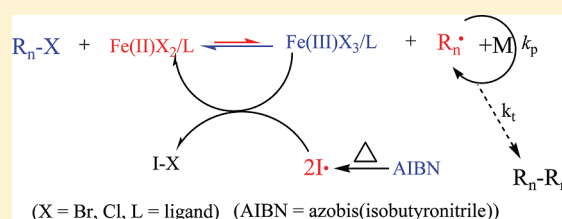


Iron-Mediated ICAR ATRP of Methyl Methacrylate

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ABSTRACT: An iron(III) ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) catalyst was found to be an active catalyst for initiators for continuous activator regeneration atom transfer radical polymerization (ICAR ATRP) of methyl methacrylate (MMA), using triphenylphosphine (PPh_3) as a ligand and azobis(isobutyronitrile) (AIBN) as a thermal radical initiator, and 1,4-(2-bromo-2-methylpropionato)benzene (BMPB_2) as an ATRP initiator. Effects of reaction temperature, catalyst concentration and AIBN concentration on polymerization were investigated. These results showed that the catalyst was highly efficient for the ICAR ATRP of MMA. For example, even if the catalyst concentration decreased to 34 ppm, the polymerization with the molar ratio of $[\text{MMA}]_0/[\text{BMPB}_2]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[\text{PPh}_3]_0/[\text{AIBN}]_0 = 500/1/0.03/1.5/0.1$ could be carried out at 60°C with a conversion 70.4% in 32 h. At the same time, the molecular weight of the obtained PMMA with a narrow molecular weight distribution ($M_w/M_n = 1.37$) was consistent with the theoretical one.



INTRODUCTION

Atom transfer radical polymerization (ATRP), one of the “living”/controlled radical polymerizations (LRPs), has become a power tool for preparing new polymeric materials with controlled molecular weights and well-defined architectures in recent years.^{1–9} It is mediated by a transition-metal complex that establishes a dynamic equilibrium between active and dormant species.¹⁰ By now, many improved ATRP techniques have been developed to overcome the intrinsic limitations of the traditional ATRP system,^{11–14} such as reverse ATRP,¹⁵ simultaneous reverse and normal initiation (SR&NI) ATRP or initiators for continuous activator regeneration ATRP (ICAR ATRP),^{16–21} activators generated by electron transfer ATRP (AGET ATRP),^{22–27} activators regenerated by electron transfer ATRP (ARGET ATRP),^{28–31} and LRP in the presence of zerovalent metal.^{32–41}

For a typical ICAR ATRP system, an alkyl halide initiator is necessary and a very small amount of higher oxidation state transition metal is used as catalyst. The activators, lower oxidation state transition-metal complex, are produced by an in situ reduction with a thermal radical initiator such as azobis(isobutyronitrile) (AIBN). The advantage of ICAR ATRP over AGET ATRP is that the amount of catalyst can be decreased to a very low (often ppm level). Using catalytic level of metal complex is a great improvement for traditional ATRP process, which has an attractive potential for its application in industrial scale. Many kinds of transition metals have been successfully used in ATRP systems, such as copper,⁴² iron,^{43–48} nickel,^{49,50} and ruthenium.^{51–54} Among them, copper is used most extensively. On the basis of its high activity, polymerizations can be realized using very low amount of copper. Matyjaszewski et al. have reported some excellent works about copper-mediated ARGET and ICAR ATRP.^{20,21,29,55} They have also studied ICAR ATRP of styrene and MMA catalyzed by ruthenium complex.⁵⁶

Nowadays, the use of iron catalyst is attractive because of its low toxicity, biocompatibility, and potential application in biomaterials. Actually, some excellent works about iron-mediated AGET ATRP have been reported recently.^{25–27,57–62} Iron-catalyzed ARGET ATRP of acrylonitrile (AN) provided a novel way to synthesize poly(AN) with high molecular weight and low polydispersity.⁶³ Our group has reported the first iron-mediated ICAR ATRP of styrene and MMA in the absence of thermal radical initiator very recently.⁶⁴ This system showed a higher activity for the polymerization of styrene; however, a very low catalyst activity for the polymerization of MMA was observed in this catalyst system⁶⁴ due to the intrinsic lower activity of iron catalyst for the polymerization of the polar monomer.⁶⁵

In this work, combining the advantages of the iron catalyst and ICAR ATRP technique, the ICAR ATRP of MMA was investigated using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as the catalyst, triphenylphosphine (PPh_3) as the ligand, bifunctional 1,4-(2-bromo-2-methylpropionato)benzene (BMPB_2) as the initiator, and AIBN as thermal radical initiator. Compared to the reported iron-mediated ICAR ATRP of MMA,⁶⁴ the current ICAR ATRP catalyst system showed higher activity, and even if the amount of catalyst decreased to ppm level (~ 30 ppm), the polymerization could be carried out successfully.

EXPERIMENTAL SECTION

Materials. The monomer, methyl methacrylate (MMA) (>99%), was purchased from Shanghai Chemical Reagents Co. (Shanghai, China). It was washed with an aqueous solution of sodium hydroxide (5 wt %) three times, followed by deionized water until neutralization,

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and then dried over an anhydrous magnesium sulfate, distilled under reduced pressure and stored at $-18\text{ }^{\circ}\text{C}$. Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (>99%), triphenylphosphine (PPh_3) were purchased from Shanghai Chemical Reagents Co. (Shanghai, China) and used as received. Azobis(isobutyronitrile) (AIBN) and benzoyl peroxide (BPO) were obtained from Shanghai Chemical Reagents Co. and purified by recrystallizing twice from methanol. Toluene (analytical reagent), tetrahydrofuran (THF) (analytical reagent) and all other chemicals were obtained from Shanghai Chemical Reagents Co. and used as received unless mentioned. The bifunctional initiator 1,4-(2-bromo-2-methylpropionato) benzene (BMPB_2) was synthesized according to the literature.⁶⁶

Synthesis of 1,4-(2-Bromo-2-methylpropionato)benzene (BMPB_2). 1,4-Dihydroxybenzene (5.51 g, 0.05 mol), triethylamine (23 mL, 0.165 mol), and THF (250 mL) were added in a 500 mL three-necked round-bottom flask. The solution was bubbled with argon and cooled by an ice bath with stirring at $0\text{ }^{\circ}\text{C}$. 2-Bromoisobutyryl bromide (14.9 mL, 0.12 mol) was added slowly to the mixture and the reaction mixture was allowed to react overnight with stirring at room temperature. After reaction, the triethylammonium bromide was removed by filtration and the solvent was removed by rotatory evaporation from the reaction mixture. The product was recovered as a yellow powder that was recrystallized three times from methanol to give a white crystalline powder (BMPB_2): yield 17.7 g (86.8%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.18$ ppm (s, 4 H), 2.07 ppm (s, 12 H).

General Procedure for ICAR ATRP of MMA. A typical bulk polymerization procedure for the molar ratio of $[\text{MMA}]_0/[\text{BMPB}_2]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[\text{PPh}_3]_0/[\text{AIBN}]_0 = 500/1/0.5/1.5/0.1$ is as follows: a mixture was obtained by adding $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (15.4 mg, 0.057 mmol), PPh_3 (44.8 mg, 0.171 mmol), MMA (6.0 mL, 56.9 mmol), BMPB_2 initiator (46.4 mg, 0.114 mmol), and AIBN (1.89 mg, 0.0115 mmol) to a dried ampule. The mixture was thoroughly bubbled with argon for about 20 min to eliminate the dissolved oxygen, then flame-sealed and transferred into an oil bath held by a thermostat at the desired temperature ($60\text{ }^{\circ}\text{C}$) to polymerize under stirring. After the desired polymerization time, the ampule was cooled by immersing it into iced water. Afterward, it was opened and the contents were dissolved in THF (~ 2 mL), and precipitated into a large amount of methanol (~ 200 mL). The polymer obtained by filtration was dried under vacuum until constant weight at $50\text{ }^{\circ}\text{C}$. The monomer conversion was determined gravimetrically.

For the polymerization procedures with other molar ratios of $[\text{MMA}]_0/[\text{BMPB}_2]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[\text{PPh}_3]_0/[\text{AIBN}]_0$ are the same as that described above except for different amounts of corresponding chemicals and different polymerization temperatures (50 , 70 , 75 , and $80\text{ }^{\circ}\text{C}$) used. For the solution polymerization of MMA, another 2 mL of toluene was added into the reaction mixture; for the polymerizations using BPO as the thermal initiator, BPO was used instead of AIBN; and the other procedures are the same as that of the bulk polymerization.

Chain Extension of PMMA. A predetermined quantity of PMMA (obtained by bulk ICAR ATRP of MMA) was added to a dried ampule, and then the predetermined quantity of MMA, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, PPh_3 , and AIBN was added. The rest of the procedure was the same as that described above. The chain-extension polymerization was carried out in bulk under stirring at $60\text{ }^{\circ}\text{C}$.

Characterization. The number-average molecular weight ($M_{n,\text{GPC}}$) values and molecular weight distribution (M_w/M_n) values of the polymers were determined using Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive index detector (Waters 2414), using HR 1, HR 2, and HR 4 (7.8×300 mm, $5\text{ }\mu\text{m}$ beads' size) columns with measurable molecular weights in the range 10^2 to 5×10^5 g/mol. THF was used as an eluent at a flow rate of 1.0 mL/min at $30\text{ }^{\circ}\text{C}$. The GPC samples were injected using a Waters 717 plus autosampler and calibrated with poly(methyl methacrylate) standards from Waters.

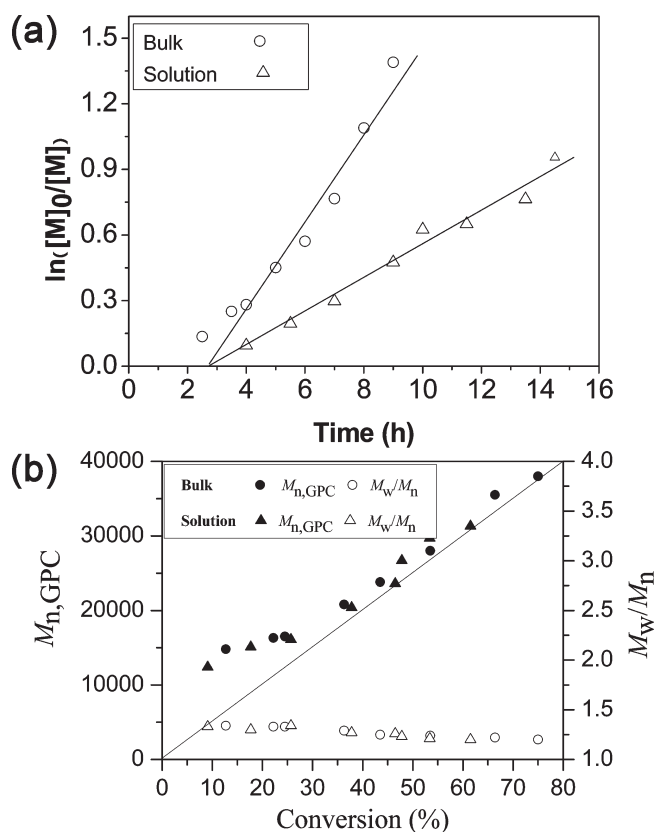


Figure 1. $\ln([M]_0/[M])$ versus reaction time (a) and number-average molecular weight ($M_{n,\text{GPC}}$) and molecular weight distribution (M_w/M_n) versus the conversion (b) for bulk and solution ICAR ATRP of MMA with molar ratio of $[\text{MMA}]_0/[\text{BMPB}_2]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[\text{PPh}_3]_0/[\text{AIBN}]_0 = 500/1/0.5/1.5/0.1$ at $60\text{ }^{\circ}\text{C}$. Bulk polymerization conditions: MMA = 6 mL. Solution polymerization conditions: MMA = 6 mL, solvent = toluene, toluene/MMA = 1/3 (v/v).

The ^1H NMR spectrum was recorded on an Inova 400 MHz nuclear magnetic resonance (NMR) instrument using CDCl_3 as the solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature.

RESULTS AND DISCUSSION

Typical Polymerization of MMA. The bulk and solution polymerization of MMA was first investigated with the same molar ratio of $[\text{MMA}]_0/[\text{BMPB}_2]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[\text{PPh}_3]_0/[\text{AIBN}]_0 = 500/1/0.5/1.5/0.1$ at $60\text{ }^{\circ}\text{C}$. As shown in Figure 1a, the linearity of kinetic plots indicated that the propagating radical concentrations remained constant in the polymerization process. It can be seen that there is an induction period (~ 2.8 h) in the beginning of both polymerization conditions. This is because it needs some time to decompose AIBN and establish a dynamic equilibrium between the Fe(II) and Fe(III) species as the reaction proceeds. According to the kinetic slopes, the apparent rate constants of the polymerization k_p^{app} ($R_p = -d[M]/dt = k_p[P_n^*][M] = k_p^{\text{app}}[M]$) can be obtained. The k_p^{app} values of $6.66 \times 10^{-5}\text{ s}^{-1}$ and $2.16 \times 10^{-5}\text{ s}^{-1}$ for the bulk and solution polymerizations were obtained, respectively. The former is 3.08 times of the later due to decreasing of monomer concentration in toluene. Figure 1b shows that the molecular weight ($M_{n,\text{GPC}}$) values of the polymers increased linearly with

Table 1. Comparison of Molecular Weights from GPC and NMR Results

entry	R^a	time (h)	convn (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_n^1 NMR (g/mol)	M_w/M_n
1	500/1/0.5/1.5/0.1	6	42.1	21 100	24 500	23 500	1.27
2	500/1/0.4/1.2/0.1	5.5	40.8	20 400	24 400	24 100	1.24

^a Polymerization conditions: temperature = 60 °C. $R = [MMA]_0/[BMPB_2]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[AIBN]_0$. ^b $M_{n,th} = ([MMA]_0/[BMPB_2]_0) \times M_{w,MMA} \times \text{conversion}\%$.

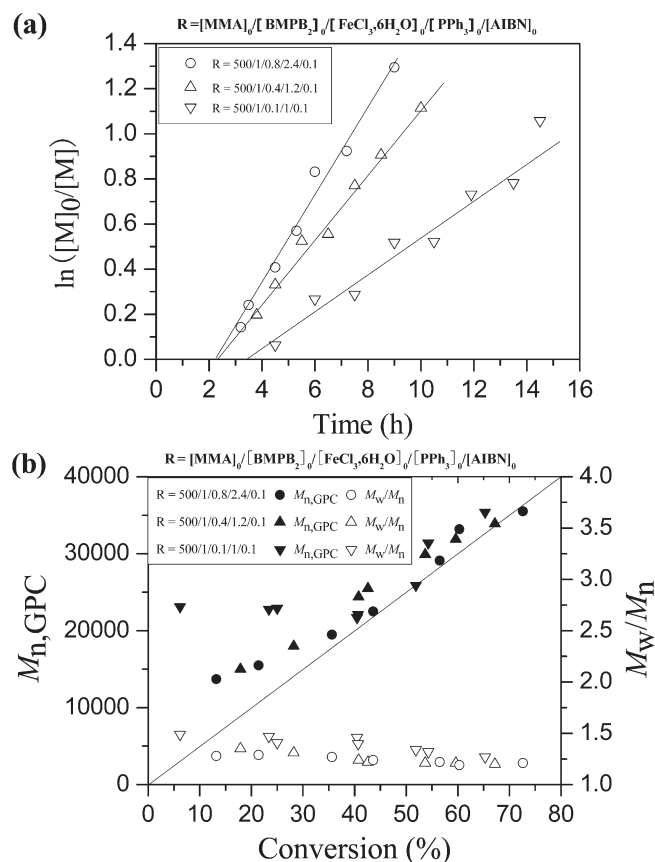


Figure 2. $\ln([M]_0/[M])$ versus reaction time (a) and number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) versus the conversion (b) for bulk ICAR ATRP of MMA with different catalyst concentrations. Polymerization conditions: MMA = 6 mL.

monomer conversion, and meanwhile, the molecular weight distribution (M_w/M_n) values (1.20–1.34) of the obtained PMMAs remained low during the polymerization process. It can be seen from Table 1 that the $M_{n,GPC}$ values are consistent with the molecular weight values calculated by 1H NMR. From the results above, it can be concluded that the iron-mediated ICAR ATRP of MMA keeps the controlled/living radical polymerization characteristics of ATRP.

Effect of Molar Ratio of $[FeCl_3 \cdot 6H_2O]_0/[AIBN]_0$ on Polymerization of MMA. In an ICAR ATRP system, the initial molar ratio of higher oxidation state catalyst to AIBN has significant effect on the controllability over molecular weight and molecular weight distribution. In this work, the bulk polymerizations of MMA were investigated using different molar ratios of $[FeCl_3 \cdot 6H_2O]_0/[AIBN]_0$ at 60 °C. Figure 2(a) shows the kinetic plots with molar ratios of $[MMA]_0/[BMPB_2]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[AIBN]_0 = 500/1/0.8/2.4/0.1$, $500/1/0.4/1.2/0.1$ and $500/1/0.1/1/0.1$, respectively. The time

dependence of $\ln([M]_0/[M])$ was linear for various ratios of $FeCl_3 \cdot 6H_2O$ to AIBN, indicating that propagating radical species remained constant during the three polymerization processes. From Figure 2b, it can be seen that the molecular weights of PMMAs increased linearly with monomer conversion and the molecular weight distributions remained low ($M_w/M_n = 1.19$ – 1.31) for the both cases of the molar ratios of $FeCl_3 \cdot 6H_2O$ to AIBN = 0.8/0.1 and 0.4/0.1. However, if the molar ratio of $FeCl_3 \cdot 6H_2O$ to AIBN changed to 0.1/0.1, the molecular weights of the obtained PMMAs were larger than the theoretical molecular ones; meanwhile the M_w/M_n values kept broader (1.27–1.49), indicating a relatively poorly controlled polymerization process.

Effect of Catalyst Concentration on Polymerization of MMA.

For an excellent polymerization system, the high activity of the catalyst is necessary. In the ICAR ATRP reaction, a lower amount of catalyst is used compared to normal ATRP. The polymerizations with different amount of catalyst (112 ppm to 12 ppm) were carried out. The results are shown in Table 2. It can be seen that the polymerizations were well controlled with catalyst concentration at 112–34 ppm, the $M_{n,GPC}$ values were consistent with the corresponding $M_{n,th}$ ones with molecular weight distribution (1.28–1.37). If the catalyst concentration further decreased to 23 and 12 ppm, the polymerizations were out of control with broad molecular weight distribution (1.51–1.77), but their $M_{n,GPC}$ values were close to the $M_{n,th}$ ones. Anyway, these results indicated the current iron-mediated ICAR ATRP is a highly active catalyst system.

Effect of AIBN Concentration on Polymerization of MMA.

As we know, the reducing agent plays a very important role for a typical AGET ATRP system: increasing the amount of reducing agent resulted in a higher concentration of the situ formed active species, which increased the propagating radical concentrations and lead to a higher polymerization rate. To better understand the effect of AIBN concentration in the polymerization process, we studied ICAR ATRP of MMA with different amount of AIBN at 60 °C. From Table 3, it can be seen that increasing the amount of AIBN (i.e., $[AIBN]_0/[BMPB_2]_0$ from 0/1, 0.1/1, 0.2/1 to 0.3/1) resulted in enhancement of polymerization rate, and that the $M_{n,GPC}$ values were close to their corresponding theoretical ones while keeping low M_w/M_n values (<1.27) for the obtained polymers. However, when in the presence of larger amount of AIBN (i.e., $[AIBN]_0/[BMPB_2]_0 = 0.5/1$, entry 5 in Table 3), radical termination can not be neglected and the M_w/M_n became broad ($M_w/M_n = 1.44$). This is because the relatively larger amount of AIBN would result in some side reactions such as radical termination and initiation induced directly by AIBN, especially at the beginning of polymerization.

Effect of Reaction Temperature on Polymerization of MMA.

For an ICAR ATRP process, catalyst regeneration depends on the decomposition of a thermal radical initiator such as AIBN; so reaction temperature controls the concentrations of propagating radicals. From Table 4, it can be seen that the

Table 2. Effect of the Amount of Catalyst on the Bulk ICAR ATRP of MMA at 60 °C

entry	R ^a	Fe (ppm)	time (h)	convn (%)	M _{n,th} ^b (g/mol)	M _{n,GPC} (g/mol)	M _w /M _n
1	500/1/0.1/1/0.1	112	24	57.1	28 600	32 100	1.28
2	500/1/0.07/1/0.1	78	27	62.5	31 300	32 500	1.30
3	500/1/0.05/1/0.1	56	30	71.3	35 600	34 800	1.32
4	500/1/0.03/1.5/0.1	34	32	70.4	35 200	34 300	1.37
5	500/1/0.02/1.5/0.1	23	36	79.3	39 600	40 400	1.51
6	500/1/0.01/2/0.1	12	36	73.6	36 800	50 300	1.77

^a R = [MMA]₀/[BMPB₂]₀/[FeCl₃·6H₂O]₀/[PPh₃]₀/[AIBN]₀. ^b M_{n,th} = ([MMA]₀/[BMPB₂]₀) × M_{w,MMA} × conversion%.

Table 3. Effect of AIBN Concentration on the Bulk ICAR ATRP of MMA at 60 °C

entry	R ^a	time (h)	convn (%)	M _{n,th} ^b (g/mol)	M _{n,GPC} (g/mol)	M _w /M _n
1	500/1/0.1/1/0	36	61.4	30 800	32 500	1.27
2	500/1/0.1/1/0.1	28	68.5	34 300	35 000	1.25
3	500/1/0.1/1/0.2	27	81.3	40 700	39 200	1.24
4	500/1/0.1/1/0.3	24	72.7	36 400	36 900	1.26
5	500/1/0.1/1/0.5	11	79.8	39 900	39 500	1.44

^a R = [MMA]₀/[BMPB₂]₀/[FeCl₃·6H₂O]₀/[PPh₃]₀/[AIBN]₀. ^b M_{n,th} = ([MMA]₀/[BMPB₂]₀) × M_{w,MMA} × conversion %.

Table 4. Effect of Reaction Temperature on Polymerization of MMA

entry	R ^a	T (°C)	time (h)	convn (%)	M _{n,th} ^b (g/mol)	M _{n,GPC} (g/mol)	M _w /M _n
1	500/1/0.1/1/0.1	50	33	68.8	34 400	33 800	1.40
2	500/1/0.1/1/0.1	60	28	68.5	34 300	35 000	1.25
3	500/1/0.1/1/0.1	70	18.5	63.3	31 700	33 000	1.27
4	500/1/0.1/1/0.1	75	8.5	69.7	34 900	33 600	1.26
5	500/1/0.1/1/0.1	80	9	63.1	31 600	33 800	1.34
6	500/1/0.4/1.2/0.3	50	18	70.0	35 100	35 000	1.22
7	500/1/0.2/0.6/0.3	50	23	76.6	38 300	38 500	1.24
8	500/1/0.1/1/0.3	50	23	71.1	35 600	32 900	1.36
9	500/1/0.05/1/0.3	50	45	59.4	29 700	31 600	1.39

^a R = [MMA]₀/[BMPB₂]₀/[FeCl₃·6H₂O]₀/[PPh₃]₀/[AIBN]₀. ^b M_{n,th} = ([MMA]₀/[BMPB₂]₀) × M_{w,MMA} × conversion%.

polymerization rate increased with temperature enhanced from 50 to 75 °C while keeping good controllability over the polymerization. However, when the temperature increased to 80 °C, a lower polymerization rate compared to the reaction at 75 °C was observed. This is because the higher decomposition rate of AIBN at this case made AIBN consumed in a short period and resulted in no enough radicals from AIBN decomposition to continuously regenerate active Fe(II) species. In order to generate the radical benignly and persistently, we designed experiments at lower temperature (50 °C) with higher concentrations of AIBN. From entries 6–7 in Table 4 ([FeCl₃·6H₂O]₀/[AIBN]₀ = 0.4/0.3, 0.2/0.3, respectively), a well-controlled polymerization system was obtained with M_{n,GPC} values of obtained PMMAs consisted with the M_{n,th} ones and low M_w/M_n values (<1.24). Even if decreased the iron catalyst concentration to 0.05/500 ([FeCl₃·6H₂O]₀/[MMA]₀, entry 9 in Table 4), the reaction system remained good controllability over the polymerization of MMA just the M_w/M_n value (<1.40) increased slightly.

BPO as Thermal Initiator. Figure 3 shows the bulk polymerization of MMA with the same molar ratio of [MMA]₀/[BMPB₂]₀/[FeCl₃·6H₂O]₀/[PPh₃]₀/[BPO]₀ = 500/1/0.2/0.6/0.1 at 60 and 75 °C, respectively. As shown in Figure 3(a), first-order kinetics was

observed in both cases, indicating that the propagating radical concentrations remained constant in the polymerization process. From Figure 3b, it can be seen that the molecular weights of PMMAs increased with monomer conversion linearly and the M_w/M_n values decreased to 1.19 from 1.47 gradually. These results demonstrated that BPO can also be used as efficient thermal initiator in ICAR ATRP process.

ICAR ATRP with Different Feed Ratios of [Monomer]₀/[Initiator]₀. In order to better understand the controlled/living features of this polymerization system, we studied the ICAR ATRP of MMA with different molar feed ratios of [monomer]₀/[initiator]₀ at 60 °C. From Figure 4, it can be seen that the molecular weights increased with the feed ratios of [MMA]₀/[initiator]₀, while the M_{n,GPC} values were consistent with their corresponding theoretical ones; the molecular weight distributions (M_w/M_n) kept low (1.20–1.24). At the same time, the initiator efficiency (I_{eff}) kept high (about 100%). All of these results indicated that this polymerization system has high activity, even under higher feed ratios of [monomer]₀/[initiator]₀ = 1500/1.

Analysis of Chain End and Chain Extension. The chain end of the PMMA was analyzed by ¹H NMR spectroscopy, as shown in Figure 5. The chemical shift at δ = 7.02 ppm (c in Figure 5) corresponded to the aromatic protons of the initiator BMPB₂.

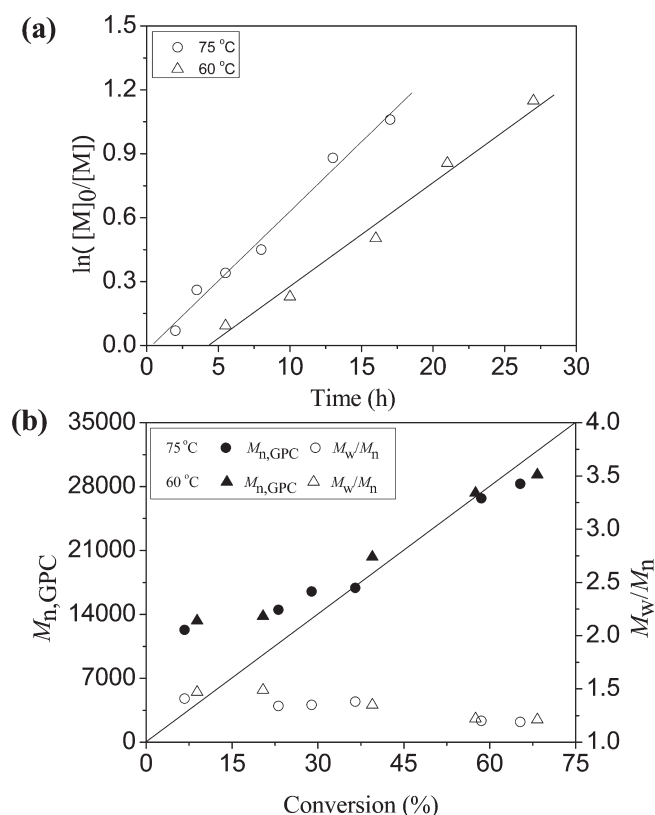


Figure 3. $\ln([M]_0/[M])$ versus reaction time (a) and number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) versus the conversion (b) for bulk ICAR ATRP of MMA with molar ratio of $[MMA]_0/[BMPB_2]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[BPO]_0 = 500/1/0.2/0.6/0.1$ at 60 and 75 °C, respectively. Bulk polymerization conditions: MMA = 6 mL.

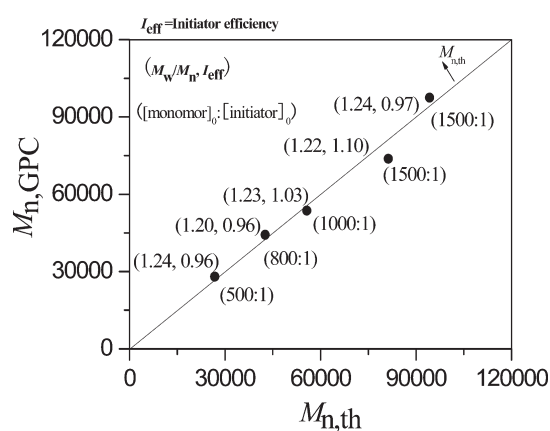


Figure 4. Relationship of theoretical molecular weight ($M_{n,th}$) and molecular weight from GPC results ($M_{n,GPC}$) under different molar feed ratios of $[MMA]_0/[initiator]_0$ at 60 °C. MMA = 6 mL. Initiator efficiency (I_{eff}) = $M_{n,th}/M_{n,GPC}$.

The chemical shift at $\delta = 3.75$ ppm (**b** in Figure 5) was attributed to the methyl ester group at the chain end, as mentioned by Sawamoto et al.,⁴³ which deviated from the chemical shift (3.58 ppm, **a** in Figure 5) of other methyl ester group in PMMA because of the electron-attracting function of ω -Cl atom. Therefore, the obtained PMMA could be used as a macroinitiator

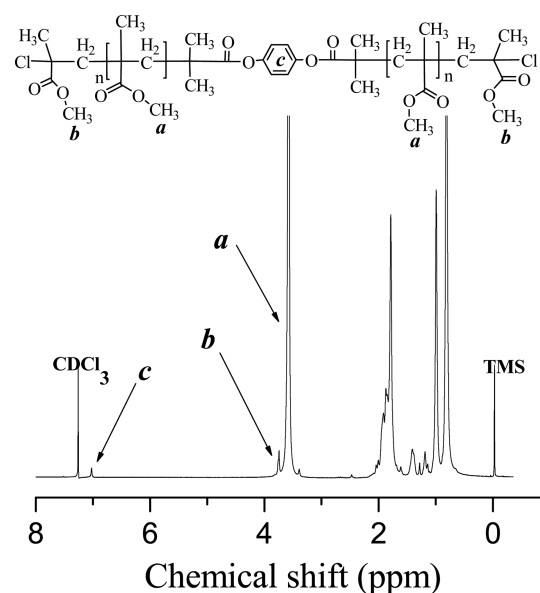


Figure 5. 1H NMR spectrum of PMMA ($M_{n,GPC} = 22500$ g/mol, $M_w/M_n = 1.24$) with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Polymerization conditions: $[MMA]_0/[BMPB_2]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[AIBN]_0 = 500/1/0.8/2.4/0.1$, MMA = 6 mL, time = 5.3 h, conversion = 43.6%, temperature = 60 °C.

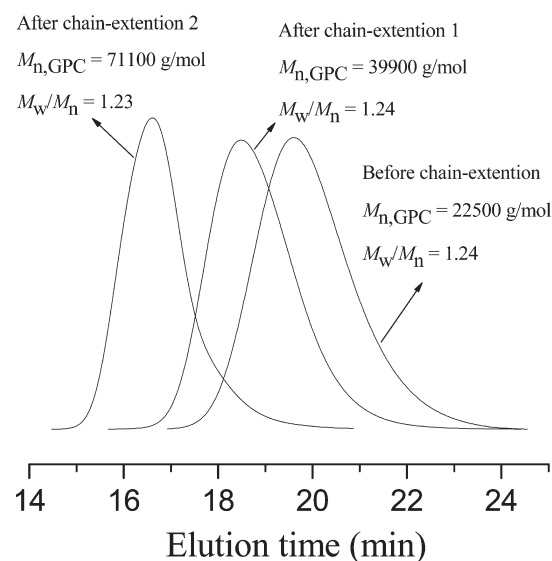
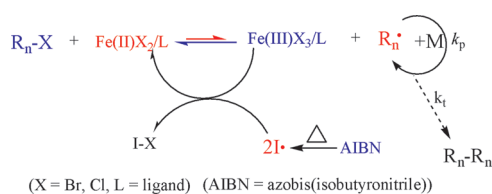


Figure 6. GPC curves before and after chain extension with PMMA as macroinitiator. Original PMMA: $[MMA]_0/[BMPB_2]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[AIBN]_0 = 500/1/0.8/2.4/0.1$, MMA = 6 mL, time = 5.3 h, conversion = 43.6%, temperature = 60 °C. Chain extended PMMA 1: $[MMA]_0/[PMMA]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[AIBN]_0 = 500/1/1/3/0.1$, MMA = 3 mL, time = 7.2 h, conversion = 39%, temperature = 60 °C. Chain extended PMMA 2: $[MMA]_0/[PMMA]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[AIBN]_0 = 1200/1/1/3/0.1$, MMA = 6 mL, time = 16 h, conversion = 46.5%, temperature = 60 °C.

to conduct a chain extension reaction via ICAR ATRP method. The obtained PMMA ($M_{n,GPC} = 22500$ g/mol, $M_w/M_n = 1.24$) was used as the predecessor in chain-extension experiment. As shown in Figure 6, there was a peak shift from the macroinitiator to the chain extended PMMA with $M_{n,GPC} = 39900$ g/mol and

Scheme 1. Plausible Mechanism for the Iron-Mediated ICAR ATRP



$M_w/M_n = 1.24$, and $M_{n, GPC} = 71100$ g/mol and $M_w/M_n = 1.23$, respectively. The successful chain extension reaction further verified the features of “living”/controlled free-radical polymerization of MMA in this catalyst system.

Mechanism of ICAR ATRP. Radical termination reactions will lead to irreversible accumulation of persistent radical or deactivator ($X-Fe(III)$ complex). In other words, if the initial catalyst concentration is too low, all of the activator will eventually be consumed as a persistent radical and polymerization will only reach limited conversions. In this work, as shown in Scheme 1, free radicals I^\bullet are slowly and continuously generated by conventional radical initiators AIBN throughout the polymerization, to constantly reduce the iron(III) complex that accumulates as a persistent radical to iron(II) complex. Then the propagating radical R_n^\bullet can be regenerated by the reversible redox reaction between iron(II) complex and ATRP initiator R_n-X as proceeded by normal ATRP mechanism. It is noted that even if the initial catalyst concentration is very low (i.e., 34 ppm as shown in entry 4 of Table 2), the polymerization can be successfully carried out up to higher conversion (more than 70%) because the free radicals I^\bullet were slowly and continuously generated by AIBN to reduce the iron(III) complex into iron(II) complex throughout the polymerization, which is similar to the copper-mediated ICAR ATRP reported by Matyjaszewski group.²⁰

CONCLUSION

“Living”/controlled radical polymerization of MMA was successfully carried out via iron-mediated ICAR ATRP even if the amount of iron catalyst decreased to 34 ppm. Well-defined PMMAs with narrow molecular weight distributions can be obtained by this catalyst system, and this catalyst system shows efficient activity.

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