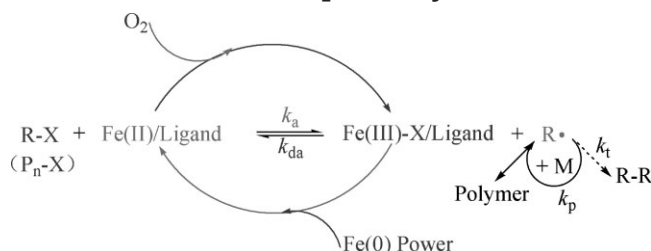


A Highly Efficient Iron-Mediated AGET ATRP of Methyl Methacrylate Using Fe(0) Powder as the Reducing Agent

Jian Qin, Zhenping Cheng, Lifen Zhang,* Zhengbiao Zhang, Jian Zhu, Xiulin Zhu*

A new method, AGET ATRP mediated by an iron(III) catalyst using Fe(0) powder as a reducing agent and MMA as a model monomer, is reported. The polymerizations can be carried out in the absence or presence of a limited amount of air and show the features of a “living”/controlled radical polymerization. MMA conversions of 90.3 and 80.0% can be obtained in 3.5 and 4.0 h in the absence/presence of a limited amount of air, respectively, for the iron-mediated AGET ATRP with a molar ratio of $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[Fe(0)]_0 = 600:1:0.5:2:0.1$ at 90 °C. PMMA with molecular weights of 55 060 and 47 790 g · mol⁻¹ and with molar-mass dispersity of 1.24 and 1.28, respectively, can be obtained correspondingly.



Introduction

Atom-transfer radical polymerization (ATRP) provides excellent control to create well-defined polymeric materials with complex architectures in a predictable manner including control over the molecular weight.^[1] Recently, several new ATRP techniques including simultaneous reverse and normal initiation (SR&NI) ATRP^[2] or initiators for continuous activator regeneration (ICAR) ATRP,^[3] activators generated by electron transfer (AGET) ATRP,^[4] and activators regenerated by electron transfer (ARGET) ATRP^[5] have been developed to reduce the amount of catalyst needed.

Various metal catalysts such as palladium, rhodium, nickel, ruthenium, chromium, copper, iron, and cobalt have been investigated in normal ATRP,^[1,6–13] but few have been reported except copper or iron in A(R)GET ATRP systems. Matyjaszewski and coworkers have done a number of excellent works using copper salts as the catalyst.^[4,5] In view of the intrinsic toxicity of the copper compounds, iron has attracted extensive attentions owing to its low toxicity, readily abundance, and biocompatibility although iron complexes were generally considered to be inferior to copper complexes for the control over polymerization.^[1c,14] Recently, an environmentally friendly iron(III)-mediated AGET ATRP system has been reported by our and Sen's groups in 2008.^[14c,15] Subsequently, we reported the iron-mediated AGET ATRPs of styrene^[14b,16] using vitamin C as the reducing agent. Chen et al. studied the AGET ATRP of acrylonitrile (AN) using iron catalyst.^[17] However, the reported iron(III)-mediated AGET ATRP catalyst systems for the polar monomers such as MMA and AN show lower catalytic activity even though they work efficiently for styrene.

J. Qin, Z. Cheng, L. Zhang, Z. Zhang, J. Zhu, X. Zhu
Jiangsu Key Laboratory of Advanced Functional Polymer Design
and Application, College of Chemistry, Department of Chemical
Engineering and Materials Science, Soochow University, Suzhou
215123, China
E-mail: zhanglifen@suda.edu.cn, xlzhu@suda.edu.cn

On the other hand, in an AGET ATRP process, a reducing agent is introduced to react with the higher oxidation state catalyst to generate (or regenerate) the activator (lower oxidation state catalyst); therefore, it plays an important role to achieve high catalyst activity in an AGET ATRP process. Recently, these groups of Matyjaszewski,^[18] Percec,^[19] Perrier,^[20] and Haddleton^[21] have reported that well-controlled radical polymerizations can be obtained in the presence of zerovalent metal such as copper(0) powder. Very recently, Matyjaszewski et al. reported a copper-mediated AGET ATRP process using zerovalent copper(0) wire as the reducing agent.^[22] In this work, an iron(III)-catalyzed AGET ATRP of MMA in the absence/presence of limited amounts of air using Fe(0) powder as the reducing agent was investigated for the first time. The polymerization showed the features of controlled/"living" free-radical polymerizations such as average-number molecular weights increasing linearly with monomer conversion and narrow molecular weight distributions for the obtained PMMAs. The current Fe(III)/Fe(0) catalyst system presents higher catalytic activity as compared with the reported AGET ATRP of MMA catalyzed by iron catalyst.

Experimental Part

Materials

The monomer, methyl methacrylate (MMA, >99%), was purchased from Shanghai Chemical Reagents Co. (Shanghai, China). It was passed through an alumina column, and stored at -18°C . Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (>99%), triphenylphosphine (PPh_3) (>99%), and Fe(0) powder (>99%, -200 mesh) were purchased from Shanghai Chemical Reagents Co. and used as received. Ethyl 2-bromoisobutyrate (EBiB) (98%) was purchased from Acros and used as received. Toluene (analytical reagent), anisole (analytical reagent), and all other chemicals were obtained from Shanghai Chemical Reagents Co. and used as received unless mentioned.

General Procedure for AGET ATRP of MMA

A typical bulk polymerization procedure was as follows: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (12.6 mg, 0.047 mmol), PPh_3 (49 mg, 0.187 mmol), anisole (2.0 mL), MMA (6.0 mL, 56.0 mmol), and EBiB initiator (13.8 μL , 0.093 mmol), Fe(0) powder (0.53 mg, 0.00946 mmol) were added to a dried ampoule under stirring. For the deoxygenated system, the ampoule was thoroughly bubbled with argon for 20 min to eliminate the dissolved oxygen in the solution. Then the ampoule was flame sealed and transferred into an oil bath held by a thermostat at the desired temperature (90, 60, or 25°C) to polymerize under stirring. For the oxygenated system, the solution containing of predetermined amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, PPh_3 , MMA, and EBiB initiator, Fe(0) powder was quickly added to a dried ampoule under air atmosphere at room temperature; then the ampoule was flame sealed directly (no bubbling with argon) and transferred into an oil bath held by a thermostat at the desired

temperature to polymerize under stirring. For the systems with anisole and toluene as the solvent, the procedures were similar to the bulk polymerization except the corresponding solvent added. The oxygen concentration $\{[\text{O}_2]_0 = 6.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, based solely on the reaction solution (8 mL)} was roughly calculated from the residual volume (air volume, 5.6 mL) of ampoule after adding the reaction solution but the solubility of oxygen in the liquids was not taken into account. After the desired polymerization time, the ampoule was cooled by immersing it into iced water. Afterwards, it was opened and the contents were dissolved in THF (2 mL), 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.

Chain Extension of PMMA Macroinitiator with MMA

A predetermined quantity of PMMA (obtained by polymerization of MMA in the absence of oxygen) was dissolved in 1.0 mL of anisole in a dried ampoule. The predetermined quantity of MMA, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, PPh_3 , and Fe(0) powder was added. The rest of the procedure was the same as the deoxygenated system described above. The chain extension polymerization was carried out under stirring at 90°C .

Characterization

The number-average molecular weight ($\overline{M}_{n,\text{GPC}}$) and molar-mass dispersity ($\overline{M}_w/\overline{M}_n$) of the polymers were determined using a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive-index detector (Waters 2414), using HR1, HR2, and HR4 ($7.8 \times 300 \text{ mm}^2$, 5 mm beads size) columns with measurable molecular weights in the range of 10^2 – $5 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$. THF was used as an eluent at a flow rate of $1.0 \text{ mL} \cdot \text{min}^{-1}$ and 30°C . The GPC samples were injected using a Waters 717 plus autosampler and calibrated with poly(MMA) standards from Waters. ^1H NMR spectrum was recorded on an Inova 400 MHz NMR instrument using CDCl_3 as the solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature.

Results and Discussion

Bulk Polymerization of MMA in the Absence of Oxygen

The polymerizations of MMA in the absence of oxygen using Fe(0) powder as the reducing agent were first studied in bulk. Figure 1a shows the kinetic plot of $\ln([M]_0/[M])$ against time for the AGET ATRP of MMA at 90°C . The first order kinetics with respect to the monomer concentration indicates that the propagating free-radical concentration was invariably stationary during the polymerization. Meanwhile, an induction period (≈ 50 min) was also observed in Figure 1a. As Zhang et al.^[15b] reported, in the beginning of polymerization, if no enough Fe(II) complexes were generated duly, the reaction shifted toward producing dormant radicals in the presence of a large amount of Fe(III)

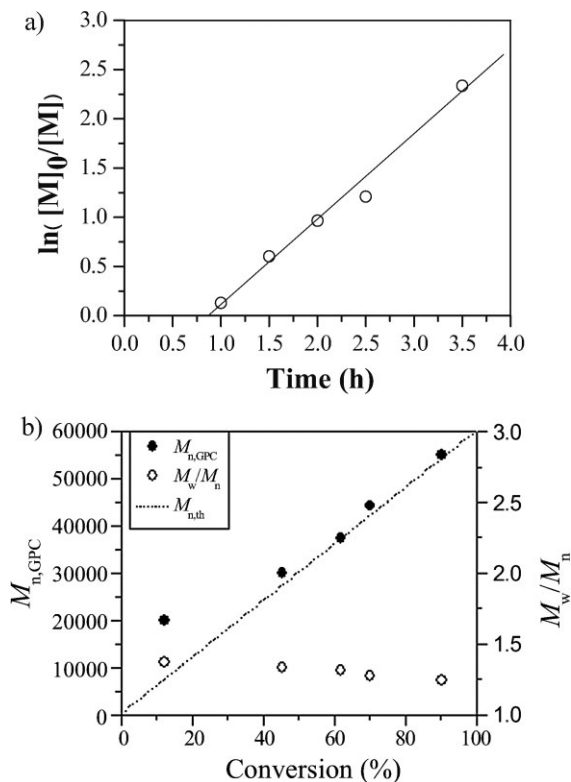


Figure 1. (a) $\ln([M]_0/[M])$ as a function of time and (b) $\bar{M}_{n,GPC}$ and PDI versus conversion for the bulk AGET ATRP of MMA in the absence of oxygen. Polymerization conditions: $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[Fe(o)]_0 = 600:1:0.5:2:0.1$, MMA = 6 mL, temperature = 90 °C.

species, resulting in too low radical concentration to polymerize with the appearance of the induction period. However, the concentration of Fe(II) complexes will increase continuously until establishing a dynamic equilibrium between the concentration of Fe(II) and Fe(III) species as the reaction proceeded. From Figure 1b, it is evident that the molecular weights ($\bar{M}_{n,GPC}$) of the polymers increased linearly with conversion while the molar-mass dispersity ($PDI = \bar{M}_w/\bar{M}_n$) of the obtained PMMAs remained low (less than 1.37). And moreover, $\bar{M}_{n,GPC}$ s were consistent with the corresponding theoretical values ($\bar{M}_{n,th}$) calculated according to the molar ratio of initial concentration of MMA to initiator EBiB, which indicated a high initiator efficiency ($I_{eff} = \bar{M}_{n,th}/\bar{M}_{n,GPC}$), almost up to 100%, in this case.

Solution Polymerization of MMA in the Absence of Oxygen

Solvent has significant effects on the solubility and coordination ability of catalyst with ligand, and then affects the activity of the catalyst. Figure 2a shows the kinetics of AGET ATRP of MMA in anisole in the absence of

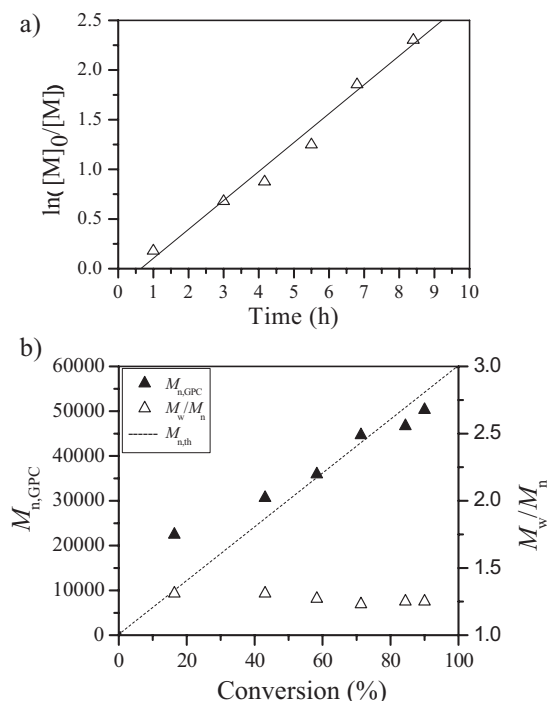


Figure 2. (a) $\ln([M]_0/[M])$ as a function of time and (b) $\bar{M}_{n,GPC}$ and PDI versus conversion for the solution AGET ATRP of MMA in anisole in the absence of oxygen. Polymerization conditions: $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[Fe(o)]_0 = 600:1:0.5:2:0.1$, MMA = 6 mL, anisole = 2 mL, temperature = 90 °C.

air. A first-order kinetic plot with an induction period of about 40 min was observed. Figure 2b shows that $\bar{M}_{n,GPC}$ s increased linearly with the monomer conversion and the $\bar{M}_w/\bar{M}_n$ of the obtained polymers remained low (less than 1.31), a little lower than that in bulk as mentioned above ($\bar{M}_w/\bar{M}_n < 1.37$). Similarly, the polymerization of MMA in toluene was also investigated. A first-order kinetic plot with an induction period of about 30 min was observed as shown in Figure 3a. Moreover, $\bar{M}_{n,GPC}$ s increased linearly with the monomer conversion and the $\bar{M}_w/\bar{M}_n$ of the obtained polymers remained low (Figure 3b). In addition, all the theoretical molecular weights were close to their corresponding experimental ones. These results indicated that excellent control over the polymerization of MMA could be obtained in solvents.

Bulk Polymerization of MMA in the Presence of Oxygen

As reported by Zhu's and Matyjaszewski's groups,^[14b,15b,15d,16a,23] AGET ATRP can be carried out in the presence of a limited amount of oxygen, which makes it easy to conduct polymerization especially for industrial scale. Therefore, no special deoxygenation procedures are required in order to obtain consistent polymerization

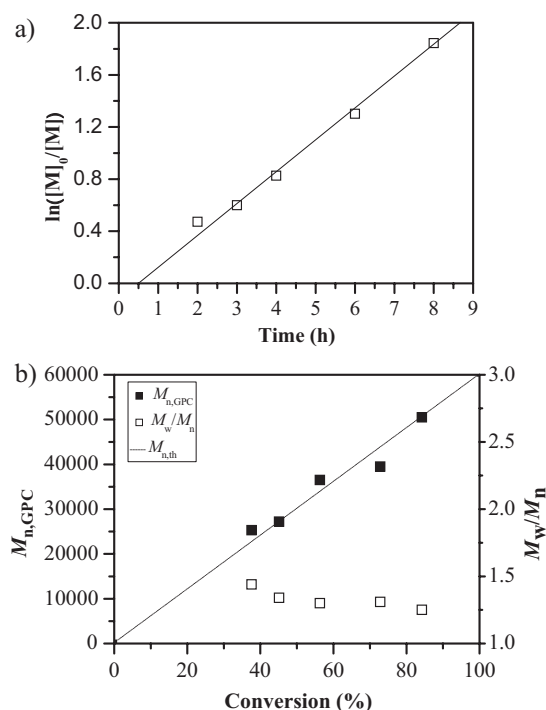


Figure 3. (a) $\ln([M]_0/[M])$ as a function of time and (b) $\bar{M}_{n,GPC}$ and PDI versus conversion for the solution AGET ATRP of MMA in toluene in the absence of oxygen. Polymerization conditions: $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[Fe(0)]_0 = 600:1:0.5:2:0.1$, MMA = 6 mL, toluene = 2 mL, temperature = 90 °C.

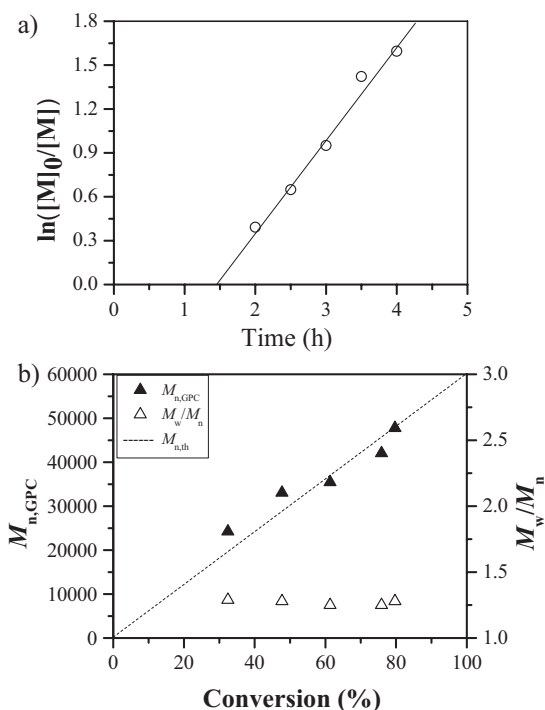
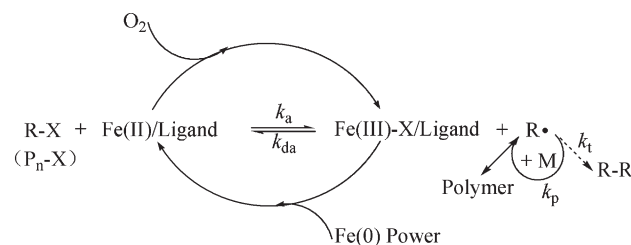


Figure 4. (a) $\ln([M]_0/[M])$ as a function of time and (b) $\bar{M}_{n,GPC}$ and PDI versus conversion for the bulk AGET ATRP of MMA in the presence of air. Polymerization conditions: $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[Fe(0)]_0 = 600:1:0.5:2:0.1$, MMA = 6 mL, $[O_2]_0 = 6.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, temperature = 90 °C.

kinetics. In this work, the polymerization of MMA in the presence of a limited amount of air (oxygen) was investigated, and the kinetic plot is shown in Figure 4a. As expected, a first-order kinetics with an induction period of about 85 min was observed, indicating the propagating radical concentration kept constant in the presence of a limited amount of air. From Figure 4b, $\bar{M}_{n,GPC}$ s increased linearly with the monomer conversion and the $\bar{M}_w/\bar{M}_n$ of the obtained PMMAs remained low (<1.29) during the polymerization process. Furthermore, the $\bar{M}_{n,GPC}$ s were consistent with the corresponding theoretical molecular weights, indicating excellent controllability over the polymerizations in this case. Thus, the iron-mediated AGET ATRP using Fe(0) powder as the reducing agent can not only be conducted in the presence of air but also does not destroy the controlled/"living" radical polymerization features of ATRP. The plausible polymerization mechanism is shown in Scheme 1, which is similar to the mechanism of AGET ATRP mediated by iron complexes with vitamin C (VC) as the reducing agent in the presence of a limited amount of air suggested by Zhang et al.^[15b] In the presence of the reducing agent Fe(0) powder, the electron transfer from Fe(0) powder to Fe(III) complexes would be the first step in this reaction. The Fe(II) complexes so formed can then react with organic halide to form propagating radicals or with oxygen to form

Fe(III) complexes. Then the formed Fe(III) complexes can be reduced to Fe(II) complexes by Fe(0) powder again. Finally, a dynamic equilibrium between the concentration of Fe(II) and Fe(III) species was established.

In addition, by calculating the apparent rate constant of the polymerization, k_p^{app} ($R_p = -d[M]/dt = k_p[P_n][M] = k_p^{app}[M]$), as determined from the kinetic plots, k_p^{app} of $2.37 \times 10^{-4} \text{ s}^{-1}$ for the bulk polymerization in the absence of air (Figure 1a), $0.81 \times 10^{-4} \text{ s}^{-1}$ for the solution polymerization in anisole in the absence of air (Figure 2a), $0.65 \times 10^{-4} \text{ s}^{-1}$ for the solution polymerization in toluene in the absence of air (Figure 3a), and $1.77 \times 10^{-4} \text{ s}^{-1}$ for the bulk polymerization in the presence



Scheme 1. Proposed mechanism for iron-mediated AGET ATRP using Fe(0) powder as a reducing agent.

of air (Figure 4a), respectively, were obtained. By comparison of these k_p^{app} values, it can be seen that the bulk polymerization rate in the presence of air and in anisole or toluene decreased due to the presence of oxygen in the air or the decreasing of monomer concentration in solution as compared with that in the absence of air. At the same time, from Figure 1a, 2a, 3a, and 4a, it can also be seen that the induction period shortened to ≈ 30 –40 min in the case of solution since the solvent anisole or toluene could improve the solubility of the catalyst complexes and facilitate to establish the dynamic equilibrium between the concentration of Fe(II) and Fe(III) species; and it increased to 85 min in the case of air due to the oxygen in the air could delay the establishment of dynamic equilibrium between the

concentration of Fe(II) and Fe(III) species as compared with that (50 min) in the case of bulk polymerization in the absence of air.

Effect of Temperature on Polymerization

It is well known that increasing the polymerization temperature can enhance the decomposition rate of initiator. In this work, the polymerizations were conducted in anisole or toluene at 25, 60, 90 °C, respectively, as shown in Table 1. From Table 1, it can be seen that 74.6% of conversion could be obtained after 2 h in anisole at 90 °C while only 67.4% of conversion was obtained after 16 h at 60 °C. In addition, the polymerization could also be carried

Table 1. Effect of solvent and temperature on the polymerization of MMA. Polymerization conditions: $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[Fe(0)]_0 = 300:1:0.5:1.5:0.1$, MMA = 3.0 mL; solvent = 1 mL.

Entry	Solvent	Temperature	Time	Conversion	$\overline{M}_{n,th}^a)$	$\overline{M}_{n,GPC}$	$\overline{M}_w/\overline{M}_n$
		[°C]	[h]	[%]	[g · mol ⁻¹]	[g · mol ⁻¹]	
1	anisole	90	2	74.6	22 800	23 300	1.27
2	anisole	60	16	67.4	20 400	24 500	1.28
3	anisole	25	281	66.5	20 100	27 200	1.33
4	toluene	90	3	76.1	23 200	23 600	1.22
5	toluene	60	40.2	59.7	18 100	21 400	1.29
6	toluene	25	338.2	59.1	17 900	26 100	1.29

$$^a)\overline{M}_{n,th} = ([M]_0/[EBiB]_0) \times M_{MMA} \times \text{conversion} + M_{EBiB}$$

Table 2. Effect of concentration of iron(III) on the polymerization of MMA. Polymerization conditions: MMA = 6.0 mL, solvent = 2 mL, temperature = 90 °C.

Entry	R ^{a)}	Fe ^{b)}	Time	Conversion	$\overline{M}_{n,th}^c)$	$\overline{M}_{n,GPC}$	$\overline{M}_w/\overline{M}_n$
		[ppm]	[h]	[%]	[g · mol ⁻¹]	[g · mol ⁻¹]	
1	600:1:1.0:2:0.1	1 020	8.5	95.5	57 500	46 600	1.22
2	600:1:0.8:2:0.1	840	8.7	99.0	59 600	46 600	1.25
3	600:1:0.6:2:0.1	650	10.5	97.6	58 700	54 700	1.23
4	600:1:0.5:2:0.1	560	10.3	96.3	57 900	57 100	1.21
5	600:1:0.4:2:0.1	470	11	94.1	56 600	47 800	1.29
6	600:1:0.1:2:0.1	190	76	81.6	49 200	51 000	1.42
7	400:1:0.5:2:0.1	840	7.3	98.8	39 700	38 500	1.21
8	800:1:0.5:2:0.1	420	8	85.7	68 700	60 700	1.30
9	1 200:1:0.5:2:0.1	280	21	82.9	99 600	81 300	1.33
10	1 600:1:0.5:2:0.1	210	10.5	72.6	116 000	96 400	1.37
11	2 000:1:0.5:2:0.1	170	20.5	65.9	132 000	109 000	1.36
12	5 000:1:0.5:16.6:0.1	70	19.5	40.0	200 000	141 600	1.46

^{a)}R = $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[Fe(0)]_0$; ^{b)}Total amount of Fe including Fe(III) from $FeCl_3 \cdot 6H_2O$ and Fe(0) powder;

$$^c)\overline{M}_{n,th} = ([M]_0/[EBiB]_0) \times M_{MMA} \times \text{conversion} + M_{EBiB}$$

out at a lower temperature (25 °C) although the polymerization rate was very slow, being 66.5% of monomer conversion after 281 h. Similar results were obtained for the polymerizations in toluene as shown in entries 4–6 of Table 1. At the same time, the PDI of the obtained polymers remained low (<1.33), indicating that the polymerization could be conducted in a wide range of temperature (25–90 °C) successfully.

Effect of Fe Concentration on Polymerization

From the discussion mentioned above, the balance of concentrations of Fe(III) and Fe(II) plays a key role in the polymerization. Thus, the effect of the concentration of Fe(III) was investigated in this work. The results are shown in Table 2. From entries 1–6 in Table 2, the polymerization rate increased with the concentration of Fe(III) as expected. This resulted from the increase concentration of Fe(II) reduced by the reducing agent Fe(0) powder in anisole. However, the features of the “living”/controlled polymerization were not destroyed while increasing the amount of Fe(III). As shown in entries 1–6, The $\bar{M}_w/\bar{M}_n$ values of the obtained PMMAs remained low (<1.42) and the $\bar{M}_{n, GPC}$ were close to the corresponding theoretical ones. Therefore, a wide range ratios of Fe(III)/Fe(0) (10/1–1/1) can be used in the AGET ATRP process at 90 °C.

In order to better understand the effect of concentration of the catalyst on AGET ATRP, different ratios of monomer to initiator were also investigated at 90 °C in anisole. The results are listed in entries 7–12 of Table 2. The polymerization rate decreased with the increase of the ratio of monomer to initiator. The polymer with higher molecular weight (more than 140 000 g · mol⁻¹, entry 12 in Table 2) could be obtained even if 70 ppm of Fe catalyst was used while the $\bar{M}_w/\bar{M}_n$ of the obtained PMMA remained relatively low (1.46), indicating a highly efficient catalyst system for the iron-mediated AGET ATRP of MMA using Fe(0) powder as the reducing agent.

Analysis of Chain End and Chain Extension

The chain end of the PMMA prepared in the presence of oxygen with anisole as a solvent was analyzed by ¹H NMR spectroscopy, as shown in Figure 5. The peak at $\delta = 4.09$ (**a** in Figure 5) corresponded to the methylene protons of the ethyl ester unit in the initiator EBiB, which revealed that the initiator EBiB moieties were attached to the polymer chain ends (α chain end). The signal at $\delta = 3.78$ (**c** in Figure 5) was attributed to the methyl ester group at the chain end, which deviates from the chemical shift ($\delta = 3.60$, **b** in Figure 5) of other methyl ester groups in PMMA because of the electron-attracting function of the ω -Cl atom.^[15b,24] These results suggested that the PMMA obtained in the presence of air was end-capped by the EBiB moieties at both α and ω chain

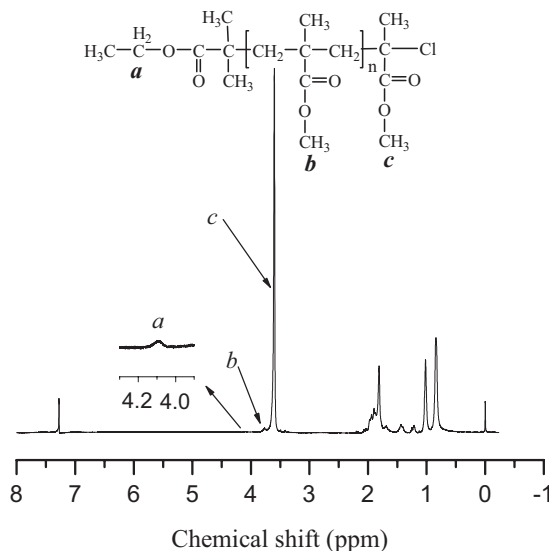


Figure 5. ¹H NMR spectrum of PMMA ($\bar{M}_{n, GPC} = 20\,300\text{ g} \cdot \text{mol}^{-1}$, $\bar{M}_w/\bar{M}_n = 1.17$) obtained in the presence of oxygen with CDCl₃ as a solvent and TMS as an internal standard. Polymerization conditions: [MMA]₀/[EBiB]₀/[FeCl₃ · 6H₂O]₀/[PPh₃]₀/[Fe]₀ = 200:1:0.5:1.5:0.1, [MMA]₀ = 3 mL, [O₂]₀ = $6.0 \times 10^{-3}\text{ mol} \cdot \text{L}^{-1}$, anisole = 1 mL, temperature = 90 °C, time = 0.9 h.

ends, being consistent with the mechanism of ATRP. Therefore, the obtained PMMA was used as macroinitiator to conduct chain-extension reaction. Figure 6 shows the GPC traces before and after extension of PMMA. The PMMA ($\bar{M}_{n, GPC} = 21\,500\text{ g} \cdot \text{mol}^{-1}$, $\bar{M}_w/\bar{M}_n = 1.23$) was used as the predecessor in chain extension experiment. The elution

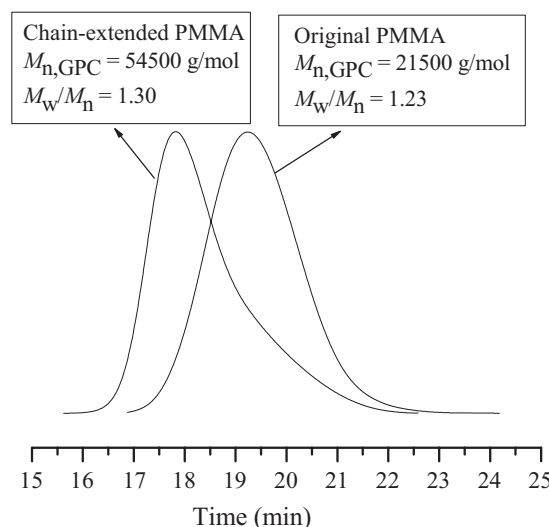


Figure 6. GPC traces before and after chain extension with PMMA as a macroinitiator. Original PMMA: [MMA]₀/[EBiB]₀/[FeCl₃ · 6H₂O]₀/[PPh₃]₀/[Fe(0)]₀ = 300:1:0.5:1.5:0.1, MMA = 3.0 mL, anisole = 1 mL, time = 1.5 h, conversion = 52.3%, chain-extended PMMA: [MMA]₀/[EBiB]₀/[FeCl₃ · 6H₂O]₀/[PPh₃]₀/[Fe(0)]₀ = 600:1:0.5:2:0.1, MMA = 2.3 mL, anisole = 1 mL, time = 5.1 h, conversion = 67.4%, temperature = 90 °C.

peak of the macroinitiator obviously shifted to the chain-extended PMMA with $\overline{M}_{n, \text{GPC}} = 54\,500 \text{ g} \cdot \text{mol}^{-1}$ and low $\overline{M}_w/\overline{M}_n$ (1.30). The successful chain extension reaction further verified the features of “living”/controlled free-radical polymerization of MMA.

Conclusion

Fe(0) powder can be used as a highly active reducing agent for the iron(III)-mediated AGET ATRP of MMA. The polymerization can be conducted in the presence of a limited amount of air and does not destroy the “living”/controlled radical polymerization characteristics of ATRP.

Acknowledgements: Financial support from the *National Natural Science Foundation of China* (Nos. 20874069, 50803044, 20974071, and 20904036), the *Specialized Research Fund for the Doctoral Program of Higher Education* (Nos. 200802850005, 20103201110005), and the *Qing Lan Project* and the *Program of Innovative Research Team of Soochow University* is gratefully acknowledged.

Received: December 4, 2010; Revised: January 24, 2011; Published online: March 15, 2011; DOI: 10.1002/macp.201000737

Keywords: atom-transfer radical polymerization (ATRP); iron catalyst; Fe(0) powder; kinetics (polym.); living radical polymerization

- [1] [1a] K. Matyjaszewski, J. H. Xia, *Chem. Rev.* **2001**, *101*, 2921; [1b] K. Kamigaito, T. Ando, T. Sawamoto, *Chem. Rev.* **2001**, *101*, 3689; [1c] N. V. Tsarevsky, K. Matyjaszewski, *Chem. Rev.* **2007**, *107*, 2270.
- [2] [2a] J. Gromada, K. Matyjaszewski, *Macromolecules* **2001**, *34*, 7664; [2b] M. Li, K. Min, K. Matyjaszewski, *Macromolecules* **2004**, *37*, 2106; [2c] M. Li, N. M. Jahed, K. Min, K. Matyjaszewski, *Macromolecules* **2004**, *37*, 2434.
- [3] [3a] L. Mueller, W. Jakubowski, W. Tang, K. Matyjaszewski, *Macromolecules* **2007**, *40*, 6464; [3b] A. Plichta, W. W. Li, K. Matyjaszewski, *Macromolecules* **2009**, *42*, 2330; [3c] L. F. Zhang, J. Miao, Z. P. Cheng, X. L. Zhu, *Macromol. Rapid Commun.* **2010**, *31*, 275.
- [4] [4a] K. Min, H. F. Gao, K. Matyjaszewski, *J. Am. Chem. Soc.* **2005**, *127*, 3825; [4b] W. Jakubowski, K. Matyjaszewski, *Macromolecules* **2005**, *38*, 4139; [4c] J. K. Oh, H. C. Dong, R. Zhang, K. Matyjaszewski, H. Schlaad, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4764; [4d] P. Kwiatkowski, J. Jurczak, J. Pietrasik, W. Jakubowski, L. Mueller, K. Matyjaszewski, *Macromolecules* **2008**, *41*, 1067; [4e] W. W. Li, K. Min, K. Matyjaszewski, F. Stoffelbach, B. Charleux, *Macromolecules* **2008**, *41*, 6387; [4f] Y. Kitayama, Y. Kagawa, Hideto. Minami, M. Okubo, *Langmuir* **2010**, *26*, 7029; [4g] H. C. Dong, K. Matyjaszewski, *Macromolecules* **2010**, *43*, 4623.
- [5] [5a] W. Jakubowski, K. Min, K. Matyjaszewski, *Macromolecules* **2006**, *39*, 39; [5b] W. A. Braunecker, K. Matyjaszewski, *Prog. Polym. Sci.* **2007**, *32*, 93; [5c] R. Nicolay, Y. Kwak, K. Matyjaszewski, *Angew. Chem.* **2010**, *122*, 551.
- [6] P. Lecomte, I. Drapier, P. Dubois, P. Teyssié, R. Jérôme, *Macromolecules* **1997**, *30*, 7631.
- [7] G. Moineau, C. Granel, P. Dubois, R. Jérôme, P. Teyssié, *Macromolecules* **1998**, *31*, 542.
- [8] [8a] R. Gong, S. Maclaughlin, S. P. Zhu, *Appl. Surf. Sci.* **2008**, *254*, 6802; [8b] M. Stol, D. J. M. Snelders, M. D. Godbole, R. W. A. Havenith, D. Haddleton, G. Clarkson, M. Lutz, A. L. Spek, G. P. M. van Klink, G. van Koten, *Organometallics* **2007**, *26*, 3985; [8c] E. Duquesne, Ph. Dege, J. Habimana, Ph. Dubois, *Chem. Commun.* **2004**, 640; [8d] P. Li, K. Y. Qiu, *Polymer* **2002**, *43*, 5873; [8e] E. Duquesne, J. Habimana, P. Degée, P. Dubois, *Macromolecules* **2005**, *38*, 9999.
- [9] [9a] T. Shibata, K. Satoh, M. Kamigaito, Y. Okamoto, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 3609; [9b] K. Nakatani, T. Terashima, M. Sawamoto, *J. Am. Chem. Soc.* **2009**, *131*, 13600; [9c] T. Terashima, R. Motokawa, S. Koizumi, M. Sawamoto, M. Kamigaito, T. Ando, T. Hashimoto, *Macromolecules* **2010**, *43*, 8218.
- [10] Y. H. Champouret, K. C. MacLeod, M. K. Smith, O. B. Patrick, R. Poli, *Organometallics* **2010**, *29*, 3125.
- [11] J. M. Muñoz-Molina, T. R. Belderrain, P. J. Pérez, *Macromolecules* **2010**, *43*, 3221.
- [12] [12a] K. Matsubara, M. Matsumoto, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4222; [12b] H. Kaneyoshi, K. Matyjaszewski, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 447; [12c] S. Maria, H. Kaneyoshi, K. Matyjaszewski, R. Poli, *Chem. Eur. J.* **2007**, *13*, 2480; [12d] X. H. Zhong, Y. M. Zhang, H. Li, Y. H. Luan, Y. G. Liu, *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1416.
- [13] [13a] S. M. Zhu, D. Y. Yan, *Macromol. Rapid Commun.* **2000**, *21*, 1209; [13b] S. M. Zhu, D. Y. Yan, *Macromolecules* **2000**, *33*, 8233; [13c] K. Matyjaszewski, M. Wei, J. Xia, N. E. McDermott, *Macromolecules* **1997**, *30*, 8161; [13d] G. Moineau, P. Dubois, R. Jerome, T. Senninger, P. Teyssié, *Macromolecules* **1998**, *31*, 545; [13e] S. Zhu, D. Yan, G. Zhang, M. Li, *Macromol. Chem. Phys.* **2000**, *201*, 2666; [13f] C. Hou, R. Qu, C. Sun, C. Ji, C. Wang, L. Ying, N. Jiang, F. Xiu, L. Chen, *Polymer* **2008**, *49*, 3424.
- [14] [14a] L. J. Bai, L. F. Zhang, J. Zhu, Z. P. Cheng, X. L. Zhu, *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 2002; [14b] Z. G. Xue, D. He, S. K. Noh, W. S. Lyoo, *Macromolecules* **2009**, *42*, 2949; [14c] L. F. Zhang, Z. P. Cheng, S. P. Shi, Q. H. Li, X. L. Zhu, *Polymer* **2008**, *49*, 3054.
- [15] [15a] R. Luo, A. Sen, *Macromolecules* **2008**, *41*, 4514; [15b] L. F. Zhang, Z. P. Cheng, F. Tang, Q. H. Li, X. L. Zhu, *Macromol. Chem. Phys.* **2008**, *209*, 1705.
- [16] [16a] L. F. Zhang, Z. P. Cheng, Y. T. Lü, X. L. Zhu, *Macromol. Rapid Commun.* **2009**, *30*, 543; [16b] L. J. Bai, L. F. Zhang, Z. B. Zhang, Y. F. Tu, N. C. Zhou, Z. P. Cheng, X. L. Zhu, *Macromolecules* **2010**, *43*, 9283; [16c] L. F. Zhang, Z. P. Cheng, Z. B. Zhang, D. Y. Xu, X. L. Zhu, *Polym. Bull.* **2010**, *64*, 233.
- [17] [17a] H. Chen, L. X. Yang, Y. Liang, Z. N. Hao, Z. X. Lu, *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 3202; [17b] G. X. Zong, H. Chen, C. H. Wang, D. L. Liu, Z. H. Hao, *J. Appl. Polym. Sci.* **2010**, *118*, 3673.
- [18] [18a] K. Matyjaszewski, S. Coca, S. G. Gaynor, M. Wei, B. E. Woodworth, *Macromolecules* **1997**, *30*, 7348; [18b] K. Matyjaszewski, J. Pyun, S. G. Gaynor, M. Wei, B. E. Woodworth, *Macromol. Rapid Commun.* **1998**, *19*, 665;

- [18c] K. Matyjaszewski, N. V. Tsarevsky, W. A. Braunecker, H. C. Dong, J. Y. Huang, W. Jakubowski, Y. Kwak, R. Nicolay, W. Tang, J. A. Yoon, *Macromolecules* **2007**, *40*, 7795.
- [19] [19a] V. Percec, T. Guliashvili, J. S. Ladislaw, A. Wistrand, A. Stjerndahl, M. J. Sienkowska, M. J. Monteiro, S. Sahoo, *J. Am. Chem. Soc.* **2006**, *128*, 14156; [19b] B. M. Rosen, V. Percec, *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 5663; [19c] N. H. Nguyen, B. M. Rosen, G. Lligadas, V. Percec, *Macromolecules* **2009**, *42*, 2379; [19d] N. H. Nguyen, B. M. Rosen, V. Percec, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 1752.
- [20] [20a] J. Tom, B. Hornby, A. West, S. Harrisson, S. Perrier, *Polym. Chem.* **2010**, *1*, 420; [20b] B. Hornby, A. West, J. Tom, C. Waterson, S. Harrisson, S. Perrier, *Macromol. Rapid Commun.* **2010**, *31*, 1276.
- [21] M. E. Levere, I. Willoughby, S. O'Donohue, A. de Cuendias, A. J. Grice, C. Fidge, C. R. Becer, D. M. Haddleton, *Polym. Chem.* **2010**, *1*, 1086.
- [22] A. J. D. Magenau, Y. Kwak, K. Matyjaszewski, *Macromolecules* **2010**, *43*, 9682.
- [23] [23a] F. Tang, L. F. Zhang, J. Zhu, Z. P. Cheng, X. L. Zhu, *Ind. Eng. Chem. Res.* **2009**, *48*, 6216; [23b] Q. Li, L. F. Zhang, Z. B. Zhang, N. C. Zhou, Z. P. Cheng, X. L. Zhu, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2006; [23c] K. Min, W. Jakubowski, K. Matyjaszewski, *Macromol. Rapid Commun.* **2006**, *27*, 594; [23d] K. Matyjaszewski, H. C. Dong, W. Jakubowski, J. Pietrasik, A. Kusumo, *Langmuir* **2007**, *23*, 4528.
- [24] [24a] T. Audo, M. Kamigaito, M. Sawamoto, *Macromolecules* **1997**, *30*, 4507; [24b] Z. P. Cheng, X. L. Zhu, G. J. Chen, W. J. Xu, J. M. Lu, *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3823.