

# A new complex catalytic system $\text{CuX}/\text{bpy}/\text{Al}(\text{OR})_3$ for atom transfer radical polymerization

Jianhua Guo, Zhewen Han<sup>\*</sup>, Pingping Wu

*Department of Polymer Science and Engineering, East China University of Science and Engineering, Shanghai 200237, People's Republic of China*

## Abstract

A new complex catalytic system, consisting of copper (I) halide ( $\text{CuBr}$ )/2,2'-bipyridine ( $\text{bpy}$ )/aluminum triisopropoxide [ $\text{Al}(\text{OiPr})_3$ ], has been successfully used in the atom transfer radical polymerization (ATRP) of methacrylates for the first time. The effect of the catalytic system on ATRP has been studied systematically. The mechanism of ATRP promoted by  $\text{Al}(\text{OiPr})_3$  has been elucidated. The study results showed that  $\text{Al}(\text{OiPr})_3$ , which was used as a catalytic promoter, decreased polymerization temperature and increased the rate and the controllability of polymerization. With adding proper amount of deactivator,  $\text{CuBr}_2$ , both MMA and BMA could be polymerized rapidly at low temperature in a living manner with  $\text{CuBr}/\text{bpy}/\text{Al}(\text{OiPr})_3$  as a ternary catalytic system. The polymers have the designed degrees of polymerization by  $\Delta[M]/[I]_0$  and narrow polydispersity ( $M_w/M_n = 1.20\text{--}1.50$ ). The linear increase of molecular weight vs. conversion of monomer was observed. The molecular weight distributions (MWD) were narrow and became narrower as conversion increased. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Metal complex catalysis; Copper halide; Aluminum trialkoxide; Atom transfer radical polymerization; Methacrylate

## 1. Introduction

Many living radical polymerization techniques [1,2], which require a low stationary concentration of growing radicals that are in a fast dynamic equilibrium with the dormant species, have been developed in recent years. Atom transfer radical polymerization (ATRP) [3–5]

employs a redox process with transition metal complexes in which a halogen atom is transferred reversibly between transition metal and polymer chain end. ATRP is a new “living” radical polymerization technique developed in 1995. Various catalytic systems, such as  $\text{CuX}/2,2'$ -Bipyridine ( $\text{bpy}$ ) [3–5],  $\text{RuCl}_2(\text{PPh}_3)_3/\text{Al}(\text{OiPr})_3$  [6,7],  $\text{FeX}_2/\text{PPh}_3$  [8,9] and  $\text{NiX}_2(\text{O}, \text{O}'\text{-(CH}_2\text{NMe)}_2\text{C}_6\text{H}_3)$  [10], have been used to control the radical polymerization of many monomers. Some active organic halides are used as initiators. ATRP can be considered as a catalytic polymerization technique. The proportion of radicals, consequently the rate and controllability of polymerization, can be easily con-

<sup>\*</sup> Corresponding author. Tel.: +86-21-64253060; fax: +86-21-64233269.

E-mail address: zhwhan@ecust.edu.cn (Z. Han).

trolled based on the components and activity of catalytic system. The key for a successful ATRP is to employ proper catalytic system with high activity and selectivity.

Matyjaszewski at first reported the ATRP catalyzed by CuX/bpy in 1995 [3–5]. For the low catalytic activity of CuX, many kinds of monomers only can be polymerized in a living style at high temperature (80 – 140°C). Sawamoto et al. [6,7] found that  $\text{RuCl}_2(\text{PPh}_3)_3$  (Ph =  $\text{C}_6\text{H}_5$ ) induced living radical polymerization of methacrylates (MMA and BMA), when coupled with organic halides and aluminum compounds such as  $\text{Al}(\text{OiPr})_3$ . No polymer was obtained at 60 – 80°C in the absence of  $\text{RuCl}_2(\text{PPh}_3)_3$  or aluminum compounds. In sharp contrast, the polymer with narrow polydispersities was only produced with  $\text{RuCl}_2(\text{PPh}_3)_3$ /aluminum compounds as a binary catalytic system.

It occurred to us that since CuX has higher catalytic activity than  $\text{RuCl}_2(\text{PPh}_3)_3$ , the ternary catalytic system consisting of CuX, bpy and  $\text{Al}(\text{OiPr})_3$  must have higher catalytic activity than  $\text{RuCl}_2(\text{PPh}_3)_3$ / $\text{Al}(\text{OiPr})_3$  system, and may catalyze the living polymerization of many kinds of monomers at lower temperature. Based on this idea, a Lewis acid, aluminum triisopropoxide [ $\text{Al}(\text{OiPr})_3$ ], was tried to be used in this paper as a catalytic promoter with combining CuBr/bpy. The oxidized transition-metal species,  $\text{Mt}^{n+1}$ , can be called as a deactivator, which is an essential part of the catalytic system. The deactivator reduces the polymerization rate, as well as polydispersities [11,12]. But high concentration of deactivator also participates in some side reactions at high temperature. Thus, the control of the amount of the deactivator and its structure is extremely important [13].

This paper reports the ATRP of MMA and BMA with ethyl 2-bromoisobutyrate (2-(EiB)-Br) as an initiator and a new ternary catalyzing system consisting of copper(I) halide (CuBr)/2,2'-bipyridine (bpy)/aluminum triisopropoxide [ $\text{Al}(\text{OiPr})_3$ ]. A series of polymerizations have been carried out in cyclohexanone at lower

temperature, and deeply discussed the influence of [ $\text{Al}(\text{OiPr})_3$ ] and  $\text{CuBr}_2$  on ATRP of BMA and MMA.

## 2. Experimental

### 2.1. Materials

Monomer BMA and MMA was purified by vacuum distillation, the inhibitor in which was removed by passing through the  $\text{Al}_2\text{O}_3$  column. Cyclohexanone was stirred over active carbon, and then distilled under vacuum. CuBr was stirred in glacial acetic acid, washed with  $\text{CH}_3\text{OH}$ , and then dried under vacuum. bpy was recrystallized by acetone. 2-(EiB)-Br (99%),  $\text{CuBr}_2$  and  $\text{Al}(\text{OiPr})_3$  were used as received.

### 2.2. General procedure

All materials except CuBr were added to a round-bottom flask. The mixture was stirred till all solid materials were well distributed. Then CuBr was added. The reaction flask was degassed three times by “freeze–pump–aerate” cycles. The reaction mixture was immersed in an oil bath heated at certain temperature. Samples for kinetic measurements were taken after a specific time interval from the reaction mixture. Adding a small amount of inhibitor to the samples stopped the polymerization reaction.

Poly(methacrylate) was isolated by precipitation with the mixture of methanol and water (4/1). The precipitated polymer was solved with THF, precipitated for the second time, and then dried under vacuum at 40°C until its weight was constant.

### 2.3. Characterization

Monomer conversion was determined by weight method. Molecular weight ( $M_w$ ,  $M_n$ ) and molecular weight distribution (MWD) were measured by GPC with the calibration of the

commercially available polystyrene standards and THF as solvent.

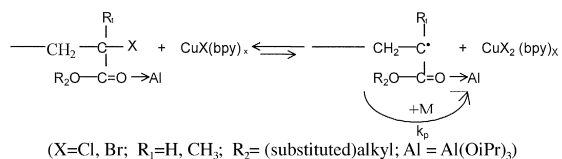
### 3. Results and discussion

#### 3.1. Effect of the catalytic promoter $\text{Al}(\text{OiPr})_3$ on ATRP

At the first, BMA was polymerized with  $\text{CuBr}/\text{bpy}/\text{Al}(\text{OiPr})_3$  as complex catalytic system at  $28^\circ\text{C}$ . The experimental results are shown in Table 1. The data showed that the polymerization rate was high even at  $28^\circ\text{C}$ , but the produced polymers had wider MWD ( $M_w/M_n = \text{MWD} > 3$ ) and the molecular weights were much less than the predicted ones. The results showed that the controllability of polymerization was poor and the polymerization process was not in a “living” manner.

It can be inferred that the radical could not be rapidly deactivated to become a dormant species due to the lack of deactivator,  $\text{Cu}(\text{II})$  compound, under the above reaction conditions (see Scheme 1). Therefore, the radical concentration was higher with the  $\text{CuX}/\text{bpy}/\text{Al}(\text{OiPr})_3$  system than that with the  $\text{CuX}/\text{bpy}$  system, but high concentration of radicals also induced the high probability of termination reaction and poor controllability of the polymerization process.

In order to solve the above problem, the proper amount of  $\text{CuBr}_2$  was added to the reaction system as the deactivator. The reaction



Scheme 1. Mechanism of redox dynamic equilibrium reaction.

temperature was increased to  $52^\circ\text{C}$  to gain the proper polymerization rate.

Table 2 shows the experimental results with different concentrations of  $\text{Al}(\text{OiPr})_3$  as catalytic promoter and with  $\text{CuBr}_2$  as deactivator when monomer conversion was about 80%. The experimental data showed that the produced polymers had narrower polydispersities with  $\text{Al}(\text{OiPr})_3$  ( $M_w/M_n = 1.29\text{--}1.54$ ) than that without  $\text{Al}(\text{OiPr})_3$  ( $M_w/M_n = 2.69$ ). By increasing the concentration of  $\text{Al}(\text{OiPr})_3$ , it took less time to reach the same monomer conversion (about 80%). The MWD became wider with increasing amount of  $\text{Al}(\text{OiPr})_3$ .

The polymerization kinetics of BMA was investigated systematically. Fig. 1 illustrates the logarithmic conversion data, i.e.,  $\ln([M]_0/[M])$  vs. polymerization time, where  $[M]_0$  and  $[M]$  denote the monomer concentrations at time 0 and  $t$ , respectively. Without adding  $\text{Al}(\text{OiPr})_3$  (a), the first-order kinetic plot was curved, which indicates the polymerization was not internally in the first order. It can be inferred that the probability of termination reaction was high during the longer polymerization process. In contrast, after adding  $\text{Al}(\text{OiPr})_3$  as catalytic promoter, the first-order rate plots were rather linear. It indicates the polymerization was internally in the first kinetic order and the concentrations of radicals were constant. Moreover, Fig. 1 obviously shows that the polymerization rate increased with increasing concentration of  $\text{Al}(\text{OiPr})_3$ .

The slopes of the straight kinetic plots in Fig. 1 allow the calculation of the apparent propagation constants of ATRP of BMA with different concentrations of  $\text{Al}(\text{OiPr})_3$  as catalytic promoter. Assuming propagation occurs via “normal” free radicals, the stationary concentration

Table 1  
ATRP of BMA with  $\text{Al}(\text{OiPr})_3$  as catalytic promoter without adding  $\text{CuBr}_2$  at  $28^\circ\text{C}$ <sup>a</sup>

Time (h)	Conversion (%)	$M_{n,\text{th}} \times 10^{-3b}$	$M_{n,\text{GPC}} \times 10^{-3}$	$M_w/M_n$
4	54.6	11.8	5.00	3.35
5	65.2	14.1	6.72	3.30
6	68.2	14.7	7.01	3.27
8	84.7	18.3	7.76	3.29

<sup>a</sup> Cyclohexanone/BMA = 2:1 (v/v),  $[\text{BMA}]_0 = 2.09$  M,  $[\text{2-(EtB)-Br}]_0 = 0.0139$  M,  $[\text{2-(EtB)-Br}]_0/[\text{CuBr}]_0/[\text{bpy}]_0/[\text{Al}(\text{OiPr})_3]_0 = 1:1:3:1$ .

<sup>b</sup>  $M_{n,\text{th}} = (\text{MW})_0 \{ [\text{BMA}]_0 \times \text{Conv.} (\%) / [\text{2-(EtB)-Br}]_0 \}$ ;  $(\text{MW})_0$  = Molecular weight of monomer BMA.

Table 2

ATRP of BMA with different concentrations of Al(OiPr)<sub>3</sub> in the presence of CuBr<sub>2</sub> at 52°C<sup>a</sup>

[Al(OiPr) <sub>3</sub> ] <sub>0</sub> /[2-(EiB)-Br] <sub>0</sub>	Time (h)	Conversion (%)	$M_{n,th}^b \times 10^{-3}$	$M_{n,GPC} \times 10^{-3}$	$M_w/M_n$
0	12	80.5	17.2	17.0	2.69
0.5	9	76.8	16.4	15.2	1.30
1.0	7	87.3	18.6	16.9	1.29
2.0	5	86.3	18.4	16.2	1.46
4.0	3	79.0	16.9	15.5	1.54

<sup>a</sup>Cyclohexanone/BMA = 2:1 (v/v), [BMA]<sub>0</sub> = 2.09 M, [2-(EiB)-Br]<sub>0</sub> = 0.0139 M, [2-(EiB)-Br]<sub>0</sub>/[CuBr]<sub>0</sub>/[CuBr<sub>2</sub>]<sub>0</sub>/[bpy]<sub>0</sub>/[Al(OiPr)<sub>3</sub>]<sub>0</sub> = 1:1:0.2:3.6:1.

<sup>b</sup> $M_{n,th} = (MW)_0 \{ [M]_0 \times \text{Conv.} (\%) / [2-(EiB)-Br]_0 \}$ .

of radicals [ $P^\cdot$ ] can be estimated from the ratio of the apparent propagation rate constant  $k_p^{app}$  to the available rate constant of radical propagation  $k_p$  [14]

$$R_p = -d[M]/dt = k_p [P^\cdot] [M] = k_p^{app} [M] \quad (1)$$

$$\ln([M]_0/[M]) = k_p^{app} t \quad (2)$$

$$[P^\cdot] = k_p^{app}/k_p \quad (3)$$

$$\ln k_p = \ln A_p - E_p/RT = 14.01 - 2454/T \quad (4)$$

Table 3 shows the kinetic data and estimated concentrations of growing radicals in ATRP of BMA. The concentration of growing radicals increased with the concentration of Al(OiPr)<sub>3</sub>,

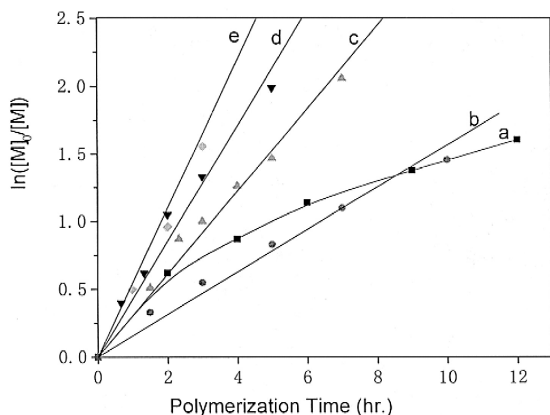


Fig. 1. First-order plot for the ATRP of BMA with different concentrations of Al(OiPr)<sub>3</sub> in the presence of CuBr<sub>2</sub> at 52°C. Cyclohexanone/BMA = 2:1 (v/v), [BMA]<sub>0</sub> = 2.09 M, [2-(EiB)-Br]<sub>0</sub> = 0.0139 M, [2-(EiB)-Br]<sub>0</sub>/[CuBr]<sub>0</sub>/[CuBr<sub>2</sub>]<sub>0</sub>/[bpy]<sub>0</sub> = 1:1:0.2:3.6; (a) [Al(OiPr)<sub>3</sub>]<sub>0</sub> = 0; (b) 0.00694; (c) 0.0139; (d) 0.0278; (e) 0.0556 M.

but was not in direct proportion to it. This was due to the low solubility of Al(OiPr)<sub>3</sub> in cyclohexanone. Al(OiPr)<sub>3</sub> became more and more difficult to be well distributed with the increase of its concentration.

Fig. 2 is the plot of number-average molecular weight ( $M_n$ ) and MWD vs. monomer conversion in the case that the molar ratio of Al(OiPr)<sub>3</sub> to 2-(EiB)-Br was 1. The  $M_n$  values increased linearly with conversion, though a little less than the calculated values, assuming that one polymer chain was formed per molecule of 2-(EiB)-Br. The  $M_w/M_n$  of polymers was fairly narrow and became narrower as the conversion increased ( $M_w/M_n = 1.54$ – $1.29$ ).

### 3.2. Effect of the deactivator Cu(II) compound on ATRP

Since ATRP is a catalytic process, the proportion of radicals and the polymerization rate can be controlled easily by adjusting the amount

Table 3

Kinetic data and estimated concentration of propagating radicals, [ $P^\cdot$ ], for ATRP of BMA at 52°C  
Cyclohexanone/BMA = 2:1 (v/v), [BMA]<sub>0</sub> = 2.09 M, [2-(EiB)-Br]<sub>0</sub> = 0.0139 M, [2-(EiB)-Br]<sub>0</sub>/[CuBr]<sub>0</sub>/[CuBr<sub>2</sub>]<sub>0</sub>/[bpy]<sub>0</sub> = 1:1:0.2:3.6.

Al(OiPr) <sub>3</sub> / 2-(EiB)-Br	$k_p$ ( $10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ )	$k_p^{app}$ ( $10^{-4} \text{ s}^{-1}$ )	[ $P^\cdot$ ] ( $10^{-7} \text{ mol l}^{-1}$ )
0.5	0.632	0.54	0.86
1	0.632	0.88	1.39
2	0.632	1.25	1.97
4	0.632	1.78	2.82

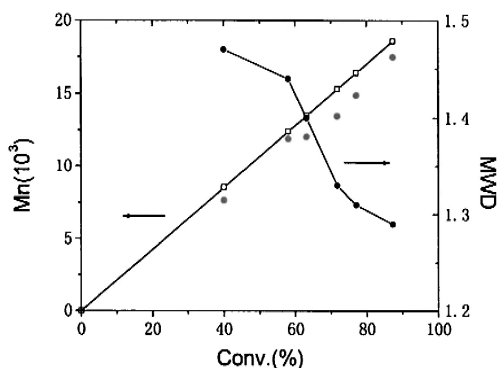


Fig. 2. Dependence of  $M_{n,th}$ ,  $M_{n,GPC}$  and  $M_w/M_n$  on conversion for the ATRP of BMA at 52°C. Cyclohexanone/BMA = 2:1 (v/v),  $[BMA]_0 = 2.09$  M,  $[2-(\text{EiB})-\text{Br}]_0 = 0.0139$  M,  $[2-(\text{EiB})-\text{Br}]_0/[CuBr]_0/[CuBr_2]_0/[bpy]_0/[Al(OiPr)_3]_0 = 1:1:0.2:3:6:1$ .  $M_{n,th} = (M_w)_0\{[M]_0 \times \text{Conv.}(\%)/[2-(\text{EiB})-\text{Br}]_0\}$ .

and activity of the transition-metal components including Cu(I) catalyst and Cu(II) deactivator. The proportion of radicals was reduced and the polymerization rate was consequently decreased with increasing the concentration of deactivator  $CuBr_2$ .

Table 4 shows the experimental results of ATRP of MMA by adding different concentrations of  $CuBr_2$  as deactivator when the polymerization conversions reach over 55%. Apparently, the reaction time was the shortest without adding  $CuBr_2$ , but the MWD was the widest ( $M_w/M_n = 1.94$ ), the reaction times became longer and the polydispersities of polymer became lower ( $M_n/M_w = 1.26 - 1.47$ ) after adding the deactivator  $CuBr_2$ .

Fig. 3 displays the logarithmic conversion data,  $\ln([M]_0/[M])$  vs. time. The initial part of first-order plot (a) was curved in the initial stage

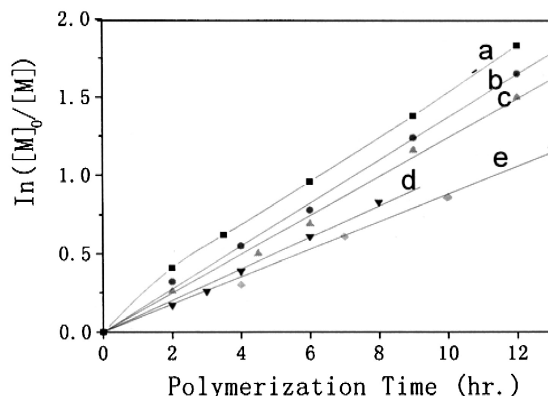


Fig. 3. Kinetics of ATRP of MMA with different concentrations of  $CuBr_2$  at 40°C. Cyclohexanone/MMA = 2:1 (v/v),  $[MMA] = 3.11$  mol l,  $[2-(\text{EiB})-\text{Br}] = 0.0462$  mol l,  $[2-(\text{EiB})-\text{Br}]/[CuBr]/[bpy]/[Al(OiPr)_3] = 1:0.5:3:1$ ; (a)  $[CuBr_2]/[2-(\text{EiB})-\text{Br}] = 0$ ; (b) 0.005; (c) 0.025; (d) 0.01; (e) 0.5.

without adding  $CuBr_2$ , but the other parts were linear. That indicates that the polymerization of MMA was not really in the first-order reaction without adding  $CuBr_2$ . It can be inferred that the probability of radical termination was high during the initial period, as there was not enough Cu(II) to deactivate the radicals to dormant species. Then, the equilibrium between free radicals and dormant species was established with gradually generated Cu(II), and so the radical concentration was constant in a later period. In contrast, when adding  $CuBr_2$ , the first-order rate plots were linear; it indicates that the ATRP was really in the first-order reaction manner, and the concentrations of the growing species remained constant. The conversion of MMA monomer was slower with the increase in the

Table 4  
ATRP data of MMA with different concentrations of  $CuBr_2$  at 40°C<sup>a</sup>

$[CuBr_2]/[2-\text{EiB}-\text{Br}]$	Time (h)	Conversion (%)	$M_{n,th} \times 10^{-3b}$	$M_{n,GPC} \times 10^{-3}$	$M_w/M_n$
0	6	61.7	12.4	14.9	1.94
0.005	6	59.7	12.0	15.0	1.47
0.025	9	68.5	13.7	15.4	1.39
0.1	8	56.4	11.3	13.8	1.30
0.5	10	57.5	11.5	10.6	1.26

<sup>a</sup> Cyclohexanone/MMA = 2:1 (v/v),  $[MMA] = 3.11$  mol l<sup>-1</sup>,  $[2-(\text{EiB})-\text{Br}] = 0.0154$  mol l<sup>-1</sup>,  $[2-(\text{EiB})-\text{Br}]/[CuBr]/[bpy]/[Al(OiPr)_3] = 1:0.5:3:1$ .

<sup>b</sup>  $M_{n,th} = M_{MMA}\{\Delta[M]/[2-(\text{EiB})-\text{Br}]\}$ .

concentration of  $\text{CuBr}_2$ . As the amount of the added  $\text{CuBr}_2$  was too much, the  $\text{CuBr}_2/\text{bpy}$  complex was dispersed heterogeneously; the polymerization rate did not decrease greatly by adding  $\text{CuBr}_2$ .

Fig. 4 shows the number-average molecular weights ( $M_n$ ) and polydispersities ( $M_w/M_n$ ) of the poly(methyl methacrylate) vs. conversion when the molar ratio of  $\text{CuBr}_2$  to 2-(EiB)-Br was 0.1. The  $M_w/M_n$  of the polymers was fairly narrow and became narrower as conversion increased ( $M_w/M_n = 1.41\text{--}1.26$ ).

The slopes of the straight kinetic plots in Fig. 3 allow for calculating the apparent propagation rate constants  $k_p^{\text{app}}$  of ATRP of MMA with different concentration of  $\text{CuBr}_2$ . Assuming propagation occurs in “normal” free radicals, the stationary concentrations of radicals  $[P^\cdot]$  can be estimated from the ratio of the apparent rate constant  $k_p^{\text{app}}$  and the rate constant of radical propagation  $k_p^\cdot$  according to Eqs. (1)–(4)

The kinetic data and estimated concentrations of growing radicals are shown in Table 5. It is shown that the concentrations of growing radicals decreased by increasing the concentration of  $\text{CuBr}_2$ . The data also show that the active radical concentrations ( $\times 10^{-7}$ ) were much less than the initiator concentration ( $\times 10^{-2}$ ).

The above mentioned results show that  $\text{Cu(II)}$  really plays a vital role in ATRP with  $\text{CuX}$  as catalyst. Under the above condition,  $\text{Cu(II)}$ ,

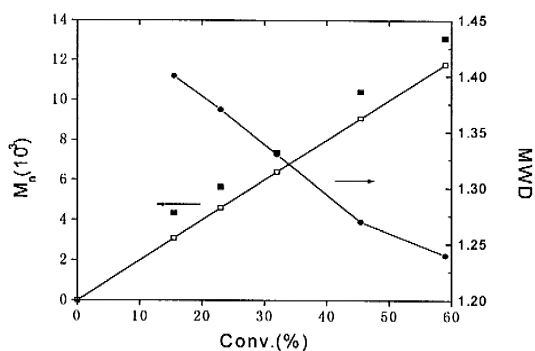


Fig. 4.  $M_{n,th}$ ,  $M_{n,GPC}$  and  $M_w/M_n$  dependence on monomer conversion for ATRP of MMA at 40°C. Cyclohexanone/MMA = 2:1 (v/v),  $[\text{MMA}] = 3.11 \text{ mol l}^{-1}$ ,  $[\text{2-(EiB)-Br}] = 0.0154 \text{ mol l}^{-1}$ ,  $[\text{2-(EiB)-Br}]/[\text{CuBr}]/[\text{CuBr}_2]/[\text{bpy}]/[\text{Al(OiPr)}_3] = 1:0.5:0.1:3:1$ .

Table 5

Kinetic data and estimated concentrations of propagating radicals  $[P^\cdot]$  for ATRP of MMA at 40°C  
Cyclohexanone/MMA = 2:1 (v/v),  $[\text{MMA}] = 3.11 \text{ mol l}^{-1}$ ,  $[\text{2-(EiB)-Br}] = 0.0154 \text{ mol l}^{-1}$ ,  $[\text{2-(EiB)-Br}]/[\text{CuBr}]/[\text{bpy}]/\text{Al(OiPr)}_3 = 1:0.5:3:1$ .

$\text{CuBr}_2 /$ 2-(EiB)-Br	$k_p$ ( $10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ )	$k_p^{\text{app}}$ ( $10^{-4} \text{ s}^{-1}$ )	$[P^\cdot]$ ( $10^{-7} \text{ mol l}^{-1}$ )
0.005	0.298	0.374	1.26
0.025	0.298	0.343	1.15
0.1	0.298	0.277	0.930
0.5	0.298	0.237	0.795

generated in redox process, was not enough to rapidly transfer the radicals to dormant species. Addition of  $\text{CuX}_2$  is essential to gain the polymer with narrow MWD because the radical concentration was reduced by  $\text{CuBr}_2$  and, subsequently, the bimolecular termination between radicals was suppressed.

### 3.3. Mechanism of the influence of $\text{Al(OiPr)}_3$ and $\text{Cu(II)}$ on ATRP

The results indicated that the catalytic promoter,  $\text{Al(OiPr)}_3$ , really decreased reaction temperature and increased the rate and controllability of polymerization. The reasons for this were analyzed. First, in the presence of the Lewis acid, this bulky Lewis acid may coordinate with the carbonyl group of initiator and dormant species (polymer chains with halogen atom at their end units); therefore, the carbon–halogen bond next to the ester carbonyl was activated, consequently increasing the rate of initiation and propagation [6,7] in ATRP. Secondly, due to the hinder and electronic effects of the coordinate  $\text{Al(OiPr)}_3$ , the radical species were stabilized by the coordination of Lewis acid, and so have lower termination rate constant, which suppresses the biradical termination reaction and increases the controllability of polymerization. Moreover, from the thermodynamic point of view, the apparent propagation activation enthalpy in ATRP is composed of the radical propagation activation enthalpy and activation enthalpy of halogen atom transfer. The coordi-

nation of Lewis acid reduces the activation enthalpy of halogen atom transfer, and consequently reduces the apparent propagation activation enthalpy [15]. Therefore, the dynamic equilibrium constant ( $K_{ep}$ ) between radicals and dormant species increases, and so does the stable concentration of radicals.

The results also indicated that Cu(II) compound can improve the controllability of ATRP. The oxidized transition-metal compounds, such as Cu(II) compound, can be called as deactivator in ATRP. They cannot only be generated in the ATRP process, but can also be added to the reaction system before polymerizing. The deactivation reaction must be controlled by the diffusion rate,  $k_d = 10^{8 \pm 1} \text{ mol}^{-1} \text{ l s}^{-1}$ . If the deactivation rate is not less than propagation rate, one, or less than one, the monomer unit will be incorporated at each activation step. In this case, the polymerization process is well controlled and may be considered an “insertion” proceeding via radical intermediates. Well-defined polymers with low MWD can be generated. According to Eq. (5), the MWD of polymers was decreased with increasing conversion  $P$  [11,12]:

$$M_w/M_n = 1 + (2/P - 1) \left\{ ([RX]_0 - [RX])k_p \right\} / (k_{deact}[Cu(II)]) \quad (5)$$

This equation can be simplified for complete conversion ( $p = 1$ ) and complete initiation:

$$M_w/M_n = 1 + ([RX]_0 k_p) / (k_{deact}[Cu(II)]) \quad (6)$$

Thus, the MWD is higher for shorter chains (higher  $[RX]_0$ ) and for higher  $k_p/k_{deact}$  ratios. When increasing the deactivator concentration,  $[D] = [Cu(II)]$ , the chain radicals will be rapidly deactivated to form the dormant species. The

radical concentration  $[P \cdot]$  is reduced and subsequently the bimolecular termination between chain radicals is suppressed greatly. Consequently, the MWD should decrease with increasing deactivator concentration.

#### 4. Conclusion

The complex catalytic system, consisting of CuBr/bpy/Al(OiPr)<sub>3</sub>, has high catalytic activity. With proper amount of CuBr<sub>2</sub> as deactivator, many kinds of monomers, such as methacrylates, can be polymerized at low temperature in a living manner with the complex catalytic system and yield well-defined polymers with narrow MWD.

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