Photoinduced controlled/"living" polymerization of methyl methacrylate with flavone as photoinitiator

Bin-Hong He,[1] Jieyu He,[2] Guo-Xiang Wang,[1] Li-Chao Liu,[1] Hu Wu,[1] Ming Zhong[1]

[1]College of Chemistry and Chemical Engineering, Hunan Institute of Science and Technology, Yueyang, Hunan Province 414006, China
[2]Experimental Center of Science and Technology, Hainan Tropical Ocean University, Sanya, Hainan Province 572022, China
Correspondence to: J. He (E-mail: hejieyu555@163.com) and G.-X. Wang (E-mail: wanggxwzl@163.com)

ABSTRACT: Photochemically mediated controlled/"living" polymerization of methyl methacrylate (MMA) triggered by flavone was studied. The polymerization was performed in ethanol at ambient temperature with $CuBr_2$/Tris(2-dimethylaminoethyl)amine (Me_6T-REN) as complex catalyst and ethyl 2-bromoisobutyrate (EBiB) as initiator. The molar mass of poly(methyl methacrylate) (PMMA) was obtained and exhibited relatively narrow molecular weight distribution (M_w/M_n) which was characterized by gel permeation chromatography (GPC). Chain extension further indicated that the living nature was maintained in the photopolymerization system. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43845.

INTRODUCTION

The design and control of precision synthesis of polymers with well-defined compositions, and regular structure remains a challenge. Living polymerization has provided synthetic methods and strategies for the preparation of well-defined macromolecules since first reported by Szwarc et al. in 1956.[1] After sixty years of development, living polymerization has been divided into three classes of powerful techniques: nitroxide mediated radical polymerization (NMP),[2] reversible addition-fragmentation transfer polymerization (RAFT),[3] and atom transfer radical polymerization (ATRP).[4–6] Among them, ATRP is one of the most rapidly developing areas in living polymerization. ATRP is suitable for a number of monomers under a variety of reaction conditions. ATRP is based on the metal complex-mediated fast equilibrium between dormant and active species through a reversible redox reaction. One of the disadvantages of ATRP is consumption of higher amount of catalyst. Thus, the principal problem is decreasing loading. Promising techniques were reported recently, for example, use of initiators for continuous activator regeneration ATRP (ICAR ATRP),[7–9] activator generation by electron transfer ATRP (AGET ATRP),[10–12] activator regeneration by electron transfer ATRP (ARGET ATRP),[13–16] single-electron-transfer living radical polymerization (SET-LRP),[17–19] e-ATRP,[20–22] and photo-induced ATRP.[23–26]

Photopolymerization is environmentally friendly, facile, rapid, and well-controlled, and suitable for a variety of monomers.[27]

More importantly, photo-induced ATRP reduced the amount of catalyst required.[27] Using organic copper salt (Cu(SC(S)N(C_2H_5)_2)_2) as a photocatalyst, N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) as a ligand, ethyl 2-bromophenylacetate (EBPA) as an ATRP initiator, and (2,4,6-trimethylbenzoyl) diphenylphosphine oxide (TPO) as a radical photoinitiator, photo-induced homogeneous ATRP was performed. The amount of copper catalyst was decreased to a 1.56 ppm level.[25] Metal-free ATRP mediated by light and catalyzed by an organic-based photoredox catalyst has been reported by Hawker and coworkers and You groups.[26,28] In photopolymerization system, photoinitiators are essential. However, many photoinitiators exhibit poor compatibility with polymer.

Flavonoids, a large group of plant polyphenol secondary metabolites, are widely presented in medicinal plants, fruit juices, and teas.

UV absorption of many flavonoids is in the regions 240–280 nm and 300–380 nm.[29] Flavone as photoinitiator has been successfully used in polymerization of tripropylene glycol diacrylate.[30] The conventional photoinitiator remains in polymer and leads to photodegradation and yellowing. The presence of residual initiator was reduced when falvone is used as photoinitiator. To-date, there is no report of using flavone as photoinitiator in photo-ATRP.

In this study, flavone was used as photoinitiator, photo-induced ATRP of MMA was investigated for the first time with $CuBr_2$/
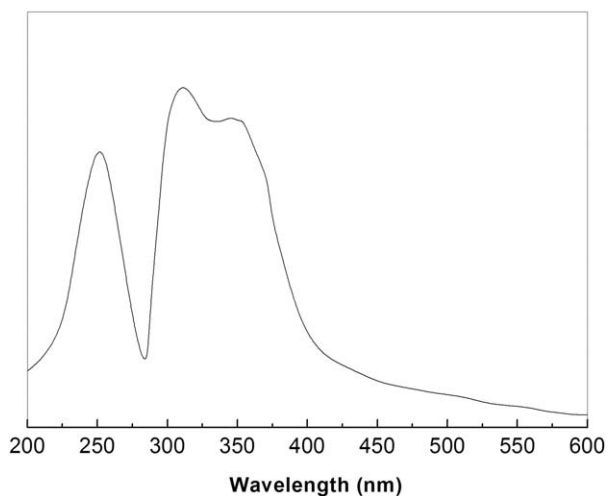
Figure 1. The UV-spectrum of flavone in ethanol solution. 1 cm quartz cuvette.

Me$_6$TREN as catalyst, and EBiB as ATRP initiator. The polymerization mechanism was discussed.

EXPERIMENTAL

Materials

MMA was of analytical grade and purchased from Tianjin Bodi Chemical Co (Tianjin, China). MMA was further purified by reduced pressure distillation prior to use. CuBr$_2$ and ethanol were used as supplied from Sinopharm Chemical Reagent Co., Ltd. Shanghai, China. Flavone and tris(2-dimethylaminoethyl)-amine (Me$_6$TREN) with a purity of 99% were purchased from Alfa Aesar. Other chemicals were commercially available and used as received without further purification.

General Procedure for Photo-Induced ATRP of MMA

In an example for a typical photo-induced ATRP procedure of MMA with flavone as photoinitiator, CuBr$_2$ (0.022 g, 0.00001 mol) was added to a solution of MMA (1 g, 0.01 mol) and ethanol (20 mL) in a 50-mL three-necked flask equipped with a magnetic stirring bar. Then Me$_6$TREN (0.0069 g, 0.00003 mol),
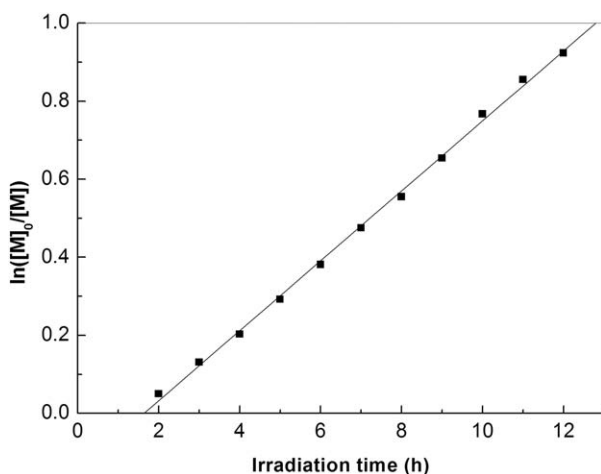
flavone (0.000001 mol), and EBiB (0.0195 g, 0.0001 mol) were added into the flask. The final concentration of flavone was 5×10^{-5} mol/L. The reaction mixture was consecutively evacuated and refilled with N$_2$ three times. The photo-induced ATRP of MMA with CuBr$_2$/Me$_6$TREN as catalyst, EBiB as ATRP initiator, and flavone as photoinitiator was performed in ethanol at 25 °C. The molar ratio of MMA to EBiB to CuBr$_2$ to Me$_6$TREN to flavone was 100/1/0.1/0.3/0.01. The mixture in flask was irradiated with LED lamp (350 nm–440 nm) at light density of 100 μW/cm^{-2} at 380 nm at 25 °C. After a predetermined interval, the polymerization was stopped and the mixture was dropped into a large excess of methanol. The PMMA was obtained by filtration and dried at 60 °C under vacuum. The monomer conversion was determined by weight.

Chain Extension Experiments

Chain extension was performed at 25 °C in ethanol with 12 W LED lamp at intensity of 100 μW/cm^{-2} at 380 nm with the molar ratio of [MMA]$_0$/[macroinitiator]$_0$/[CuBr$_2$]$_0$/[Me$_6$TREN]$_0$/[flavone]$_0$ = 100:1:0.1:0.3:0.01. After 7 h polymerization, a chain extended PMMA ($M_{n,GPC}$ = 16,400 g/mol, M_w/M_n = 1.32) as compared to the macroinitiator was obtained.

Characterizations

The number average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) were measured by gel permeation chromatography GPC (Waters 1515), with THF eluent at 30 °C and flow rate of 1.00 mL/min.

The apparent molecular weights and molecular weight distribution were determined with a calibration based on linear poly(methyl methacrylate) (PMMA) standards.

UV spectrum was recorded on a TU-1901 Double beam UV–visible spectrophotometer in 1 cm quartz cuvette. The wavelength range is 200–900 nm.

^{1}H-NMR spectrum of polymer in CDCl$_3$ was collected on a Bruker ARX 400 NMR spectrometer at room temperature. Tetramethylsilane was used as internal standard.

Figure 2. Dependence of ln([M]$_0$/[M]) on irradiation time. Reaction conditions: MMA/EBiB/CuBr$_2$/Me$_6$TREN/flavone =100:1:0.1:0.3:0.01, 25 °C.
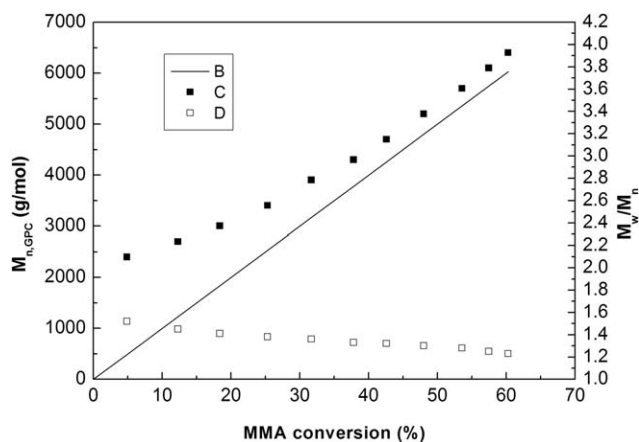

Figure 3. Dependence of number-average molecular weights ($M_{n,GPC}$) on MMA conversions. Reaction conditions were the same as in Figure 1.

Table I. Effect of Concentration of Flavone on the Polymerization[a]

Run	Concentration of flavone (mol/L)	Time (h)	Conversion (%)	$M_{n,th}$[b] (g/mol)	$M_{n,GPC}$[c] (g/mol)	M_w/M_n[c]
1	5×10^{-6}	6	10.75	1075	2100	1.42
2	1×10^{-5}	6	18.23	1823	2800	1.38
3	5×10^{-5}	6	31.68	3168	3900	1.36
4	10×10^{-5}	6	43.18	4318	5100	1.34

[a] $[MMA]_0/[EBiB]_0/[CuBr_2]_0/[Me_6-TREN]_0 = 100:1:0.1:0.3$.
[b] $M_{n,th} = ([MMA]_0/[EBiB]_0) \times M_{w,MMA} \times$ Conversion.
[c] Determined by GPC.

RESULTS AND DISCUSSION

Photo-induced ATRP of MMA in Ethanol with Flavone as Photoinitiator

The UV spectrum of flavone has the maximum absorption peaks centered at 251 nm and 350 nm in ethanol solution (Figure 1).

According to the study by Matyjaszewski group and other groups, the "livingness" of this polymerization process can be ascertained from a linear first-order kinetic plot, accompanied by a linear increase in polymer molecular weight with conversion, with the lower M_w/M_n value.[31]

Figure 2 shows the kinetic plot of the photo-induced ATRP system. Kinetic evaluation demonstrated pseudo-first order kinetic plots during the polymerization. It indicated that the concentration of active species remained constant throughout the reaction. An induction period (about 1.6 h) was observed at the beginning of polymerization, implying that some time is needed to establish the equilibrium between $Cu(II)/Me_6TREN$ and $Cu(I)/Me_6TREN$ species. The apparent rate constant according to the line slope in Figure 2 was 2.47×10^{-5} s^{-1}.

Figure 3 shows the dependence of number-average molecular weight ($M_{n,GPC}$) and M_w/M_n with MMA conversion in the photo-induced ATRP of MMA at 25 °C. For ATRP systems,

$M_{n,GPC}$ increased linearly with respect to MMA conversion and it was in a close correlation with the theoretical values. The M_w/M_n values decreased with increasing MMA conversion and the M_w/M_n values of the obtained polymer were less than 1.5 in many cases. Lower M_w/M_n values indicated that the polymerization proceeded in a living fashion.

On the basis of the above discussion, it was concluded that photo-induced ATRP of MMA in ethanol with flavone as photoinititor was effective for ATRP techniques.

Effect of Flavone Concentration on the Polymerization

A series of experiments were carried out to investigate the effect of flavone concentration on the polymerization. The wavelength of light was set to 380 nm and the temperature was 25 °C. The results are shown in Table I.

As seen from Table I, the conversion increased with increasing flavone concentration. The $M_{n,GPC}$ values increased with the monomer consumption and they were in agreement with the theoretical values $M_{n,th}$ [$M_{n,th} = ([MMA]_0/[EBiB]_0) \times M_{w,MMA} \times$ Conversion[32,33]]. Low M_w/M_n values ($M_w/M_n = 1.34-1.42$) were obtained in all cases. All these results further supported that flavone initiated efficiently the photo-induced ATRP of MMA in ethanol.
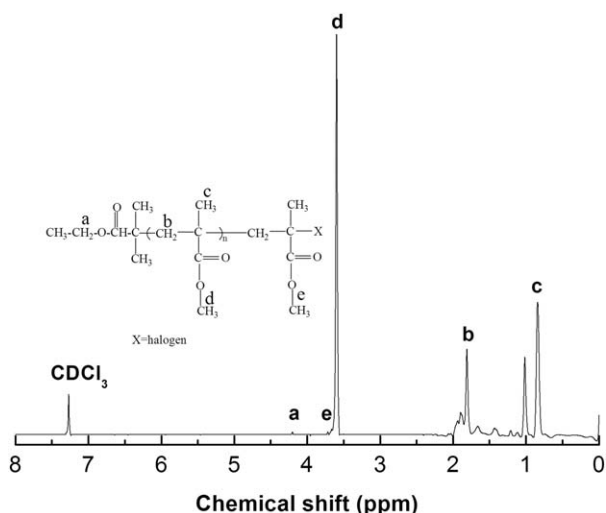

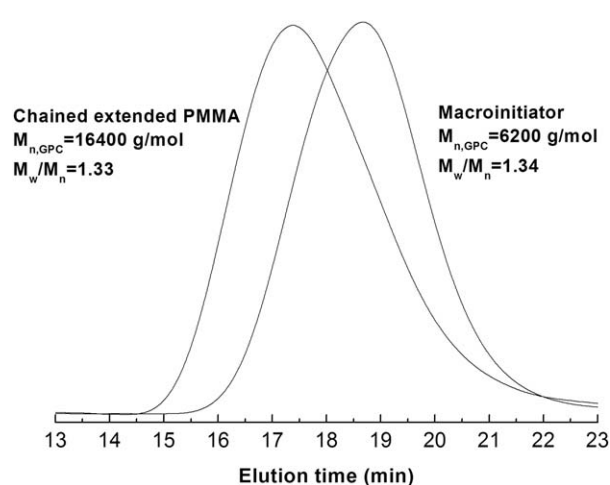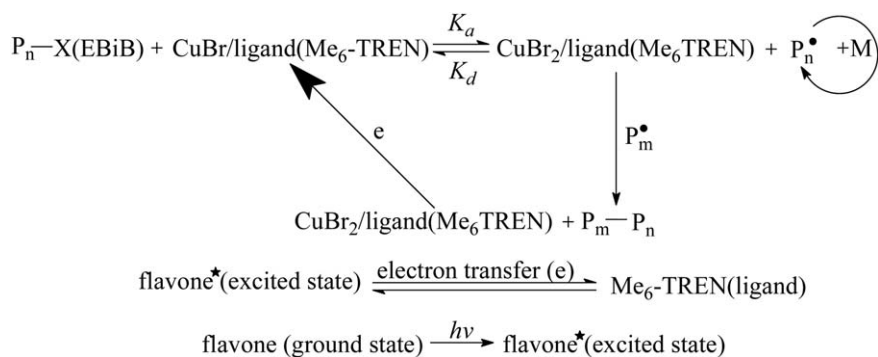**Figure 4.** ^{1}H-NMR spectrum (CDCl$_3$, 400 MHz) of PMMA.

Figure 5. M_w/M_n of PMMA-X macroinitiator before and after chain extension with MMA.

Scheme 1. A probable mechanism for photo-induced ATRP of MMA with flavone as photoinitiator.

End-Group Analysis of Obtained PMMA and Chain Extension with MMA

The chemical structure of PMMA obtained using flavone photoinitiator system in ethanol at $25\,^{\circ}C$ was characterized by ^{1}H-NMR spectrum. Figure 4 presents the ^{1}H-NMR spectrum of PMMA samples. The peaks at 3.60 ppm (3H, CH_3—O—, d in Figure 4), 0.67–1.13 ppm (3H, CH_3—, c in Figure 4), and 1.39–2.07 ppm (2H, —CH—, b in Figure 4) were in agreement with the expected PMMA chemical structure. The peak at 3.72 ppm (3H, CH_3—O—, e in Figure 4) corresponds to methyl protons next to the halogen chain end.[34] The signal at 4.2 ppm (a in Figure 4) is derived from methylene group of EBiB.

To verify the controlled/living nature of the polymerizations, chain extension of MMA from macroinitiator ($M_{n,GPC}$ = 6200 g/mol, M_w/M_n = 1.34) was carried out. The results were shown in Figure 5. The monomodal and symmetrical GPC traces was observed, demonstrating the living character of PMMA-X macroinitiator.

Analysis of Mechanism

A probable mechanism consistent with of photoinitiation kinetic with flavone as photoinitiator is presented in Scheme 1, which is similar to some reports.[35,36] Excited state of flavone is formed upon UV light irradiation.[37] It might be that the electron transferred between the excited state flavone and the Me_6T-REN (amine). Then CuBr was generated by the reduction of $CuBr_2$ by the electrons. P_n-X reacted with CuBr to generate $CuBr_2$ and free radical P·. Then it initiated the polymerization.

CONCLUSIONS

Photo-induced ATRP of MMA with flavone as photoinitiator was investigated at $25\,^{\circ}C$ in ethanol for the first time. Well controlled polymerization was achieved. The $M_{n,GPC}$ of the resultant PMMA grew linearly with respect to MMA conversion, with M_w/M_n values remaining low during the polymerization. The living character of polymerization was demonstrated by chain extension experiments.

ACKNOWLEDGMENTS

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