Iron-Mediated ICAR ATRP of Methyl Methacrylate

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ABSTRACT: An iron(III) (FeCl₃·6H₂O) 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 (PPh₃) as a ligand and azobisisobutyronitrile (AIBN) as a thermal radical initiator, and 1,4-(2-bromo-2-methylpropionato)benzene (BMPB₂) 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 [MMA]₀/[BMPB₂]₀/[FeCl₃·6H₂O]₀/[PPh₃]₀/[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 (Mₘ/Mₙ = 1.37) was consistent with the theoretical one.

INTRODUCTION

Atom transfer 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 activation (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 azobisisobutyronitrile (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, iron, nickel,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.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.²⁰⁻²⁷

In this work, combining the advantages of the iron catalyst and ICAR ATRP technique, the ICAR ATRP of MMA was investigated using FeCl₃·6H₂O as the catalyst, triphenylphosphine (PPh₃) as the ligand, bifunctional 1,4-(2-bromo-2-methylpropionato)benzene (BMPB₂) 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.

Received: December 27, 2010
Revised: March 27, 2011
and then dried over an anhydrous magnesium sulfate, distilled under reduced pressure and stored at −18 °C. Iron(III) chloride hexahydrate (FeCl₃·6H₂O) (>99%), triphenylphosphine (PPh₃) 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 (BMPB₂) was synthesized according to the literature.⁶⁶

Synthesis of 1,4-(2-Bromo-2-methylpropionato)benzene (BMPB₂). 1,4-Dihydroxybenzene (5.51 g, 0.05 mol), triethylamine (15.4 mg, 0.11 mmol), and FeCl₃·6H₂O (15.4 mg, 0.057 mmol), PPh₃ (44.8 mg, 0.171 mmol), MMA (6.0 mL, 56.9 mmol), BMPB₂ (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 °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 °C. The monomer conversion was determined gravimetrically.

For the polymerization procedures with other molar ratios of [MMA]₀/[BMPB₂]₀/[FeCl₃·6H₂O]₀/[PPh₃]₀/[AIBN]₀ = 500/1/0.5/1.5/0.1 is as follows: a mixture was obtained by adding FeCl₃·6H₂O (15.4 mg, 0.057 mmol), PPh₃ (44.8 mg, 0.171 mmol), MMA (6.0 mL, 56.9 mmol), BMPB₂ (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 °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 °C. The monomer conversion was determined gravimetrically.

For the polymerization procedures with other molar ratios of [MMA]₀/[BMPB₂]₀/[FeCl₃·6H₂O]₀/[PPh₃]₀/[AIBN]₀ are the same as described above except for different amounts of corresponding chemicals and different polymerization temperatures (50, 70, 75, and 80 °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, FeCl₃·6H₂O, PPh₃, 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 °C.

Characterization. The number-average molecular weight (M_n,GPC) values and molecular weight distribution (Mₙ/Mₚ) values of the polymers were determined using Waters 1515 gel permeation chromatography (GPC) equipped with a refractive index detector (Waters 2414), using HR 1, HR 2, and HR 4 (7.8 × 300 mm, 5 μm beads) columns with measurable molecular weights in the range 10⁴ to 5 × 10⁵ g/mol. THF was used as an eluent at a flow rate of 1.0 mL/min at 30 °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 (Mₙ,GPC) and molecular weight distribution (Mₙ/Mₚ) values versus the conversion (b) for bulk and solution ICAR ATRP of MMA with molar ratio of [MMA]₀/[BMPB₂]₀/[FeCl₃·6H₂O]₀/[PPh₃]₀/[AIBN]₀ = 500/1/0.5/1.5/0.1 at 60 °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 CDCl₃ 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 [MMA]₀/[BMPB₂]₀/[FeCl₃·6H₂O]₀/[PPh₃]₀/[AIBN]₀ = 500/1/0.5/1.5/0.1 at 60 °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 can be obtained. The k_app values of 6.66 × 10⁻⁵ s⁻¹ and 2.16 × 10⁻⁵ 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 (Mₙ,GPC) values of the polymers increased linearly with
**Figure 2.** $\ln([M]_0/[M])$ versus reaction time (a) and number-average molecular weight ($M_n,\text{GPC}$) and molecular weight distribution ($M_n/M_m$) versus the conversion (b) for bulk ICAR ATRP of MMA with different catalyst concentrations. Polymerization conditions: MMA = 6 mL.

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]/[BMPB]$_2$ from 0/1, 0.1/1, 0.2/1 to 0.3/1) resulted in enhancement of polymerization rate, and that the $M_n,\text{GPC}$ values were close to their corresponding theoretical ones while keeping low $M_n/M_m$ values (<1.27) for the obtained polymers. However, when in the presence of larger amount of AIBN (i.e., [AIBN]/[BMPB]$_2$ = 0.5/1, entry 5 in Table 3), radical termination can not be neglected and the $M_n/M_m$ became broad ($M_n/M_m = 1.44$). 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 dependence of $\ln([M]_0/[M])$ was linear for various ratios of FeCl$_3$·6H$_2$O to AIBN, indicating that propagating radical species remained constant during the three polymerization processes. From Figure 2b, it can be seen that the polymer weights of PMMAs increased linearly with monomer conversion and the molecular weight distributions remained low ($M_n/M_m = 1.19–1.31$) for the both cases of the molar ratios of FeCl$_3$·6H$_2$O to AIBN = 0.8/0.1 and 0.4/0.1. However, if the molar ratio of FeCl$_3$·6H$_2$O to AIBN changed to 0.1/0.1, the molecular weights of the obtained PMMAs were further decreased to 23 and 11 ppm, the polymerizations were out of control with broad molecular weight distribution (1.51–1.77), but their $M_n,\text{GPC}$ values were close to the $M_n,\text{th}$ ones. Anyway, these results indicated the current iron-mediated ICAR ATRP is a highly active catalyst system.

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>$R^a$</th>
<th>time (h)</th>
<th>convn (%)</th>
<th>$M_{n,\text{th}}$ (g/mol)</th>
<th>$M_{n,\text{GPC}}$ (g/mol)</th>
<th>$M_{n,\text{NMR}}$ (g/mol)</th>
<th>$M_n/M_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500/1/0.5/1.5/0.1</td>
<td>6</td>
<td>42.1</td>
<td>21 100</td>
<td>24 500</td>
<td>23 500</td>
<td>1.27</td>
</tr>
<tr>
<td>2</td>
<td>500/1/0.4/1.2/0.1</td>
<td>5.5</td>
<td>40.8</td>
<td>20 400</td>
<td>24 400</td>
<td>24 100</td>
<td>1.24</td>
</tr>
</tbody>
</table>

$^a$Polymerization conditions: temperature = 60 °C. $R = [\text{MMA}]_0/[\text{BMPB}2]_0/[\text{FeCl}_3\cdot6\text{H}_2\text{O}]_0/[\text{PPh}_3]_0/[\text{AIBN}]_0$. $b$ $M_{n,\text{th}} = ([\text{MMA}]_0/[\text{BMPB}2]_0) \times M_{n,\text{MMA}} \times \text{conversion}\%$.
The 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 time (h) while keeping good controllability over the polymerization process. From Figure 3b, it can be seen that the molecular weights of PMMAs increased with monomer conversion linearly and the $M_n/M_w$ 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 [monomer]$_0$/[initiator]$_0$ while the $M_n$/$M_w$ values kept low (<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 $^1$H NMR spectroscopy, as shown in Figure 5. The chemical shift at $\delta = 7.02$ ppm (c in Figure 5) corresponded to the aromatic protons of the initiator BMPB$_2$.
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.,\textsuperscript{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 $\omega$-Cl atom. Therefore, the obtained PMMA could be used as a macroinitiator to conduct a chain extension reaction via ICAR ATRP method. The obtained PMMA ($M_{n,GPC} = 22500$ g/mol, $M_w/M_n = 1.24$) with CDCl$_3$ as solvent and tetramethylsilane (TMS) as internal standard. Polymerization conditions: [MMA]$_0$/[BMPB]$_0$/[FeCl$_3$·6H$_2$O]$_0$/[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, $t = 5.3$ h, conversion = 43.6%, temperature = 60 °C.

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]$_0$/[FeCl$_3$·6H$_2$O]$_0$/[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 ($I_{eff}$) = $M_{n,th}/M_{n,GPC}$.

Figure 5. $^1$H 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]$_0$/[FeCl$_3$·6H$_2$O]$_0$/[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]$_0$/[FeCl$_3$·6H$_2$O]$_0$/[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$_3$·6H$_2$O]$_0$/[PPh$_3$]$_0$/[AIBN]$_0 = 500/1/3/0.1$, MMA = 3 mL, time = 7.2 h, conversion = 39%, temperature = 60 °C. Chain extended PMMA 2: [MMA]$_0$/[PMMA]$_0$/[FeCl$_3$·6H$_2$O]$_0$/[PPh$_3$]$_0$/[AIBN]$_0 = 1200/1/3/0.1$, MMA = 6 mL, time = 16 h, conversion = 46.5%, temperature = 60 °C.
$M_n/M_w = 1.24$, and $M_n/GPC = 71100$ g/mol and $M_n/M_w = 1.23$, 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 $\Gamma$ 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 $R_n$ 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 $\Gamma$ are 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.

**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 PMMs with narrow molecular weight distributions can be obtained by this catalyst system, and this catalyst system shows efficient activity.

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**ACKNOWLEDGMENT**

The financial support from the National Natural Science Foundation of China (Nos. 20974071 and 20904036), the Specialized Research Fund for the Doctoral Program of Higher Education contract grant (Nos. 200802850005 and 2013201110005), the Qing Lan Project, the Program of Innovative Research Team of Soochow University, and a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD) is gratefully acknowledged.

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