

# CuBr<sub>2</sub>/Me<sub>6</sub>TREN Mediated ARGET ATRP of Methyl acrylate in Polyethylene Glycol

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## ABSTRACT

ARGET ATRP of methyl acrylate (MA) with low concentration of air stable-CuBr<sub>2</sub> catalyst was successfully carried out in green solvent polyethylene glycol (PEG) without any external reducing agent. The polymerizations of MA proceeded in a well-controlled manner as evidenced by kinetic studies, chain extension results, a linear increase of the molecular weights with the increasing of monomer conversion, and narrow molecular weight distribution ( $M_w/M_n=1.1$ ). Interestingly, we found that the PEG has the reduction ability to CuBr<sub>2</sub> and could play as supplement reducing agent cooperation with Me<sub>6</sub>TREN to mediate ARGET ATRP. Reduction of Cu(II)Br<sub>2</sub> to Cu(I)Br by different molecular weight PEG was proved by UV-visible spectroscopy. A. Q.-PEG with different molecular weight have strong effects on polymerization rate and the polymerization can be operated at suitable conditions where the use of catalyst concentration can decrease to 25 ppm level.

KEYWORDS: ARGET ATRP, PEG, Green Solvent, Reducing Agent, Methacrylate

## INTRODUCTION

Atom transfer radical polymerization (ATRP), one of the reversible deactivation radical polymerization (RDRP) methods, can be used to synthesize well-defined polymers and materials with complex architectures.<sup>[1-4]</sup> Aiming to enhance the possibilities of industrial application of this catalytic system, several new

ATRP methods have been developed to diminishing catalysis concentration, including activators regenerated by electron transfer (ARGET),<sup>[5-7]</sup> initiators for continuous activator regeneration (ICAR) ATRP,<sup>[8]</sup> supplementary activator and reducing agent (SARA) ATRP,<sup>[9]</sup> single-electron-transfer living radical polymerization (SET-LRP),<sup>[10]</sup> electrochemically

mediated ATRP (*e*-ATRP),<sup>[11-12]</sup> and photochemically mediated ATRP.<sup>[13-15]</sup> Among these methods, A(R) GET ATRP can be conducted in the presence of limited air and the catalyst concentration could be reduced to ppm level. In most cases, removal of the low levels of catalyst is achieved simply by precipitation of the polymer. Different from normal ATRP, transition metal catalyst in ARGET ATRP system is used in its deactivated, higher oxidation state. To activate the catalyst, an excess amount of reducing agent relative to metal catalyst is introduced to continuously reduce the catalyst to its activated state and regenerate the persistent radicals. The reducing agent choosing and related rate of reduction reaction can greatly influence the ARGET ATRP. Under careful selection of polymerization conditions, the catalyst concentration can be reduced to the ppm level without sacrificing controllability.<sup>[16-18]</sup>

A variety of reducing agents, including hydrazine(s),<sup>[18]</sup> tin(II) 2-ethylhexanoate,<sup>[19-20]</sup> ascorbic acid,<sup>[21]</sup> thiourea dioxide,<sup>[22]</sup>  $\beta$  cyclodextrin<sup>[23]</sup> have been investigated as reducing agent in ARGET ATRP. Among these, ascorbic acid and tin(II) 2-ethylhexanoate were the most widely investigated additive in ARGET ATRP system.<sup>[24]</sup> However, since ascorbic acid has a strong reducing ability and can break the balance between the higher oxidation state deactivators and lower oxidation state activators. Hence, ascorbic acid can only be used in a heterogeneous mixture where a low catalyst dosage used.<sup>[25]</sup> Interestingly, nitrogen based ligands themselves also have been exploited as reducing agent in ARGET ATRP. This means external reducing agent became unnecessary. This catalytic system is very

promising since reducing agent residue may affect the final properties of the polymer. Matyjaszewski's and our groups detailedly investigated the A(R)GET ATRP of MMA using an excess of these nitrogen based ligands in the absence of any additional reducing agents.<sup>[26-27]</sup> It is well known that Me<sub>6</sub>TREN was universally added as ligand in a typical ARGET ATRP system, giving a fast, low catalyst usage and well controlled polymerization. The using of Me<sub>6</sub>TREN both as reducing agent and ligand was firstly explored by Matyjaszewski's group in ARGET ATRP of n-butyl acrylate (BA) at 60 °C.<sup>[28]</sup> Although BA polymerization was well controlled in terms of molecular weight, values of molecular weight distribution were very higher (PDI=1.83 for a monomer conversion of 86%) and the catalyst concentration was up to 500 ppm. Subsequently, Liu reported the ARGET ATRP of MMA conducted in bulk and different solvent employed Me<sub>6</sub>TREN as both reducing agent and ligand, and found that the polymerization of MMA in DMSO shown the best controlled  $M_w$  and low PDI values.<sup>[29]</sup> However, in order to achieve good controllability, the amount of CuBr<sub>2</sub> catalyst should be kept at around 500ppm to mediate monomer polymerization.

As mentioned above, the solvent strongly effect the behaviors of ATRP including polymerization rate and molecular weight distribution where Me<sub>6</sub>TREN both as ligand and reducing agent. The use of polar solvents often leads to fast polymerization, and the activation rate constant ( $k_{act}$ ) increases with increasing solvent polarity. However, slightly higher concentrations of catalyst should be added to maintain sufficient deactivators. It is urgent to screen other polar solvent candidates to expand the scope of

application of ARGET ATRP and reduce catalyst concentration when adapted Me<sub>6</sub>TREN both as ligand and reducing agent.

Low molecular weight polyethylene glycols (PEG), due to their good biocompatibility, low cost, low toxicity to human beings and the environment, PEG act as a new kind of environmentally friendly polar solvent have attracted increasing interest and widely applied in organic synthesis,<sup>[30-31]</sup> also in polymer synthesis.<sup>[32-37]</sup> The use of PEG as solvent for ATRP polymerization was first carried out in the polymerization of MMA mediated by CuBr<sub>2</sub>/2,2'-bipyridine.<sup>[35]</sup> Our group subsequently reported AGET ATRP of MMA and SARA ATRP of MA using PEG as green solvents.<sup>[27, 36]</sup> Interestingly, PEG can act not only as a solvent, but also as a ligand. AGET ATRP of MMA using iron catalyst was carried out in PEG without any additional ligand.<sup>[37]</sup> All the results showed that polymerization in PEG exhibited a higher reaction rate compared with other solvents.<sup>[27,35-36]</sup> Some hypotheses have been proposed to explain this phenomenon.<sup>[35,38]</sup> One is contributed to be the polarity and the coordination ability of the PEG solvent; another is the terminal hydroxyl group in PEG could potentially accelerate the polymerization rate. However, the effects of PEG in radical polymerization have not fully understand.

There are no reports concerns low levels of catalyst to synthesize well controlled polymers in polar PEG solvent. The main reason may be that PEG has well excellent miscibility with these traditional strong reducing agents and can quickly convert Cu(II) into Cu(I) species.<sup>[37]</sup> Very fast reduction process of Cu(II) complexes by strong reducing agents diminishes dormant

Cu(II) species concentration to a very low level, thus increases concentration of radicals and decreases polymerization control. In a typical copper catalyst ARGET ATRP in PEG, the concentration of catalyst was always very high. In this paper we report the use of ARGET ATRP in PEG to synthesize well designed PMA with Me<sub>6</sub>TREN ligand also as reducing agent under low levels of Cu catalyst. The effects of PEG with different molecular weight and usage, and the concentration of the catalyst were investigated to find best conditions where giving well controlled polymers with defined molecular weight and low PDI values.

## EXPERIMENTAL

### Materials

Methyl acrylate (MA, AR, Aladdin Industrial Corporation (China)) was passed through a basic alumina column before use in order to remove the radical inhibitor. 2,2'-Bipyridine (Bpy, AR, Sinopharm Chemical Reagent Co. Ltd., SCRC), Ethyl 2-bromoisobutyrate (EBiB, Alfa Aesar), CuBr<sub>2</sub> (CP, SCRC), PEG(200) (CP, SCRC), PEG(400) (CP, SCRC), PEG(600) (CP, SCRC), Poly(ethylene glycol) dimethyl ether ((PEGME(400), Alfa Aesar) and Tris [2-(dimethylamino) ethyl] amine (Me6TREN, Alfa Aesar) were used as received. Puried water was obtained by reverse osmosis. Tetrahydrofuran (THF) (HPLC grade) was filtered under reduced pressure before use. Other solvents and reagents were used without further purification except as noted.

### Measurements

Monomer conversion was determined by gravimetry and number average ( $M_n$ ) and molecular weight distributions were determined by gel permeation chromatograph (GPC) on a PL GPC220 equipped with two PLgel 5  $\mu$ m MIXED-C columns using a series of standard PMMA as calibrations and THF as the eluent at a flow rate of 1.0 mL/min at 40°C. The ultraviolet-visible (UV-VIS) studies were performed with a Cary 5000 UV-visible spectrometer. The analyzes were

carried in the 200–1100 nm range at room temperature (RT). The chemical structures of the resultant PMMA were confirmed in  $\text{DCCl}_3$  using a Bruker ARX 400  $^1\text{H}$  NMR spectrometer with tetramethylsilane as the internal standard.

#### Reduction of $\text{Cu(II)Br}_2/\text{Bpy}$ complex using various PEG

Reduction of  $\text{Cu(II)}$  to  $\text{Cu(I)}$  by PEG was followed by UV–visible spectroscopy.  $\text{Cu(II)Br}_2$  (4.5 mg, 20  $\mu\text{mol}$ ), Bpy (6.3 mg, 40  $\mu\text{mol}$ ) and PEG (5 mL) were added to a dried Schlenk flask and bubbled with nitrogen for about 15 min to remove oxygen, then immersed in a thermostated oil bath at designed temperature. After an expected time, the Schlenk flask was transferred to a quartz cuvette and measured by a Cary 5000 UV–visible spectrometer. The absorbance of  $\text{Cu(II)}$  deactivator complex was records at timed intervals.

#### Typical procedure for the ARGET ATRP of MA (DP = 222) catalyzed by $\text{Cu(II)Br}_2/\text{Me}_6\text{TREN}$ in PEG

In a typical ARGET ATRP experiment,  $\text{CuBr}_2$  (3.4 mg, 15  $\mu\text{mol}$ ) was dissolved in 3 mL of relevant PEG in a dry glass tube. Then 3 mL of degassed MA (33.1 mmol) was added and the mixture was bubbled with nitrogen for 15 min, and then sealed with a rubber septum.  $\text{Me}_6\text{TREN}$  (8  $\mu\text{L}$ , 30  $\mu\text{mol}$ ), EBiB (22.9  $\mu\text{L}$ , 150  $\mu\text{mol}$ ) were subsequently introduced via a syringe, then immersed in a thermostated oil bath at designed temperature. After an expected time, the tube was opened to stop the reaction. The product PMA was obtained after precipitation in large amounts of water, decanted, and

drying in *vacuo* to constant weight. The conversion of the monomer was determined gravimetrically.

#### Chain extension experiment: polymerization from a Br terminated PMA macroinitiator

Chain extension was performed employing above ARGET ATRP technique in PEG(600). In a polymerization tube, 0.18 g ( $1.48 \times 10^{-2}$   $\mu\text{mol}$ ) of PMA ( $M_n = 12100$  g/mol) macroinitiator was dissolved in 3 mL of MA (33.1 mmol) under stirring and nitrogen atmosphere. 3.4 mg of  $\text{CuBr}_2$  was dissolved in 3 mL PEG(600) in another tube under stirring. After both solutions above were mixed, bubbled with nitrogen for 15 min, and then sealed with a rubber septum.  $\text{Me}_6\text{TREN}$  (8  $\mu\text{L}$ , 30  $\mu\text{mol}$ ) was subsequently introduced via a syringe, then placed in an oil bath at the desired reaction temperature. After 6 h, the tube was opened to stop the reaction. The chain-extended PMA was obtained after precipitation in large amounts of water, decanted, and drying in *vacuo* to constant weight.

## RESULTS AND DISCUSSION

### ARGET ATRP of MA in PEG with different molecular weight

Based on the mentioned above, ARGET ATRP of methyl acrylate (MA) was performed with various molecular weights PEG using  $\text{CuBr}_2/\text{Me}_6\text{TREN}$  as the catalyst precursor at 50 °C without external reducing agent. The polymerization results are shown in Table 1.

TABLE 1. Results of ARGET ATRP of MA in PEG at 50 °C.

Run <sup>a</sup>	Solvent	Time (h)	Conv. (%) <sup>b</sup>	$M_{n,\text{th}}^c$ (g/mol)	$M_{n,\text{GPC}}^d$ (g/mol)	$M_w/M_n$
1	PEGME(400)	12	11	2400	5500	1.11
2	PEG(200)	4	65	12500	10800	1.10
3	PEG(400)	4	46	9000	9300	1.10
4	PEG(600)	4	33	6400	7000	1.09

<sup>a</sup>Experiment conditions:  $[\text{MA}]_0/[\text{EBiB}]_0/[\text{CuBr}_2]_0/[\text{Me}_6\text{TREN}]_0 = 222/1/0.1/0.2$  in PEG at 50 °C,  $V_{\text{MA}} = 3$  mL, 0.033 mol,  $V_{\text{PEG(600)}} = 3$  mL; <sup>b</sup>Determined gravimetrically. <sup>c</sup> $M_{n,\text{th}} = M_{\text{EBiB}} + [\text{MA}]_0/[\text{EBiB}]_0 \times \text{conversion} \times M_{\text{MA}}$ . <sup>d</sup>Determined using GPC against PMMA standard.

As can be seen from Table 1 (Run 2–4), all of the polymerizations of MA can be well controlled in the presence of different molecular weight PEG, the  $M_{n,GPC}$  is similar to the  $M_{n,th}$  and the PDI is about 1.1. Having taken into account that the reaction time and conditions used are almost the same for the different PEG used, PEG(200) seems to provide the faster reaction rate since it achieved the highest monomer conversion (65%) after 4 h polymerization time. It is well known that higher polar solvent can accelerate polymerization rate in ATRP reaction, such as water and some ionic liquid.<sup>[39-40]</sup> Generally, the higher the polarity of solvent, the faster the polymerization rate. Among these three PEG, PEG(200) shows highest polarity with the highest dielectric constant ( $\epsilon = 21.1$ ), and the values of PEG(400) and PEG(600) are 13.7, 11.6 respectively.<sup>[41]</sup> As a result, PEG(200) provides the faster polymerization reaction rate.

Another possible reason may be that PEG (200) contains more hydroxyl groups, which accelerates the polymerization. Then we checked whether the hydroxyl group worked to accelerate the polymerization rate. PEGME(400) terminated by two methyl groups at the end of the PEG chains was used under comparable reaction conditions (Table 1, Run 1), the polymerization rate lowered significantly, only 11% of monomer being converted after 12 h. This may be lack of hydroxyl group in PEGME(400) which can accelerate the polymerization reaction, and caused low monomer conversion.

Since no external reducing agent was added into the polymerization solution, Me<sub>6</sub>TREN may act as an intrinsic reducing agent to reduce Cu(II) to Cu(I). However, sufficient amount of

Me<sub>6</sub>TREN needed to maintain a well-controlled polymerization. Generally, a 10-fold excess of Me<sub>6</sub>TREN (with four tertiary amine groups capable of reducing Cu(II)) was used in the absence of any other reducing agent. This is just 2 equiv. of Me<sub>6</sub>TREN relative to Cu(II)Br<sub>2</sub> using in this article. Theoretically, Me<sub>6</sub>TREN will quickly be consumed and polymerization reaches only limited conversion. However, the monomer conversion reached about 65% in PEG(200), and with the increase in molecular weight PEG (i.e. decrease the amount of hydroxyl group), the conversion of the monomer is significantly reduced. Especially, only 11% of monomer being converted in the absence of hydroxyl group where PEGME(400) used as solvent. These results mention us that the role of PEG is not simply to accelerate the polymerization reaction rate. There are some article reports that small molecular alcohol can be used as reducing agent in AGET ATRP,<sup>[42-45]</sup> PEG has similar functional hydroxyl group like alcohol, and also be used as reducing agent in nano-materials synthesis.<sup>[46]</sup> There is high possibility that PEG in ATRP can also act as reductant, react with higher oxidation metal catalyst generated highly concentrated activated species and then promoted polymerization rate. It is not surprised that PEG may play as supplement reducing agent to mediate ARGET ATRP.

#### Reduction of Cu(II) to Cu(I) by PEG

To further prove that PEG has reduction ability to Cu(II)Br<sub>2</sub>, we carried out the reduction reactions of Cu(II)Br<sub>2</sub> with PEG under the similar ARGET ATRP conditions. As the reduction of Cu(II) to Cu(I) may occurred in the presence of Me<sub>6</sub>TREN ligand. So, to avoid the ligand effect, we selected bipyridine as the

model ligand. When the reaction proceeded under the given conditions after 8 h, the color of the homogeneous solution changed gradually from blue to light yellow, indicating that Cu(II)/Bpy was reduced into Cu(I)/Bpy by PEG (Support information Figure 1s). UV-visible spectroscopy was also used to confirm the reduction of Cu(II)/Bpy to Cu(I)/Bpy. As the Figure 1 shows, it can be clearly seen that the maximum absorption of the Cu(II)/Bpy solution appears at 740 nm, the signals of the Cu(II)/Bpy complexes shows a decrease of absorption with time due to the reduction of Cu(II) to Cu(I). The formation of Cu(I) by heating Cu(II)/Bpy in PEG in the absence of any other reducing agent may occur through the oxidation of the hydroxyl group in PEG. So hydroxyl group amounts in PEG may have strong effects on this reduction reaction rate. Figure 1 displayed the

experimental UV-visible spectra of the reduction of Cu(II)/Bpy to Cu(I)/Bpy using different molecular weight PEG as reducing agent at 50 °C for 8 h. A weak decrease of Cu(II) absorption was observed when PEG(600) using, showing that Cu(I) were formed under a relatively low concentration. The intensity of this absorption was slightly decreased when PEG(400) was applied. In the case of using PEG(200), a significant decrease was observed, indicating that a high concentration of Cu(II) have been reduced to Cu(I). It is clear that the reducing reactivity of PEG was remarkably enhanced with the increase of hydroxyl group content. These results all demonstrate that Cu(II)/Bpy can be reduced into Cu(I)/bpy under the polymerization conditions by PEG.

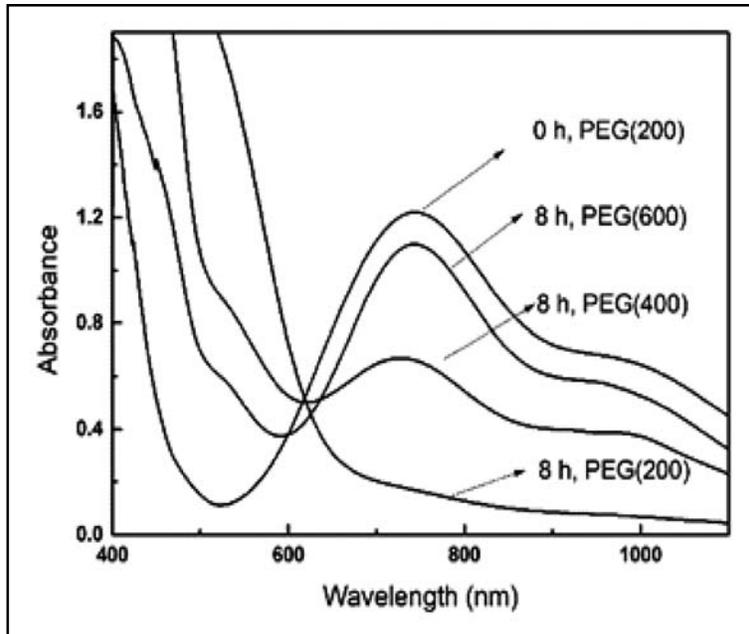


Fig. 1. UV-Vis spectra of CuBr<sub>2</sub>/Bpy in PEG (5mL) at 50 °C. Reaction time = 8h ([Cu(II)Br<sub>2</sub>]/[Bpy] = 4/8 mmol L<sup>-1</sup>).

### Effect of catalyst dosage on the ARGET ATRP of MA

It is valuable to diminish the amount of catalyst for ATRP reaction, the appropriate reducing agent and concentration of reducing agent is key point for a well-controlled polymerization. The reagent will quickly be consumed if too little is used, and too much might lead to fast and uncontrolled polymerizations or unwanted side reactions with the catalyst. The selection becomes more complicated here by the fact that Me<sub>6</sub>TREN ligand and PEG can also both act as mild reducing agent. The amounts of PEG usage, Me<sub>6</sub>TREN and concentration of catalyst had to be taken into account carefully. In our previous experiment, when we tried to mediate the polymerization in PEG200 using a low catalyst concentration, we found that polymers with higher monomer conversion

(>90) was formed after only 2h reaction time with uncontrolled molecular weight and broad molecular weight distribution (PDI > 2.0). These results are due to the stronger reduction ability of PEG(200) than PEG(600) (Figure 1). It will very quickly convert Cu(II) to Cu(I) species, and increases concentration of radicals, decreases polymerization control. In ATRP reaction, a sufficient amount of deactivating species (CuBr<sub>2</sub>) is needed for well-controlled polymerization since both molecular weight distribution and initial molecular weight depend on the ratio of the propagation and deactivation rate constants and the concentration of deactivator.<sup>[47]</sup> Taking the polymerization rate and controllability into consideration, PEG(600) was selected as the reaction media for our next polymerization, because PEG(600) is a relatively mild reducing agent.

TABLE 2. The effect of volume of PEG(600) on the ARGET ATRP of MA

Run <sup>a</sup>	Solvent	Time (h)	Conv. (%) <sup>b</sup>	M <sub>n,th</sub> <sup>c</sup> (g/mol)	M <sub>n,GPC</sub> <sup>d</sup> (g/mol)	M <sub>w</sub> /M <sub>n</sub>
5	PEG(600)	3:3	56	11000	12000	1.08
6	PEG(600)	3:2	27	5300	5200	1.08
7	PEG(600)	3:1	11	2300	2200	1.11
8	PEG(600)	3:0.5	8	1800	1700	1.20

<sup>a</sup>Experiment conditions: [MA]<sub>0</sub>/[EBiB]<sub>0</sub>/[CuBr<sub>2</sub>]<sub>0</sub>/[Me<sub>6</sub>TREN]<sub>0</sub> = 222/1/0.1/0.2 in PEG at 50 °C, reaction time = 6 h; <sup>b</sup>Determined gravimetrically. <sup>c</sup>M<sub>n,th</sub> = M<sub>EBiB</sub> + [MA]<sub>0</sub>/[EBiB]<sub>0</sub> × conversion × M<sub>MA</sub>. <sup>d</sup>Determined using GPC against PMMA standard.

As can be seen from Table 2 (Run 5–8), when the volume of PEG(600) was varied from 3 to 0.5 mL, the conversion decreased dramatically from 56 to 8 %, indicating that the polymerization rate decreased with decreasing the amount of PEG(600). Since the concentration of Cu(II)/Me<sub>6</sub>TREN is the same in all polymerization

conditions, the reason could be attributed to parts of the Cu(I) species formed by PEG involved in the reduction reaction. As a relatively weak reducing agent, a sufficient amount of PEG (3 mL) can still convert a portion of the Cu(II) species to the Cu(I) state.

Based on the above results, when polymerization was carried out with various initial  $\text{CuBr}_2/\text{Me}_6\text{TREN}$  catalyst loadings (Table 3, items 9-13), the amount of copper varied from a "high concentration" of 500 ppm to 5 ppm with respect to the monomer. It is

very important to consider the effects of PEG especially when low levels of catalyst used, since the PEG not only accelerate the polymerization reaction rate but also play as supplement reducing agent.

TABLE 3. The Effect of amounts of  $\text{CuBr}_2$  on the ARGET ATRP of MA

Run <sup>a</sup>	Solvent	$V_{\text{MA}}/V_{\text{PEG}}$ (mL: mL)	$[\text{M}]_0/[\text{I}]_0/[\text{Cu}]_0/[\text{L}]_0$	Cu (ppm)	Time (h)	Conv. <sup>b</sup> (%) <sup>b</sup>	$M_{n,\text{th}}$ <sup>c</sup> (g/mol)	$M_{n,\text{GPC}}$ <sup>d</sup> (g/mol)	$M_w/M_n$
9	PEG(600)	3:3	222/1/0.1/0.2	500	2.5	25	5200	5500	1.10
10	PEG(600)	3:3	222/1/0.01/0.02	50	2.5	23	4700	4200	1.26
11	PEG(600)	3:3	222/1/0.005/0.02	25	2.5	66	12800	11200	1.43
12	PEG(600)	3:1	222/1/0.005/0.02	25	10	63	12300	13200	1.20
13	PEG(600)	3:1	222/1/0.001/0.02	5	10	29	5700	7900	1.47

<sup>a</sup>Experiment conditions:  $[\text{MA}]_0/[\text{EBiB}]_0/[\text{CuBr}_2]_0/[\text{Me}_6\text{TREN}]_0 = 222/1/x/y$  in PEG at 50 °C, <sup>b</sup>Determined gravimetrically. <sup>c</sup> $M_{n,\text{th}} = M_{\text{EBiB}} + [\text{MA}]_0/[\text{EBiB}]_0 \times \text{conversion} \times M_{\text{MA}}$ , <sup>d</sup>Determined using GPC against PMMA standard.

It was observed that under same volume of PEG(600)(3 mL), a lower concentration of  $\text{CuBr}_2$  (25 ppm) resulted in a higher polymerization rate (Table 3, entry 11). It may be due to higher PEG(600)/ $\text{CuBr}_2$  ratio increased higher concentrations of the propagating radicals in the polymerization system, subsequently raised the polymerization rate. Meanwhile the termination reaction of propagating radicals also easily happened. Thus the broader molecular weight distributions of PMA were observed (PDI=1.43). So it is favorable to lower the ratio of PEG(600)/ $\text{CuBr}_2$  to maintained concentration of Cu(II) by balancing a slow termination process with an equally slow and steady reduction process. When polymerization conducted in 1 mL PEG(600) with 25 ppm of Cu (Table 3, Run 12), polymers with polydispersity below 1.2 were prepared. When only 5 ppm of copper was used

in the reaction medium with 1 mL PEG(600), the molecular weight of the polymer was still well controlled, but a higher PDI (1.47) was observed (Table 3, Run 13). Polymerizations carried out with 25 ppm or lower concentration of Cu resulted in the preparation of colorless polymers; therefore, catalyst removal may not be necessary in this polymerization system.

#### Kinetics of ARGET ATRP of MA in PEG

The polymerization kinetics was investigated to examine the effects of PEG and  $\text{CuBr}_2$  concentration. It can be seen from Figure 2a that polymerizations catalysed by slight higher levels of  $\text{CuBr}_2$  (500 ppm) in different types of PEG (PEG200, PEG600) proceeded with approximately first-order kinetics in both cases, indicating a constant agreement with the theoretical one, the molecular weight distribution (PDI,  $M_w/M_n$ ) remained 1.1 during

the entire polymerization period, indicating that control was quickly obtained and retained. Furthermore, the  $M_w/M_n$  values remained relatively narrow which is further demonstrated

in Figure 3. In view of these results, although no extra reducing agent was added, Cu-mediated ARGET ATRP of MA was a well-controlled polymerization process.

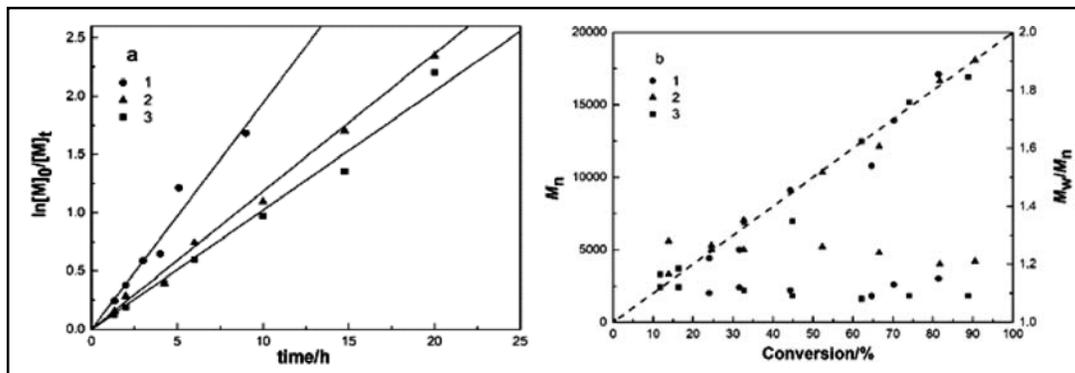


Fig. 2. (a) Kinetic plots of  $\ln[M]_0/[M]_t$  versus reaction time and (b) Dependence of molecular weights  $M_n$  and molecular weight distributions  $M_w/M_n$  on the monomer conversion for the ARGET ATRP of MA in PEG at 50 °C. Initial conditions: 1.  $[MA]_0:[EBiB]_0:[CuBr_2]_0:[Me_6TREN]_0 = [222]:[1]:[0.1]:[0.2]$ .  $V_{MA}/V_{PEG(200)} = 3\text{mL}/3\text{mL}$ ; 2.  $[MA]_0:[EBiB]_0:[CuBr_2]_0:[Me_6TREN]_0 = [222]:[1]:[0.1]:[0.2]$ .  $V_{MA}/V_{PEG(600)} = 3\text{mL}/1\text{mL}$ ; 3.  $[MA]_0:[EBiB]_0:[CuBr_2]_0:[Me_6TREN]_0 = [222]:[1]:[0.005]:[0.02]$ .  $V_{MA}/V_{PEG(600)} = 3\text{mL}/3\text{mL}$ ;

Compared with polymerization using PEG(200) as solvent, the polymerization in PEG(600) was slower, reaching 33% and 65% conversion after 4 h in PEG(600), PEG(200) respectively. The difference may be due to higher polarity and

the amounts of hydroxyl group in PEG(200) three times higher than in PEG(600), it will provide more Cu(I) active substances and cause higher polymerization rate.

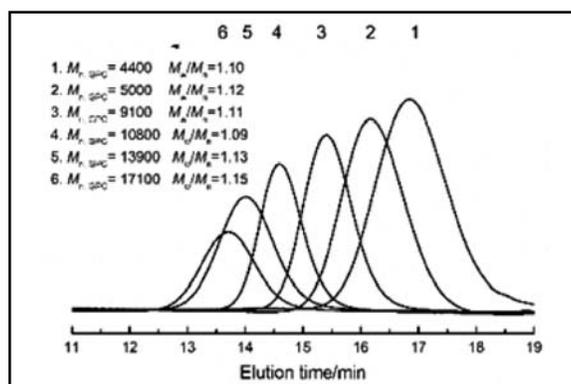


Fig. 3. GPC traces of the obtained PMA in PEG-200. Initial conditions:  $[MA]_0:[EBiB]_0:[CuBr_2]_0:[Me_6TREN]_0 = [222]:[1]:[0.1]:[0.2]$ .

It is difficult to reach well controlled polymerization under low concentration of  $\text{CuBr}_2$  when  $\text{Me}_6\text{TREN}$  used both as reducing agent and ligand. The reason is that a larger excess of ligand to Cu was required to reduce  $\text{Cu(II)Br}_2$  and stabilize copper-based ATRP catalyst as the release of acid during the oxidation of amines ligands can destabilize these catalysts. However, surplus ligands may generate higher concentration of Cu(I) species during the initial stage of polymerization, causing an increase proportion of termination reaction. However, when polymerization conducted in 1 mL PEG(600) with 25ppm  $\text{CuBr}_2$  and only 4-fold of  $\text{Me}_6\text{TREN}$  was added, as Figure 2 (a) line 2 shows, the kinetics plots of polymerization increased linearly, indicating an almost constant number of radicals throughout the polymerization process. The MA conversions reached 90% after 20 h, and the molecular weights of all the polymers increased linearly

with time and increasing monomer conversion with slightly broad PDI values (about 1.2). The results clearly illustrated that sufficient reducing agent is present in polymerization system to regenerate of the Cu(I) activator, since only 4-fold of  $\text{Me}_6\text{TREN}$  to  $\text{CuBr}_2$  was added, PEG may play as supplement reducing agent to maintain a constant number of radicals.

#### End-group analysis and chain extension of PMA

The chain end of the PMA ( $M_{n,\text{GPC}} = 4100 \text{ g mol}^{-1}$ ,  $M_w/M_n = 1.12$ ) using EBiB as the initiator and  $\text{CuBr}_2/\text{Me}_6\text{TREN}$  as the catalyst in PEG without any additional reducing agent was analyzed by  $^1\text{H NMR}$ . The assignment of proton resonances conducted according to references.<sup>[48]</sup> The PMA NMR molecular weight was calculated using the equation  $M_{n,\text{NMR}} = \{[I(e)/(I(b)/2)] + 1\} \times M_{w,\text{MA}} + M_{w,\text{EBiB}}$ , where  $I(e)$  is the integral of the PMA main chain C-H proton  $-\text{CH}_2-\text{CH}_2(\text{CO}_2\text{Me})-$  at 2.3 ppm and  $I(b)$

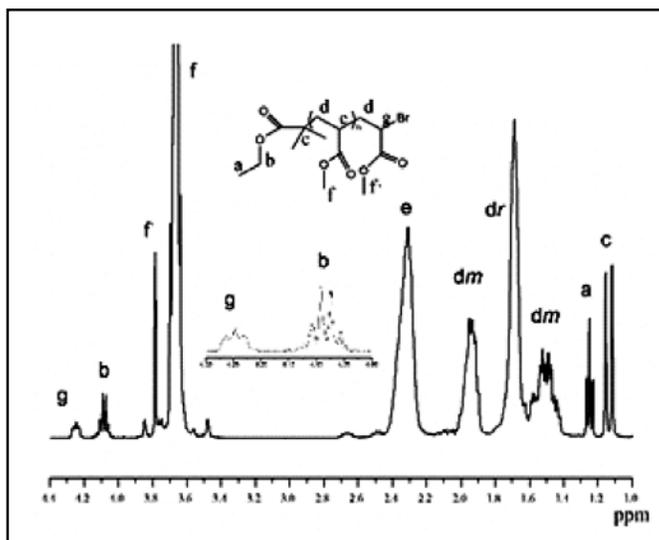


Fig. 4. The  $^1\text{H NMR}$  spectrum of PMA-Br ( $M_{n,\text{GPC}} = 4100$ ;  $M_w/M_n = 1.12$ ;  $M_{n,\text{NMR}} = 3800$ ; active chain-end functionality = 97.8 %). The solvent is  $\text{CDCl}_3$ .

is the integral of the initiator fragment – CH(CH<sub>3</sub>)<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> at 4.07 ppm. The molecular weight calculated from the <sup>1</sup>H NMR spectrum ( $M_{n,NMR}$ ) was 3800 g mol<sup>-1</sup>, which is in good agreement with  $M_{n,GPC}$ , indicating that the PMA obtained was end terminated by the Br atoms with high fidelity. The percentage of the chain-end functionality was calculated as follows: % functionality = [I(g)/I(b)/2] × 100%;

where I(g) is the integral of the PMA terminal bromo chain-end –CH<sub>2</sub>-CHgBr(CO<sub>2</sub>Me) at 4.25 ppm and I(b) is the integral of the methylene group in the initiator fragment – CH(CH<sub>3</sub>)<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> at 4.07 ppm. The percentage of chain-end functionality for the initiator fragment was 97.8%. These data all revealed that most of the resulting PMA were active with the “living” polymer chain ends.

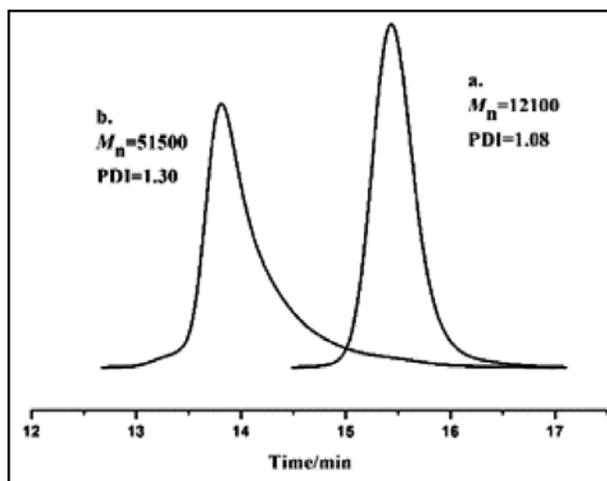


Fig. 5. GPC curves of PMA (a) before and (b) after chain extension. Original PMA:  $[MA]_0/[EBiB]_0/[CuBr_2]_0/[Me_6TREN]_0 = 100/1/0.1/0.2$ , (50:50 V/V monomer/PEG(600)) at 50 °C. Chain extended PMA:  $[MA]_0/[PMA]_0/[CuBr_2]_0/[Me_6TREN]_0 = 2220/1/1/2$ ,  $V_{MA} = 3$  mL, 0.033mol,  $V_{PEG(600)} = 3$  mL,  $T = 50$  °C.

In addition, to further prove the presence of the terminal Br chain ends in the growing polymer chains and the “living” nature of the PMA obtained by the reported method, a chain extension experiment was carried out. Figure 5 presents the GPC traces of the PMA-Br macroinitiator, PMA extended show the complete shift of the low molar mass PMA ( $M_n = 12100$ ,  $M_w/M_n = 1.08$ ) GPC trace towards a very high molar mass PMA ( $M_n = 51500$ ,  $M_w/M_n = 1.10$ ).

These results prove the “living” character of the PMA using this catalytic system.

## CONCLUSIONS

Summing up the results presented above, the ARGET ATRP of MA were successfully conducted at green solvent PEG catalyzed by CuBr<sub>2</sub>/Me<sub>6</sub>TREN without any external reducing agent. If an appropriate amount of PEG is

added, the amount of Cu species in ATRP can be reduced down to a few ppm without losing control over the polymerization. Here, PEG not only worked just as reaction media but also play as supplement reducing agent, the reduction ability of PEG was also confirmed by UV–visible spectroscopy. The present method produce polymers with controlled molecular weight, low dispersity, and well-defined chain-end functionality.

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