



AGET ATRP of methyl methacrylate catalyzed by FeCl₃/iminodiacetic acid in the presence of air

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ABSTRACT

The recently developed living free-radical polymerization system, atom transfer radical polymerization (AGET ATRP), was used for methyl methacrylate (MMA) polymerization in the presence of a limited amount of air, using a novel catalyst system based on iron (FeCl₃) complexes with iminodiacetic acid (IDA) and using ascorbic acid (VC) as a reducing agent. The kinetics of AGET ATRPs of MMA with different amounts of VC in the presence of air was investigated. The results of the polymerizations demonstrated the features of “living”/controlled free-radical polymerization such as the number-average molecular weights increasing linearly with monomer conversion and narrow molecular weight distributions ($M_w/M_n = 1.31\text{--}1.44$).

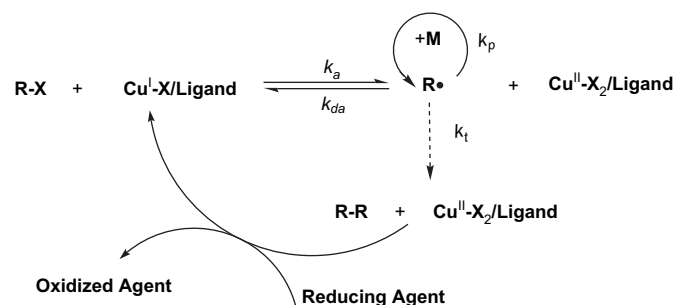
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1. Introduction

Metal-mediated atom transfer radical polymerization (ATRP) is a versatile technique for the synthesis of a wide range of materials derived from all kinds of monomers such as styrenes, methacrylates and acrylates [1]. However, normal ATRP has some limitations such as the catalyst used is sensitive to air and humidity. In order to overcome these drawbacks of normal ATRP, more recently, an improved ATRP technique, activators generated by electron transfer ATRP (AGET ATRP) process [2], has been developed. The typical mechanism is shown in Scheme 1 [2h]. In a typical AGET ATRP system, a transition-metal complex in its oxidatively stable state such as Cu(II) complex, a reverse ATRP catalyst, is used as catalyst instead of copper(I) complexes for normal ATRP system, and an alkyl halide for a normal ATRP initiator is also used as the initiator for the AGET ATRP system. However, the activators, copper(I) complexes, are produced by an in situ reduction of the copper(II) complexes with a reducing agent such as tin(II) 2-ethylhexanoate (Sn(EH)₂). For example, Jakubowski and Matyjaszewski [2a] studied the AGET ATRPs with different monomers such as styrene, methyl methacrylate, *n*-butyl acrylate and octadecyl methacrylate in toluene or anisole using Sn(EH)₂ as the reducing agent, and well-defined polymers were synthesized. Min et al. [2b] successfully introduced the AGET ATRP technique into miniemulsion to synthesize pure linear and star-shaped block copolymers. Wu et al. [2g]

successfully prepared brush macromolecules having poly(*l*-lactide) (PLLA) and poly(styrene) (PS) side chains by combination of AGET ATRP and ring-opening polymerization methods. Esteves et al. [2m] synthesized CdS quantum dot (QD)-poly(acrylate) nanocomposites using the surface-initiated AGET ATRP in a miniemulsion. From these above reported documents, the AGET ATRP shows the advantages of facile preparation, storage, and handling of ATRP catalysts, better control over the polymerization, and synthesis of pure block copolymers. Thus, the AGET ATRP has all benefits of normal ATRP and reverse ATRP [3], and remains tolerant to air during the operation.

As normal ATRP, AGET ATRP is also catalyzed by complexes of transition metals and suitable ligands that mediate a dynamic equilibrium between dormant and active polymer chains. The main role of the ligand in ATRP is to solubilize the transition-metal salt in the organic media and to adjust the redox potential of the metal



Scheme 1. Mechanism for activators generated by electron transfer for atom transfer radical polymerization (AGET ATRP).

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center for appropriate reactivity and dynamics for the atom transfer [4]. Building on the known use of ligands, nitrogen-based ligands such as 2,2'-bipyridine (bpy) and phosphorus-based ligands (i.e., triphenylphosphine (PPh₃)) are the most frequently used ones. However, they are usually toxic to human health. Thus, it is very important to find new AGET ATRP catalytic systems that are less toxic to human health, especially for the synthesis of materials for biomedical applications. Various organic acids with less toxicity such as pyromellitic acid [5], iminodiacetic acid [3c,6], succinic acid [7] and isophthalic acid [8] have been successfully employed as new ligands in the iron-mediated atom transfer radical polymerization of vinyl monomers such as styrene (St) and methyl methacrylate (MMA). The systems with different kinds of organic acids can react from 25 °C to 130 °C resulting in controlled "living" radical polymerization with relatively narrow molecular weight distributions of the resulting polymers ($M_w/M_n = 1.2\text{--}1.5$) [6a].

To the best of our knowledge, only copper-catalyzed AGET ATRP has been reported [2]. Actually, the natural capacity of the body to store and transport iron [9] as well as the advantages of AGET ATRP for the tolerance to air during the operation make this iron metal particularly attractive for use as an AGET ATRP catalyst. In this paper, the AGET ATRP of MMA was investigated using FeCl₃ as the catalyst, a less toxic organic acid, iminodiacetic acid (IDA), as the ligand, and ascorbic acid (VC) as the reducing agent. The aim of the present work is to develop a novel AGET ATRP system mediated by iron complexes with less toxic organic acid.

2. Experimental section

2.1. 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, and then dried over anhydrous magnesium sulfate, distilled under reduced pressure and stored at -18 °C. Iron(III) chloride hexahydrate (FeCl₃·6H₂O) (>99%), iminodiacetic acid (IDA) (>98%) and ascorbic acid (VC) (>99.7%) were purchased from Shanghai Chemical Reagents Co. (Shanghai, China) and used as-received. Ethyl 2-bromoisobutyrate (EBiB) (>98%) was purchased from Acros and used as-received. *N,N*-Dimethylformamide (DMF) (analytical reagent), tetrahydrofuran (THF) (analytical reagent) and all other chemicals were obtained from Shanghai Chemical Reagents Co. and used as-received unless mentioned.

2.2. General procedure for AGET ATRP of MMA

A typical polymerization procedure for the molar ratio of $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[IDA]_0/[VC]_0 = 200/1/1/2/0.75$ was as follows: FeCl₃·6H₂O (38.7 mg, 0.142 mmol), IDA (37.6 mg, 0.284 mmol), DMF (1 mL), MMA (3.0 mL, 28.4 mmol) and EBiB initiator (21 μL, 0.140 mmol) were added to a dried ampoule to give a mixed solution (solution A) under stirring. The ampoule was thoroughly bubbled with argon for 20 min to eliminate the dissolved oxygen in solution A. For the deoxygenated system, a bubbled solution of VC (18.7 mg, 0.105 mmol) in DMF (1 mL) was added, and then the ampoule was flame sealed and transferred into an oil bath held by a thermostat at the desired temperature (90 °C) to polymerize under stirring. It is noted that the method using argon bubbling to remove the oxygen in the reaction solution may not be an efficient one to obtain oxygen-free system. A better way to do this is the pump-freeze-thaw process (usually three cycles). For the air system, the bubbled solution A, containing predetermined amount of FeCl₃·6H₂O, IDA, DMF, MMA and EBiB initiator, was quickly added to a dried ampoule under air atmosphere

via syringe at room temperature, a bubbled solution of VC (18.7 mg, 0.105 mmol) in DMF (1 mL) was subsequently added, 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 (90 °C) to polymerize under stirring. The oxygen concentration from air ($[O_2] = 6.2 \times 10^{-3}$ mol/L, based on the reaction solution (5 mL)) was calculated from the residual volume (air volume, 3.3 mL) of ampoule after adding the reaction solution [10]. 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) 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.

2.3. Chain extension of PMMA using PMMA as macroinitiators

A predetermined quantity of PMMA (obtained by polymerization of MMA in the presence of air) was dissolved in 3 mL of DMF in a dried ampoule. The predetermined quantity of MMA, FeCl₃·6H₂O, IDA and VC was added in this order. The rest of the procedure was same as the deoxygenated system described above. The chain-extension polymerization was carried out under stirring at 90 °C.

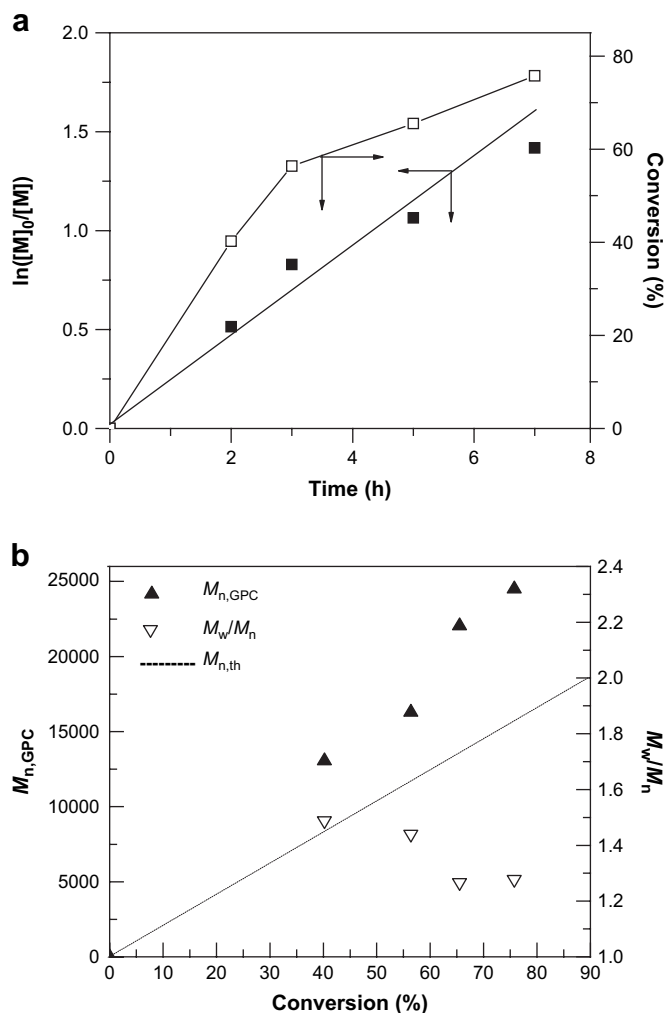


Fig. 1. $\ln([M]_0/[M])$ and conversion as a function of time (a) and average-number molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) versus the conversion (b) for AGET ATRP of MMA in the absence of oxygen. Polymerization conditions: $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[IDA]_0/[VC]_0 = 200/1/1/2/0.75$; $[MMA]_0 = 5.6$ M; temperature = 90 °C; solvent = DMF.

2.4. 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, $5 \mu\text{m}$ beads' size) columns with molecular weights in the range 10^2 – 5×10^5 g/mol. THF was used as an eluent at a flow rate of 1.0 mL/min and 30°C . The GPC samples were injected using a Waters 717 plus autosampler and calibrated with poly(methyl methacrylate) standards from Waters. ^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.

3. Results and discussion

3.1. The polymerization of MMA in the absence of oxygen (deoxygenated system)

To the best of our knowledge, reported AGET ATRPs were all mediated by copper catalyst until now. As mentioned above, iron

salts have better biocompatibility than copper salts, and a number of excellent normal ATRP systems mediated by iron catalyst have been reported [11], however, there have not been any reports on the AGET ATRP mediated by iron catalyst. To investigate feasibility of the iron(III)-mediated AGET ATRP, a typical monomer MMA was selected in this work. The polymerizations of MMA in the absence of oxygen were first investigated. We used FeCl_3 as the catalyst, IDA as the ligand, and EBiB as the initiator. Fig. 1a shows the kinetic plot of $\ln([M]_0/[M])$ versus time for the ATRP of MMA at 90°C . The linearity of the plot indicated that the polymerization was approximately first order with respect to the monomer concentration. The slope of the kinetic plots indicated that in the polymerization process, the number of active species was constant. The monomer conversion reached 76% after 7 h. From Fig. 1b, the molecular weight ($M_{n, \text{GPC}}$) values of the polymers increased linearly with conversion, meanwhile the molecular weight distribution (M_w/M_n) values of the obtained PMMAs reduced to less than 1.3 for higher monomer conversion (76%).

3.2. The polymerization of MMA in the presence of air (air system)

In normal ATRP system, oxygen acts as a scavenger for lower oxidized transition-metal salts such as copper(I) chloride. Thus special deoxygenation procedures are required in order to obtain consistent kinetics, which is not economical and time-consuming for industrial scale production. The AGET ATRP process makes it possible to overcome this problem, since reducing agents such as VC or tin(II) 2-ethylhexanoate do not generate initiating radicals but are exclusively used for the reduction of higher oxidized transition metal to lower oxidized transition-metal activating species in situ in AGET ATRP systems. Therefore, to develop a technique so that the polymerization can be carried out in the presence of air/oxygen is much appreciated for controlled/"living" radical polymerization processes. Hizal and coworkers reported a copper-catalyzed controlled/"living" radical polymerization system in the presence of air in which Cu(I) was produced in situ via electron transfer reaction between phenols and Cu(II) [12]. Jakubowski and Matyjaszewski reported a copper-mediated AGET ATRP process in the presence of air, in which the Cu(I) was produced in situ via electron transfer reaction between VC or tin(II) 2-ethylhexanoate

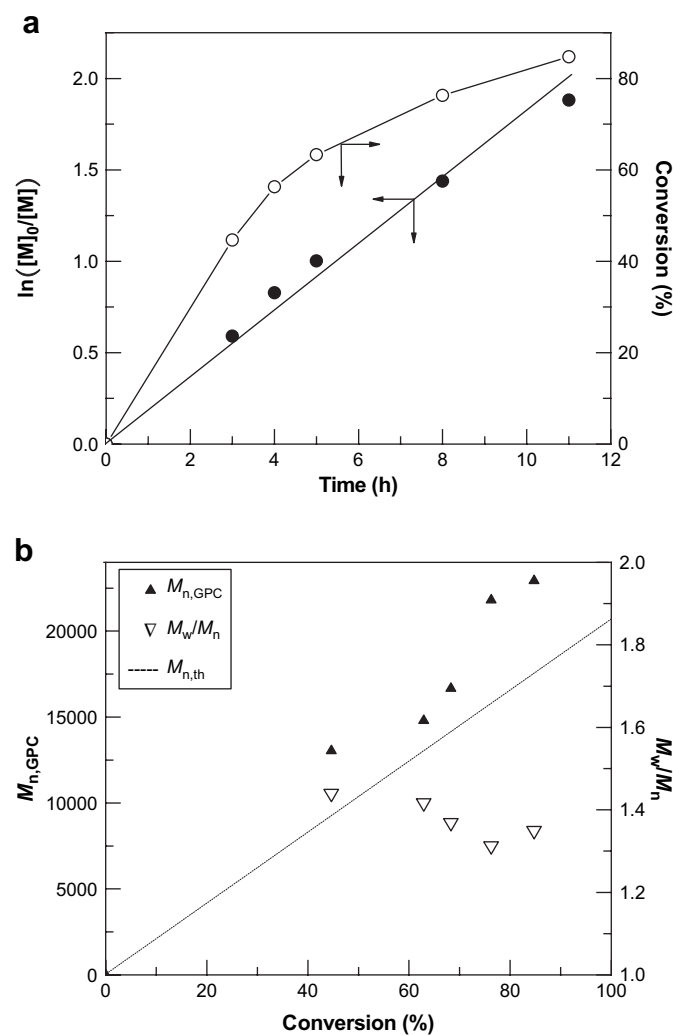
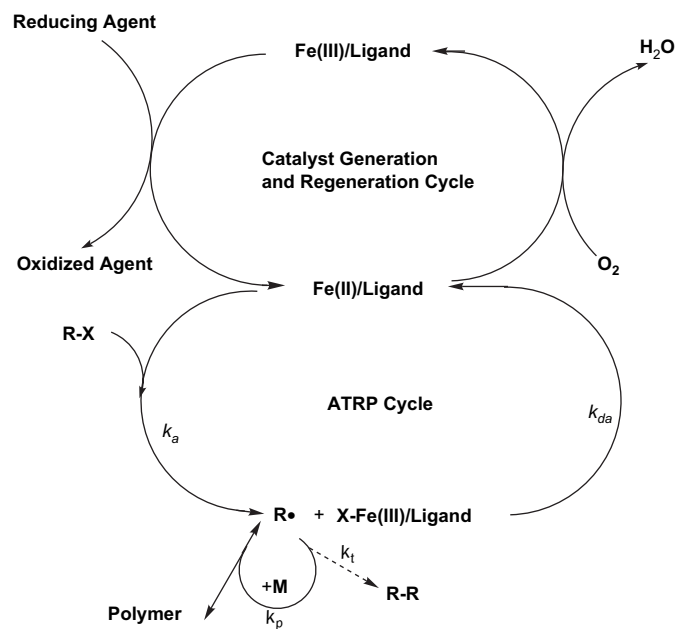


Fig. 2. $\ln([M]_0/[M])$ and conversion as a function of time (a) and average-number molecular weight ($M_{n, \text{GPC}}$) and molecular weight distribution (M_w/M_n) versus the conversion (b) for AGET ATRP of MMA in the presence of air. Polymerization conditions: $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[\text{IDA}]_0/[\text{VC}]_0 = 200/1/1/2/0.75$; $[\text{MMA}]_0 = 5.6$ M; temperature = 90°C ; solvent = DMF, $[\text{O}_2] = 6.2 \times 10^{-3}$ mol/L.



Scheme 2. Proposed mechanism for activators generated by electron transfer for atom transfer radical polymerization (AGET ATRP) in the presence of air (air system).

and Cu(II) [13]. However, to the best of our knowledge, there have been no reports on the iron-mediated AGET ATRP in the presence of air. In this work, the iron-mediated AGET ATRPs of MMA in the presence of a limited amount of air were investigated. Fig. 2a shows the kinetic plot of AGET ATRP of MMA under a molar ratio of $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[IDA]_0/[VC]_0 = 200/1/1/2/0.75$ at $90^\circ C$. A first order kinetics through zero point was still observed, indicating that the propagating radical concentration kept constant in the presence of oxygen. Fig. 2b shows that $M_{n,GPC}$ values increased linearly with the monomer conversion (up to 85%) and the M_w/M_n values of the obtained PMMAs were kept low during the polymerization process. Thus, the iron-mediated AGET ATRP not only can be conducted in the presence of oxygen but also does not destroy the controlled/"living" radical polymerization characteristics of ATRP. The plausible polymerization mechanism is shown in Scheme 2, which is similar to the mechanism of ATRP mediated by copper complexes in the presence of a limited amount of air suggested by Hizal et al. [12b]. In the presence of the reducing agent VC, the electron transfer from VC to Fe(III) complexes would be the first step in this reaction. The Fe(II) complexes so formed can then undergo two distinctly different types of reactions, reacting with organic halide to form propagating radicals and/or with oxygen from air to form iron salt in its higher oxidation state, which is then reduced to Fe(II) complexes by excess VC. Such regeneration of

Fe(II) complexes would be expected to lead to polymerization as a result of the consumption of oxygen and VC as well.

3.3. Effect of concentration of the reducing agent VC on polymerization in the presence of air

In order to better understand the AGET ATRP mechanism in the presence of air, the effect of different amounts of VC on the MMA polymerizations was also studied at $90^\circ C$. The results are shown in Figs. 3 and 4. Figs. 3 and 4 show the plots of the kinetics and effect of monomer conversions on molecular weights under a molar ratio of $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[IDA]_0/[VC]_0 = 200/1/1/2/1$ and $200/1/1/2/0.5$, respectively. In the two cases, the resulting slopes, as, respectively, shown in Figs. 3a and 4a, indicated that the polymerization proceeded with an approximately constant number active species for the duration of the polymerizations up to 89% monomer conversion. As expected, decreasing the molar ratio of $[FeCl_3 \cdot 6H_2O]_0/[VC]_0$, namely decreasing the concentrations of reducing agent VC, decreased the apparent constant of polymerization, k_p^{app} ($R_p = -d[M]/dt = k_p[P_n][M] = k_p^{app}[M]$), as determined from the kinetic slopes, indicating the decrease of the polymerization rate (R_p). According to the kinetic slopes, all k_p^{app} values can be calculated as listed in Table 1. As demonstrated in Scheme 2, the

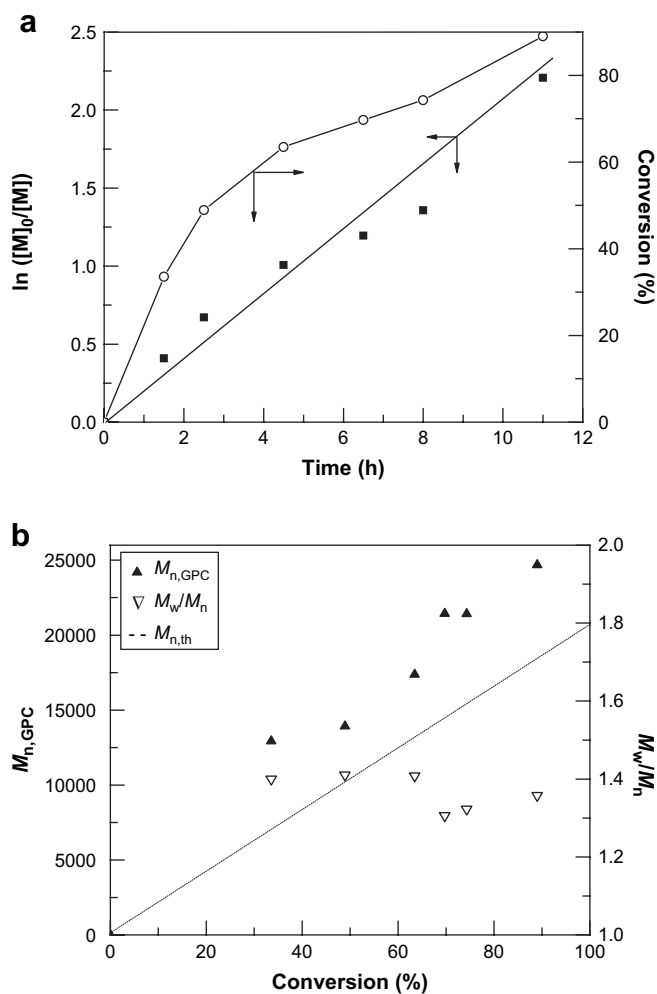


Fig. 3. $\ln([M]_0/[M])$ and conversion as a function of time (a) and average-number molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) versus the conversion (b) for AGET ATRP of MMA in the presence of air. Polymerization conditions: $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[IDA]_0/[VC]_0 = 200/1/1/2/1$; $[MMA]_0 = 5.6$ M; temperature = $90^\circ C$; solvent = DMF, $[O_2] = 6.2 \times 10^{-3}$ mol/L.

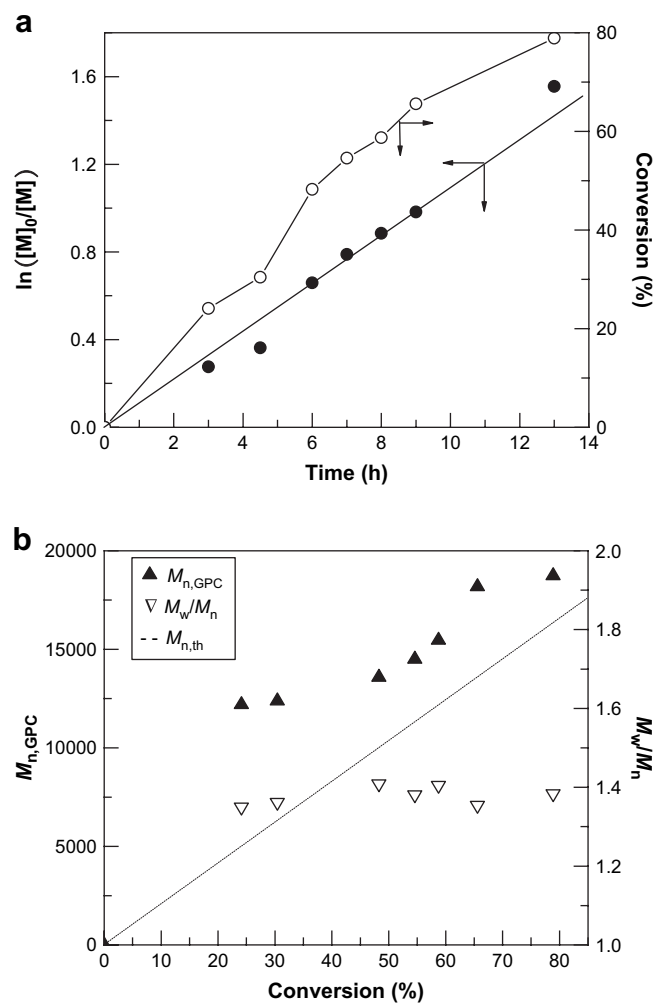


Fig. 4. $\ln([M]_0/[M])$ and conversion as a function of time (a) and average-number molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) versus the conversion (b) for AGET ATRP of MMA in the presence of oxygen. Polymerization conditions: $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[IDA]_0/[VC]_0 = 200/1/1/2/0.5$; $[MMA]_0 = 5.6$ M; temperature = $90^\circ C$; solvent = DMF, $[O_2] = 6.2 \times 10^{-3}$ mol/L.

Table 1
Comparison of k_p^{app} for the AGET ATRP of MMA under different concentrations of reducing agent (VC)

Entry	1	2	3	4
Molar ratio of $[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[\text{VC}]_0$	1/0.75 ^a	1/1 ^b	1/0.75 ^b	1/0.5 ^b
k_p^{app} (s^{-1})	5.48×10^{-5}	5.03×10^{-5}	4.69×10^{-5}	3.37×10^{-5}

Polymerization conditions: $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[\text{IDA}]_0/[\text{VC}]_0 = 200/1/1/2/x$ ($x = 1, 0.75, 0.5$); $[\text{MMA}]_0 = 5.6 \text{ M}$; temperature = 90°C ; solvent = DMF.

^a In the absence of air.

^b In the presence of air, $[\text{O}_2] = 6.2 \times 10^{-3} \text{ mol/L}$.

reducing agent VC plays a key role in the AGET ATRP process. Increasing the amount of VC resulted in the higher concentration of Fe(II) salts produced by the in situ reduction of an iron(III) complex with VC, and then increased concentrations of the propagating radicals in the polymerization system, resulting in the increase of polymerization rate. From entries 2–4 in Table 1, when the molar ratio of $[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[\text{VC}]_0$ increased from 1/0.5, 1/0.75 to 1/1, the k_p^{app} values correspondingly increased from $3.37 \times 10^{-5} \text{ s}^{-1}$, $4.69 \times 10^{-5} \text{ s}^{-1}$ to $5.03 \times 10^{-5} \text{ s}^{-1}$, indicating the increase of polymerization rate in air system. By comparison of entries 1 and 3, the k_p^{app} value of $5.48 \times 10^{-5} \text{ s}^{-1}$ for the polymerization in the absence of air was larger than that of $4.69 \times 10^{-5} \text{ s}^{-1}$ for the polymerization in the presence of air. This is due to that the oxygen in the air system consumed a part of the VC as demonstrated in Scheme 2 and that oxygen also played the role of direct inhibitor to quench the propagating radicals, resulting in reduced polymerization rate. From Figs. 3b and 4b, the M_w/M_n values of the obtained PMMAs were narrower (1.31–1.41). $M_{n,GPC}$ values increased linearly with conversion, indicating that the iron-mediated AGET ATRP of MMA with IDA as the ligand in the presence of a limited amount of air was a controlled/“living” radical polymerization.

3.4. AGET ATRP with different feed ratios of [monomer]/[initiator]

In order to define controlled/“living” natures of this polymerization system, we also studied the AGET ATRP of MMA with different molar feed ratios of [monomer]/[initiator] in the presence of air at 90°C , and the results are shown in Fig. 5. From Fig. 5 it was found that the molecular weights increased with the feed ratios of $[\text{MMA}]/[\text{initiator}]$, while the molecular weight distributions (M_w/M_n s) remain almost constant (~ 1.4). However, the molecular weights from GPC results are gradually close to their corresponding

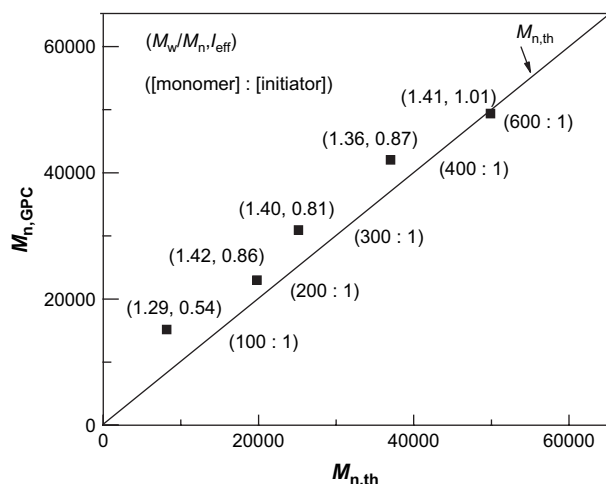


Fig. 5. Relationship of theoretical molecular weight ($M_{n,th}$) and molecular weight from GPC results ($M_{n,GPC}$) under different molar feed ratios of $[\text{MMA}]/[\text{initiator}]$ in the presence of air at 90°C . $[\text{MMA}]_0 = 5.6 \text{ M}$, solvent = DMF, $[\text{O}_2] = 6.2 \times 10^{-3} \text{ mol/L}$, time = 26 h. Initiator efficiency (I_{eff}) = $M_{n,th}/M_{n,GPC}$.

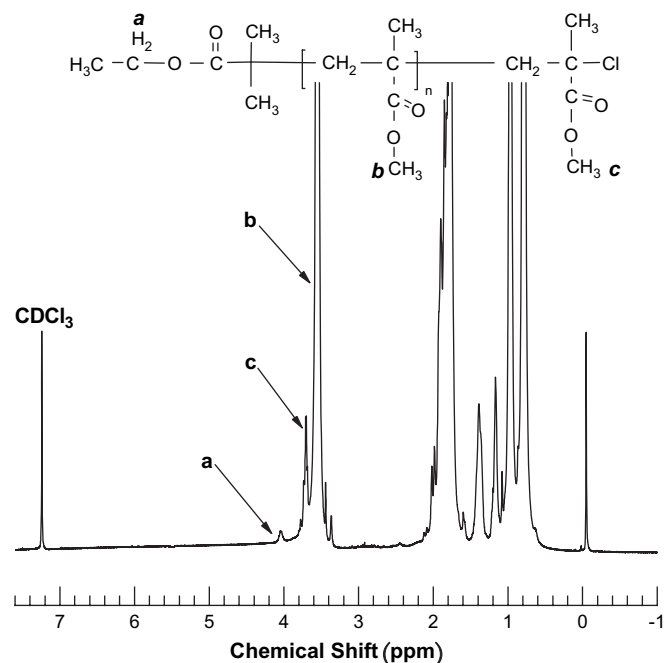


Fig. 6. ^1H NMR spectrum of PMMA ($M_{n,GPC} = 12440 \text{ g/mol}$, $M_w/M_n = 1.34$) obtained in the presence of air with CDCl_3 as solvent and tetramethylsilane (TMS) as internal standard. Polymerization conditions: $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[\text{IDA}]_0/[\text{VC}]_0 = 200/1/1/2/0.75$, $[\text{MMA}]_0 = 5.6 \text{ mol/L}$, $[\text{O}_2] = 6.2 \times 10^{-3} \text{ mol/L}$, solvent = DMF, temperature = 90°C , time = 1.5 h.

theoretical ones. The initiator efficiency (I_{eff}) increased from 0.54 for the feed ratio of $[\text{MMA}]/[\text{initiator}] = 100/1$ to 1.01 for the feed ratio of $[\text{MMA}]/[\text{initiator}] = 600/1$. These results indicated that this polymerization system has pretty high activity, especially under higher feed ratios of $[\text{monomer}]/[\text{initiator}] = 600/1$.

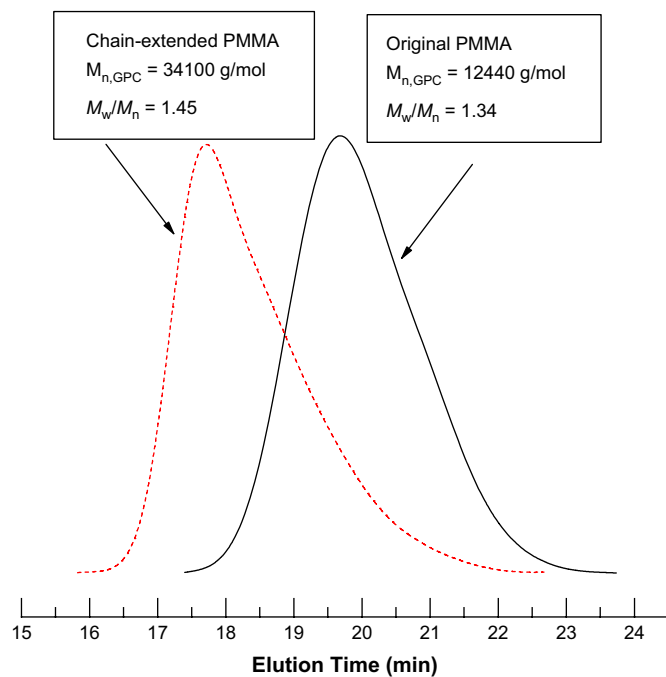


Fig. 7. GPC curves before and after chain extension with PMMA as macroinitiator. Original PMMA: $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[\text{IDA}]_0/[\text{VC}]_0 = 200/1/1/2/0.75$, $[\text{MMA}]_0 = 5.6 \text{ mol/L}$, $[\text{O}_2] = 6.2 \times 10^{-3} \text{ mol/L}$, solvent = DMF, temperature = 90°C , time = 1.5 h, conversion = 22.0%. Chain extended PMMA: $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[\text{IDA}]_0/[\text{VC}]_0 = 300/1/1/2/0.5$, $[\text{MMA}]_0 = 1.6 \text{ mol/L}$, solvent = DMF, temperature = 90°C , time = 42 h, conversion = 88%.

3.5. Analysis of chain end and chain extension

The chain end of the PMMA prepared in the presence of air was analyzed by ^1H NMR spectroscopy, as shown in Fig. 6. The chemical shift at $\delta = 4.06$ ppm (*a* in Fig. 6) was corresponded to the methylene protons of the ethyl ester unit in the initiator EBiB, which indicated that the initiator EBiB moieties were attached to the polymer chain ends (α chain end). The chemical shift at $\delta = 3.75$ ppm (*c* in Fig. 6) was attributed to the methyl ester group at the chain end, as mentioned by Sawamoto et al., which deviated from the chemical shift (3.60 ppm, *b* in Fig. 6) of other methyl ester group in PMMA because of the electron-attracting function of ω -Cl atom [14]. Therefore, the obtained PMMA should be used as macroinitiators to conduct chain-extension reaction. The PMMA ($M_{n,\text{GPC}} = 12\,440$ g/mol, $M_w/M_n = 1.34$) obtained in the presence of air was used as the predecessor in chain-extension experiment. There was a peak shift from the macroinitiator to the chain extended PMMA with $M_{n,\text{GPC}} = 34\,100$ g/mol and $M_w/M_n = 1.45$ (Fig. 7). The successful chain-extension reaction further verified the features of controlled/"living" free-radical polymerization of MMA in the presence of a limited amount of air.

4. Conclusions

A novel iron-mediated AGET ATRP system in the presence of a limited amount of air, using MMA as a model monomer, IDA as a ligand and ascorbic acid (VC) as a reducing agent, was successfully developed. The amount of the reducing agent VC had obvious effect on the polymerization rate. When the molar ratio of $[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[\text{VC}]_0$ increased from 1/0.5 to 1/1, the k_p^{app} values increased from $3.37 \times 10^{-5} \text{ s}^{-1}$ to $5.03 \times 10^{-5} \text{ s}^{-1}$, namely, the corresponding polymerization rate increased by 49%, and all the polymerizations of MMA demonstrated the controlled/"living" features. Thus, the polymerization rate could be facilely regulated by the amount of reducing agent.

Acknowledgments

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