversion increased from 9.3% to 61.8%. Moreover, the polymer with the $M_{n,\text{GPC}}$ value was a little broader M_w/M_n in the case of $[\text{EBiB}]_0/[\text{Fe}_2\text{O}_3]_0 = 1 : 0.1$. It was found that the polymers with the $M_{n,\text{GPC}}$ close to the theoretical values were obtained under these conditions with increasing the molar ratio of $[\text{EBiB}]_0/[\text{Fe}_2\text{O}_3]_0$ from 1 : 0.5 to 1 : 2. These results indicated that Fe_2O_3 functioned in the photo-induced ATRP process.

Effect of Periodic Light-on-off on the Photo-Induced ATRP of MMA in PEG-400 With Fe_2O_3 as Photoinitiator

To investigate the effect of periodic light-on-off on the photo-induced ATRP of MMA in PEG-400 with Fe_2O_3 as photoinitiator, photo-induced ATRP of MMA was further studied under the same conditions. First, the conversion 18.94% was reached in 2 h under irradiation in order to obtain sufficient primary

radicals. Thereafter, this light was periodically turned off over the duration of 2–3, 4–5, 6–7, and 8–9 h.

As shown in Figure 5, the polymerization stopped when the light was turned off. It indicated that the concentration of the free radicals generated without light was so small that the propagation reaction did not occur. The polymerization was fast when the light was turned on. These results demonstrated that the light preserved good control over the polymerization not only through photoinitiation but also by significantly activating the intermediate radicals.

Analysis of Chain End of PMMA and Chain Extension

The PMMA macroinitiator was prepared at 25°C in PEG-400 with Fe_2O_3 as photoinitiator according to the molar ratio of $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[\text{PPh}_3]_0/[\text{Fe}_2\text{O}_3]_0 = 200 : 1 : 0.01 : 0.01 : 1$. The reaction was terminated after 3 h at 33.63% conversion, yielding PMMA-Br with $M_{n,\text{GPC}} = 7900$ g/mol and $M_w/M_n = 1.39$. The resulting PMMA-Br was analyzed by ^1H NMR spectroscopy (Figure 6).

The peaks at 0.81–1.27 ppm corresponded to the protons of the methyl groups [Figure 6(a)]. The signals at 1.36–2.04 ppm were observed, which were correlated with protons of methylene

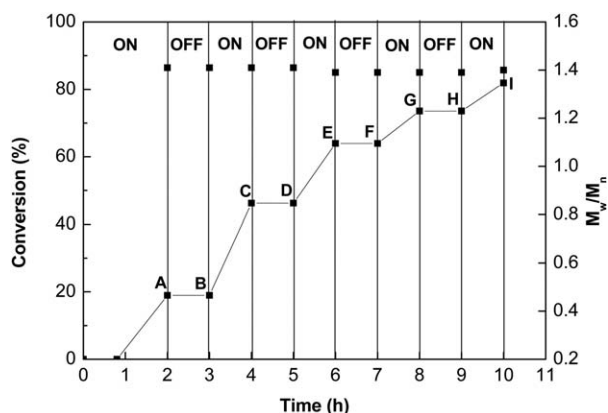


Figure 5. Photo-induced ATRP performed by periodic light-on-off. The stop-and-go characteristics and M_w/M_n of the Photo-induced ATRP are shown by development of the monomer conversion as a function of the irradiation time at room temperature. Reactions were conducted with $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[\text{PPh}_3]_0/[\text{Fe}_2\text{O}_3]_0 = 200 : 1 : 0.01 : 0.01 : 1$, $V_{\text{PEG-400}} = 20$ mL.

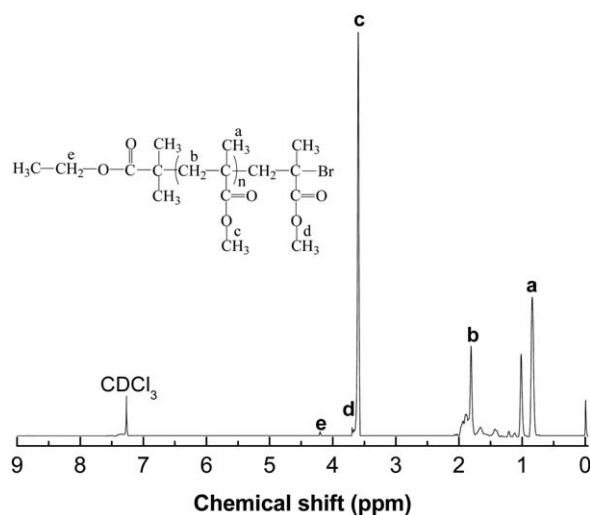


Figure 6. ^1H NMR spectrum of PMMA-Br synthesized by using Fe_2O_3 as photoinitiator in photo-induced ATRP of MMA.

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