



# Atom transfer radical polymerizations of methyl methacrylate catalyzed by EBiB/SnCl<sub>2</sub>·2H<sub>2</sub>O(FeCl<sub>2</sub>·4H<sub>2</sub>O)/FeCl<sub>3</sub>·6H<sub>2</sub>O/MA<sub>5</sub>-DETA systems

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## Abstract

The ATRP of methyl methacrylate (MMA) with the system of FeCl<sub>2</sub>·4H<sub>2</sub>O, *N,N,N',N'',N'''*-penta(methyl acrylate)diethylenetriamine (MA<sub>5</sub>-DETA) and ethyl 2-bromoisobutyrate (EBiB) showed high activity and is not well-controlled. The addition of a certain amount of FeCl<sub>3</sub>·6H<sub>2</sub>O as the additive into the above system results in the decrease of the polymerization rate and the improvement of the controllability. When SnCl<sub>2</sub>·2H<sub>2</sub>O was added instead of FeCl<sub>2</sub>·4H<sub>2</sub>O, a novel catalyst system SnCl<sub>2</sub>·2H<sub>2</sub>O/FeCl<sub>3</sub>·6H<sub>2</sub>O/EBiB/MA<sub>5</sub>-DETA formed shows better controllability, higher catalytic activity and higher initiating efficiencies (more than 90%) in comparison with the system FeCl<sub>2</sub>·2H<sub>2</sub>O/FeCl<sub>3</sub>·6H<sub>2</sub>O/EBiB/MA<sub>5</sub>-DETA. The polydispersities of the polymers kept range from  $M_w/M_n = 1.18$ –1.26. The real active species in the new system is Fe (II) formed from the reaction of FeCl<sub>3</sub>·6H<sub>2</sub>O with the active radical species produced from the reaction of SnCl<sub>2</sub>·2H<sub>2</sub>O with EBiB.

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*Keywords:* Atom transfer radical polymerization; Initiator; Additive

## 1. Introduction

Since 1995 the atom transfer radical polymerization (ATRP), which was discovered by Wang, Matyjaszewski [1] and Sawamoto [2] independently, has been developed rapidly [3,4]. In this technique, the polymerization proceeds through the reversible activation of carbon–halogen bond at the polymer terminal by the transition metal complex via a one-electron redox reaction. As a result, to build a fast equilibrium between the dormant and active growing radical species is essential for getting a well-controlled polymerization system. In most cases, the desired living polymerization system can be obtained by the design of an excellent initiation system including the choice of a transition metal, a suitable ligand and an effective initiator [3,4]. In some cases, however, an extra additive needs to add in order to get faster polymerization rate [5,6] and/or better controllability [7,8].

We have recently reported a new multidentate aliphatic amine *N,N,N',N'',N'''*-penta (methyl acrylate)diethylenetriamine (MA<sub>5</sub>-DETA), which can be used as the suitable

ligand for the CuX based ATRP of MMA [9]. Now we tried to use the ligand in the iron-based ATRP of MMA and found the ATRP of MMA can take place with the system, FeCl<sub>2</sub>·2H<sub>2</sub>O/EBiB/MA<sub>5</sub>-DETA in high polymerization rate. However, its controllability is relatively poor. When a certain amount of FeCl<sub>3</sub>·6H<sub>2</sub>O was added as the additive, the controllability of the system was improved as expected. In order to improve the controllability further, the novel system, SnCl<sub>2</sub>·2H<sub>2</sub>O/EBiB/MA<sub>5</sub>-DETA/FeCl<sub>3</sub>·6H<sub>2</sub>O, was designed based on the use of Fe (II) formed in situ gradually. The ATRP of MMA catalyzed by the novel system is well controlled and its initiation efficiencies are over 90%. Here we would like to report the results.

## 2. Experiment section

### 2.1. Materials

Methyl methacrylate (MMA) and methyl acrylate (MA) (chemically pure, Shanghai Chemical Reagent Co. Ltd.) was vacuum distilled before use. Ethyl 2-bromoisobutyrate (EBiB) (analysis pure) was purchased from Aldrich. Other reagents, such as ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), ferrous chloride tetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O), stannous

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chloride dihydrate ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ), methanol, dichloromethane and anisole were purchased from Shanghai Chemical Reagent Co. Ltd. and used without any further purification.  $N,N,N',N'',N'''$ -penta (methyl acrylate) diethylenetriamine ( $\text{MA}_5\text{-DETA}$ ) (Scheme 1) was synthesized in our lab via Michael addition reaction of methyl acrylate (MA) and diethylenetriamine (DETA).

## 2.2. Polymerization

In a typical example, EBib (0.0975 g, 0.5 mmol),  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (0.1128 g, 0.5 mmol),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.1352 g, 0.5 mmol),  $\text{MA}_5\text{-DETA}$  (0.7995 g, 1.5 mmol) and MMA (5.00 g, 50 mmol) were added to a reaction tube. After three cycles of freeze-pump-thaw to remove oxygen, the reaction tube was sealed under nitrogen, then immersed in an oil bath thermo stated at  $90^\circ\text{C}$  under stirring. After a certain time, the polymerization was stopped. The product was dissolved in dichloromethane and washed with distilled water. Finally, the polymers were isolated by precipitation in methanol and dried under vacuum.

## 2.3. Characterization

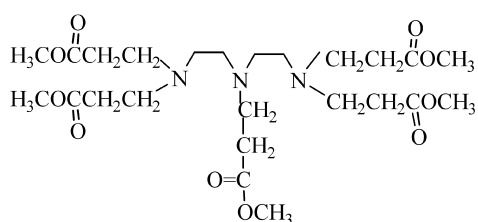
The monomer conversion of the polymerization was determined gravimetrically.

GPC measurements were carried out using a Waters 1515 liquid chromatography equipped with three columns (G 1000, 3000, 5000 HXL) with a differential refractometer detector. Polystyrene standards were used to calibrate the columns and THF as eluting solvent. Data were processed by Waters millennium32 software.

## 3. Results and discussion

### 3.1. ATRP of MMA catalyzed by EBiB/ $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ / $\text{MA}_5\text{-DETA}$ system

According to the fact that multidentate aliphatic amines, which are found to be the effective ligands in copper-based ATRP [10], have not been used in iron-based ATRP yet. We first tried to use the new tridentated amine,  $\text{MA}_5\text{-DETA}$ , as the ligand in  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  based ATRP of MMA. Table 1 listed the results obtained in bulk and in solution polymerization. Both the polymerizations went fast, the monomer conversion is as high as 75% in bulk and 65% in



Scheme 1. Structure of  $\text{MA}_5\text{-DETA}$ .

the solution within 40 min under the conditions of  $[\text{EBiB}]:[\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]:[\text{MA}_5\text{-DETA}]:[\text{MMA}] = 1:1:1:100$  at  $90^\circ\text{C}$ . For the solution polymerization, the conversion increases, while the polydispersity of the polymer decreases with the increasing time. However, the increase on the molecular weights with the conversion is not in line with the established theory of living polymerization and the molecular weights of the polymers produced at the early stage of the polymerization were larger than theoretical ones. In the bulk polymerization, the catalyst amount used has a great effect on the molecular weight distribution of the polymers. The index of the polydispersities decreases with the decrease of the catalyst amount (Table 1 entries e–j). These results indicated the present system is not well controlled.

### 3.2. The ATRP of MMA catalyzed by

$\text{EBiB}/\text{FeCl}_2 \cdot 4\text{H}_2\text{O}/\text{MA}_5\text{-DETA}$  system with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as the additive

In order to improve the controllability of the above system,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was added as the additive. The results in bulk polymerization are shown in Table 2. It is obvious that the addition of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  leads to the decrease of the polymerization rate and to the improvement of the controllability. It is reasonable because the formation rate of dormant species increases as the addition of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and the radical coupling termination was suppressed greatly. The moderate polymerization rate (conversion 52%, in 2 h) and the polymer with  $M_w/M_n$  of 1.44 can be obtained, when  $[\text{EBiB}]:[\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]:[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]:[\text{MA}_5\text{-DETA}]:[\text{MMA}] = 1:0.75:0.25:1:100$  at  $90^\circ\text{C}$ . Although the polymerization rate decreases greatly, the polymer having even narrower  $M_w/M_n$  ( $< 1.3$ ) can be produced, when the ratio of Fe (III) to Fe (II) from 0:1 increases to 3:1 (Table 2, entry a–f).

To understand more about the system, the polymerization kinetics in bulk was studied under the conditions of  $[\text{EBiB}]:[\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]:[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]:[\text{MA}_5\text{-DETA}]:[\text{MMA}] = 1:1:0.5:1.5:100$ . The increase of the conversion with the time and a linearity of the semi-logarithmic plots of  $\ln([M]_0/[M]_t)$  vs. time were observed (Fig. 1). It means that the polymerization was first-order with respect to monomer and the concentration of growing radicals remained constant. The polydispersities of the resulting polymers kept relatively low throughout the polymerization process (Fig. 2). However, a linear increase in molecular weight with the conversion was only observed after the conversion is over 30%.

### 3.3. A novel catalyst system

$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}/\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{EBiB}/\text{MA}_5\text{-DETA}$  for the ATRP of MMA

Considering the fact that the  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  is well known to be used as an effective reducing agent for the analysis of

Table 1  
Polymerizations of MMA catalyzed by EBiB/FeCl<sub>2</sub>·4H<sub>2</sub>O/MA<sub>5</sub>-DETA system (T = 90 °C)

Entry	[EBiB]:[FeCl <sub>2</sub> ·4H <sub>2</sub> O]:[MA <sub>5</sub> -DETA]:[MMA]:[anisole]	Time (h)	Conversion (%)	M <sub>n,Gpc</sub>	M <sub>w</sub> /M <sub>n</sub>
a	1:1.00:1.00:100:50	0.17	34.7	11,346	1.90
b	1:1.00:1.00:100:50	0.33	50.0	10,424	1.74
c	1:1.00:1.00:100:50	0.67	65.0	13,115	1.75
d	1:1.00:1.00:100:50	1.00	85.3	14,737	1.59
e	1:1.00:1.00:100:0	0.67	75.4	13,851	1.74
f	1:0.75:0.75:100:0	0.67	95.8	14,419	1.67
g	1:0.67:0.67:100:0	0.67	80.2	15,525	1.57
h	1:0.50:0.50:100:0	0.67	83.6	12,715	1.52
i	1:0.33:0.33:100:0	10.0	70.0	8296	1.43
j	1:0.25:0.25:100:0	10.0	14.4	11,618	1.43

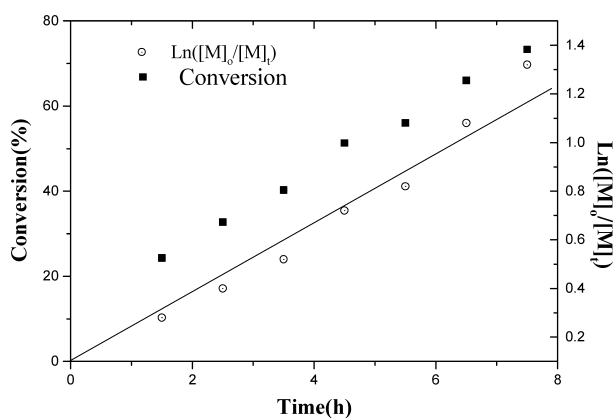


Fig. 1. Dependence of conversion and  $\ln([M]_0/[M]_1)$  on time for ATRP of MMA catalyzed by EBiB/FeCl<sub>2</sub>·4H<sub>2</sub>O/MA<sub>5</sub>-DETA with FeCl<sub>3</sub>·6H<sub>2</sub>O as additive at 90 °C; [EBiB]:[FeCl<sub>2</sub>·4H<sub>2</sub>O]:[FeCl<sub>3</sub>·6H<sub>2</sub>O]:[MA<sub>5</sub>-DETA]:[MMA] = 1:1:0.5:1.5:100.

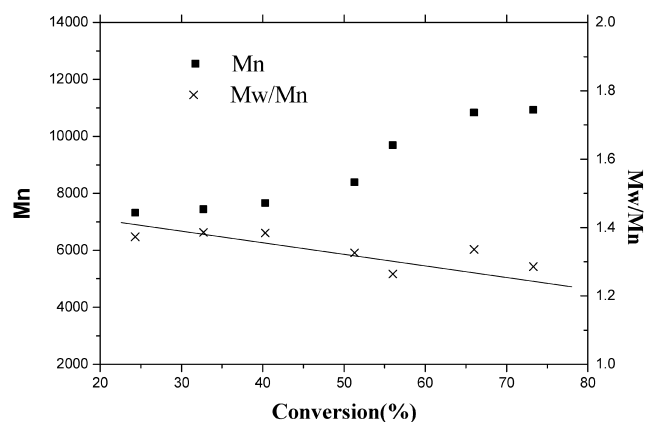


Fig. 2. Dependence of measured molecular weight and polydispersity on conversion for ATRP of MMA catalyzed by EBiB/FeCl<sub>2</sub>·4H<sub>2</sub>O/MA<sub>5</sub>-DETA and FeCl<sub>3</sub>·6H<sub>2</sub>O as the additive at 90 °C; [EBiB]:[FeCl<sub>2</sub>·4H<sub>2</sub>O]:[FeCl<sub>3</sub>·6H<sub>2</sub>O]:[MA<sub>5</sub>-DETA]:[MMA] = 1:1:0.5:1.5:100.

iron-contain in iron ore. The method used is based on the reduction of Fe (III) by SnCl<sub>2</sub> to Fe (II), then determination of the Fe (II)-contain by titration using KMnO<sub>4</sub> [11]. Thus, we tried to use this method in ATRP to see whether Fe (II) can be formed in situ gradually via the reaction of SnCl<sub>2</sub>·2H<sub>2</sub>O with FeCl<sub>3</sub>·6H<sub>2</sub>O under the polymerization conditions and whether the use of Fe (II) such formed as the catalyst will get better controlled system. The polymerizations of MMA in bulk were first conducted by the catalyst system SnCl<sub>2</sub>·2H<sub>2</sub>O/FeCl<sub>3</sub>·6H<sub>2</sub>O/EBiB/MA<sub>5</sub>-DETA at the different ratios of FeCl<sub>3</sub>·6H<sub>2</sub>O/SnCl<sub>2</sub>·2H<sub>2</sub>O at 90 °C. The results were shown in Fig. 3. All the

polymerizations gave high monomer conversions (86–99%) and the polymers with low polydispersities ( $M_w/M_n = 1.21–1.32$ ) under the conditions of (SnCl<sub>2</sub>·2H<sub>2</sub>O + FeCl<sub>3</sub>·6H<sub>2</sub>O):EBiB:MA<sub>5</sub>-DETA:MMA = 1:1:1.5:100 at 90 °C for 14 h. The slight decrease both in the conversion and in the polydispersity of the polymer with the increasing of the ratio of FeCl<sub>3</sub>·6H<sub>2</sub>O/SnCl<sub>2</sub>·2H<sub>2</sub>O was observed.

Fig. 4 shows the initiation efficiency of the system at the different ratios of FeCl<sub>3</sub>·6H<sub>2</sub>O/SnCl<sub>2</sub>·2H<sub>2</sub>O. It can be seen that the initiation efficiency of the system is high. Most of the systems have the initiating efficiency more than 90%, the best one even 96%.

Table 2  
FeCl<sub>3</sub>·6H<sub>2</sub>O as the additive in the polymerizations of MMA catalyzed by EBiB/FeCl<sub>2</sub>·4H<sub>2</sub>O/MA<sub>5</sub>-DETA (T = 90 °C)

Entry	[EBiB]:[FeCl <sub>2</sub> ·4H <sub>2</sub> O]:[FeCl <sub>3</sub> ·6H <sub>2</sub> O]:[MA <sub>5</sub> -DETA]:[MMA]	Time (h)	Conversion (%)	M <sub>n,Gpc</sub>	M <sub>n,Th</sub>	M <sub>w</sub> /M <sub>n</sub>	Initiating efficiency (%)
a	1:1.00:0:1:100	0.67	75.4	13,851	7540	1.74	54
b	1:0.75:0.25:1:100	2.0	52.0	10,382	5200	1.44	50
c	1:0.67:0.33:1:100	6.0	35.8	8087	3580	1.43	44
d	1:0.50:0.50:1:100	20.0	61.2	8769	6120	1.29	71
e	1:0.33:0.66:1:100	20.0	10.8	5853	1080	1.29	18
f	1:0.25:0.75:1:100	20.0	10.4	5544	1040	1.25	19

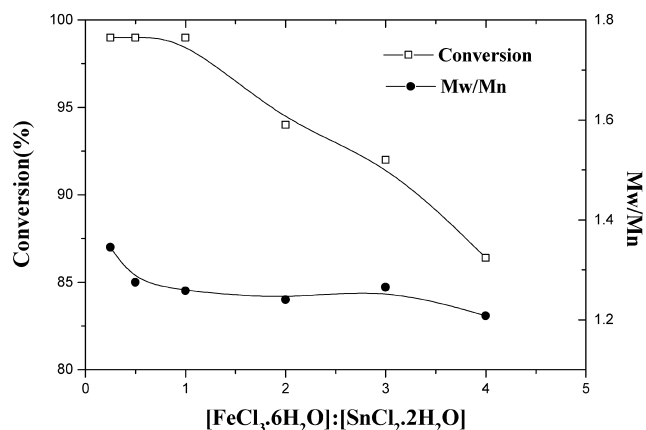


Fig. 3. Dependence of the conversion and polydispersity on different ratios of  $[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]:[\text{SnCl}_2 \cdot 2\text{H}_2\text{O}]$  for ATRP of MMA catalyzed by EBiB/ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{MA}_5\text{-DETA}$  with  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  as additive at  $90^\circ\text{C}$  after 14 h.  $[\text{EBiB}]:[\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + \text{SnCl}_2 \cdot 2\text{H}_2\text{O}]:[\text{MA}_5\text{-DETA}]:[\text{MMA}] = 1:1:1.5:100$ .

In order to know more about the system, the polymerization kinetics was measured and shown in Fig. 5. It can be seen that a long induction period (about 5 h) exists during the polymerization process. After the induction period, the conversion increases with the time and the semi-logarithmic plot of  $\ln([M]_0/[M]_t)$ -time showed a significant deviation from first-order with respect to monomer at the beginning of the polymerization and then kept a linear when the conversion is over 15%. This should be attributed to the slow initiation reaction.

The number-average molecular weights ( $M_n$ ) of the polymers linearly increase with conversion, although the  $M_n$  values are high at low conversion (lower than 15%), which is due to the slow initiation. The polydispersities of the resulting polymers kept low ( $1.18 < M_w/M_n < 1.26$ ) throughout the polymerization process (Fig. 6).

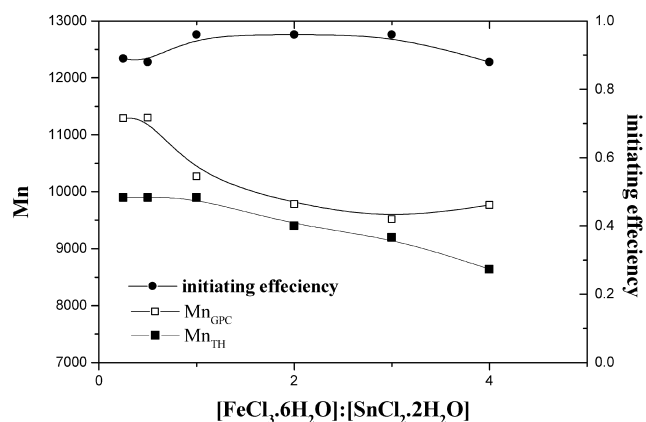


Fig. 4. Dependence on the  $M_n$  and initiating efficiency on different ratios of  $[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]:[\text{SnCl}_2 \cdot 2\text{H}_2\text{O}]$  for ATRP of MMA catalyzed by EBiB/ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{MA}_5\text{-DETA}$  with  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  as additive at  $90^\circ\text{C}$  after 14 h.  $[\text{EBiB}]:[\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + \text{SnCl}_2 \cdot 2\text{H}_2\text{O}]:[\text{MA}_5\text{-DETA}]:[\text{MMA}] = 1:1:1.5:100$ .  $M_{n,\text{TH}} = ([M]_0/[1]_0) \times M_{\text{MMA}} \times \text{conversion}\%$ , initiating efficiency =  $M_{n,\text{TH}}/M_{n,\text{GPC}}$ .

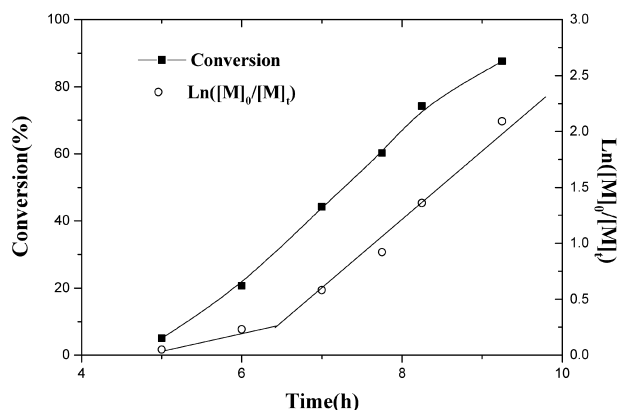


Fig. 5. Dependence of conversion and  $\ln([M]_0/[M]_t)$  on time for ATRP of MMA catalyzed by EBiB/ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{MA}_5\text{-DETA}$  with  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  as additive at  $90^\circ\text{C}$ ;  $[\text{EBiB}]:[\text{SnCl}_2 \cdot 2\text{H}_2\text{O}]:[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]:[\text{MA}_5\text{-DETA}]:[\text{MMA}] = 1:1:1.3:100$ .

All these results indicated that the novel catalyst system is really a well-controlled one for the ATRP of MMA in the wide range of the ratios of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . In comparison with the system  $[\text{EBiB}]/[\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]:[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]/[\text{MA}_5\text{-DETA}]$  above mentioned, the new system shows the following advantages: higher initiation efficiency, higher polymerization rate and better controllability.

In order to understand the role taken place by  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  more clearly, the same experiments with  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  alone, without the addition of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , were conducted. It is unexpected that the MMA polymerization does occur, but the polymerization is not controlled, just like the normal radical polymerization. The polymers produced have high molecular weights (over 150,000). The initiating efficiency of the system is very low, less than 6% (Table 3). These results indicated that the  $\text{SnCl}_2$  can react with EBiB poorly to generate the active radical species, which initiate the polymerization of MMA, but the resulting  $\text{SnCl}_4$  cannot react with propagating active species to form the dormant

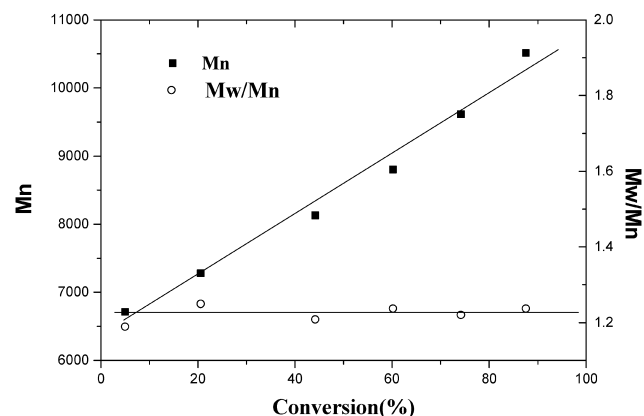


Fig. 6. Dependence of measured molecular weight and polydispersity on conversion for ATRP of MMA catalyzed by EBiB/ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{MA}_5\text{-DETA}$  and  $\text{SnCl}_2 \cdot 2\text{H}_2 \cdot 2\text{H}_2\text{O}$  as the additive at  $90^\circ\text{C}$ ;  $[\text{EBiB}]:[\text{SnCl}_2 \cdot 2\text{H}_2 \cdot 2\text{H}_2\text{O}]:[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]:[\text{MA}_5\text{-DETA}]:[\text{MMA}] = 1:1:1.3:100$ .

Table 3  
Polymerizations of MMA catalyzed by EBiB/SnCl<sub>2</sub>·2H<sub>2</sub>O/MA<sub>5</sub>-DETA system (*T* = 90 °C)

Entry	[EBiB]:[SnCl <sub>2</sub> ·2H <sub>2</sub> O]:[MA <sub>5</sub> -DETA]:[MMA]	Time (h)	Conversion (%)	<i>M</i> <sub>n,Gpc</sub>	<i>M</i> <sub>n,Th</sub>	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub>	Initiating efficiency (%)
a	1:0:3:100	14	32.8	28,7939	–	2.50	–
b	1:1:3:100	14	89.2	208,905	8920	2.17	4.3
c	1:2:3:100	14	92.4	150,467	9240	2.92	6.1
d	1:3:3:100	14	94.4	258,645	9440	2.41	3.6

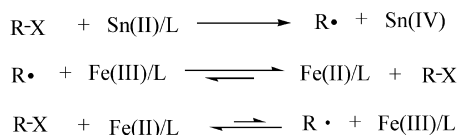
species. As a result, the polymerization with EBiB/SnCl<sub>2</sub>·2H<sub>2</sub>O/MA<sub>5</sub>-DETA proceeds only by the normal radical mechanism.

From the above results it can be concluded that the real active catalyst species in the new system of (SnCl<sub>2</sub>·2H<sub>2</sub>O + FeCl<sub>3</sub>·6H<sub>2</sub>O)/EBiB/MA<sub>5</sub>-DETA for the ATRP of MMA should not be Sn (II) itself, but the Fe (II). The Fe (II) might be produced by the reaction of FeCl<sub>3</sub>·6H<sub>2</sub>O with the active radical species produced from the reaction of SnCl<sub>2</sub>·2H<sub>2</sub>O with EBiB. Although the redox reaction of SnCl<sub>2</sub>·2H<sub>2</sub>O with FeCl<sub>3</sub>·6H<sub>2</sub>O can also give Fe (II), here we have not got the direct evidence for it. The initiation and the propagation reactions were supported as follows (Scheme 2).

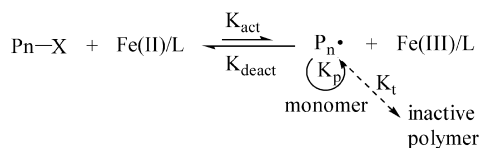
#### 4. Conclusion

The tridentate aliphatic amine MA<sub>5</sub>-DETA was first used in ATRP of MMA catalyzed by EBiB/FeCl<sub>2</sub>·4H<sub>2</sub>O. The

Initiation:



Propagation:



Scheme 2.

system showed poor controllability due to the existence of the coupling termination. The addition of extra FeCl<sub>3</sub>·6H<sub>2</sub>O as the additive resulted in the decreases of the polymerization rate and in the improvement of the controllability. A novel catalyst system SnCl<sub>2</sub>·2H<sub>2</sub>O/EBiB/FeCl<sub>3</sub>·6H<sub>2</sub>O/MA<sub>5</sub>-DETA was presented and found to be the effective and well-controlled one. The new system has high initiating efficiency (more than 90%), moderate polymerization rate and gives the polymers with low polydispersities (1.18 < *M*<sub>w</sub>/*M*<sub>n</sub> < 1.26). The real active species for the system are Fe (II), which are formed from the reaction of FeCl<sub>3</sub>·6H<sub>2</sub>O with the active radical species produced from the reaction of SnCl<sub>2</sub>·2H<sub>2</sub>O with EBiB.

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