Optimizing Activators Regenerated by Electron Transfer for Atom Transfer Radical Polymerization of Methyl Methacrylate Initiated by Ethyl 2-bromopropionate

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Abstract: In this study, we used ethyl 2-bromopropionate (EBrP) as an initiator of activators regenerated by electron transfer for atom transfer radical polymerization (ARGET ATRP) of methyl methacrylate (MMA). We investigated in detail the effect on polymerization of different kinds of reducing agents and ligands, the amounts of the reducing agent and catalyst, and reaction temperature. We determined the molecular weight and dispersity of the polymers by gel permeation chromatography (GPC). The results reveal glucose to be the best reducing agent for this system. The monomer conversion increased with increases in the reaction temperature and in the feeding amounts of the reducing agent and catalyst. The optimum amount of the reducing agent and minimal amount of catalyst required depend on the particular system. For example, we polymerized MMA with 200 ppm of catalyst and 15-fold of glucose/$CuCl_2$ resulting in a PMMA with high M_n ($M_{n,GPC}$ = 48 700, $M_{n,theo}$ = 48 500) and low dispersity (1.27). The first-order kinetics show that the molecular weights increased linearly with the monomer conversion and are consistent with the theoretical values, the chain extension reaction and end group analysis results also demonstrate that the characteristics of polymerization process belong to a typical "living"/controlled radical polymerization. Moreover, ^{1}H-NMR analysis results indicate the stereoregularity of the polymer is given priority over syndiotactic architecture and the effect of the type of ligand on the stereoregularity is very slight.

Keywords: Ethyl 2-bromopropionate, ARGET ATRP, MMA, reducing agent.

1. INTRODUCTION

In recent years, atom transfer radical polymerization (ATRP) has been recognized as one of the most successful "living"/controlled radical polymerization (CRP) techniques for its simplicity in the preparation of a polymer with a predetermined structure and a narrow molecular weight distribution. ATRP can create a dynamic equilibrium between a small amount of active species (R•) and a large amount of dormant species (P-X or P-M-X) [1, 2]. When the concentration of propagating radicals is sufficiently low, the probability of bimolecular termination reactions is reduced. However, ATRP has some limitations, such as the large dosage of catalyst required, and the sensitivity of the low-state transition metal to oxygen. To overcome these drawbacks, Matyjaszewski *et al*. developed activators regenerated by electron transfer for ATRP (ARGET ATRP) [3] and proposed a polymerization mechanism, as shown in Scheme **1**. ARGET ATRP can be conducted with a significantly lower catalyst concentration in the presence of an excess of reducing agent such as ascorbic acid [4-6], tin(II) 2-ethylhexanoate ($Sn(EH)_2$) [7, 8], glucose [7], alcohol [9], Triphenylphosphine [10] or others [11, 12]. To date, ARGET ATRP has been successfully applied in the synthesis of nanocomposite materials [13-15], hybrid materials [16, 17], block copolymers [18-20], and polymers with precisely controlled molecular weights, relatively low dispersities and controlled molecular architecture in terms of chain topologies [21, 22].

Recently, researchers have made some important advances in developing new initiator/catalytic systems [23-25]. In order to precise design and synthesize well-defined polymers, it is important to select a suitable initiator and the appropriate catalyst and reaction conditions for specific monomers. In previous reports, the most commonly used initiator for ARGET ATRP has been ethyl 2-bromoisobutyrate (EBiB) [4, 9, 26-30]. For example, using EBiB as initiator for ARGET ATRP, Matyjaszewski synthesized polymethyl methacrylate (PMMA) with $M_{n,GPC}$ =30 700 ($M_{n,theo}$ =23 260, M_w/M_n =1.27) and achieved a monomer conversion of 59% after a reaction period of 18 h. The author also synthesized a polymethyl acrylate (PMA) with $M_{n,GPC}$ = 27 700 ($M_{n,theo}$ = 30 000, M_w/M_n =1.19) and achieved a monomer conversion of 87% after reaction period of only 5.3 h [4].

Researchers have investigated the influence of different initiator structures on the activation rate

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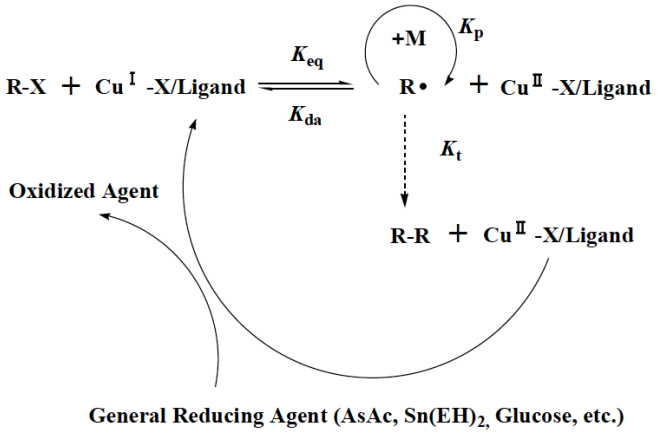
constants (K_{act}) in ATRP [31]. A variety of initiators have been investigated, including EBiB, methyl 2-bromopropionate (MBrP), and 1-phenylethyl bromide (PEBr). However, data is scarce regarding ethyl 2-bromopropionate (EBrP). To the best of our knowledge, there are no reports on the use of EBrP as an initiator of ARGET ATRP. Wang found EBrP to be an efficient initiator for the ATRP of MMA [32] and that CuCl-bpy, rather than CuBr-bpy, was a better catalyst for the controlled polymerization of MMA. In this study, we used EBrP, which has a similar molecular structure to that of EBiB, as an initiator for the ARGET ATRP of MMA. First, we compared the effect of initiator types and reducing agents on the ARGET ATRP of MMA. Then, we systematically studied the effect of the dosages of the reducing agent and ligand types, the levels of catalyst, and the temperature on the ARGET ATRP of MMA in the optimal reducing agent. In addition, we investigated the kinetics of the ARGET ATRP of MMA and the chain extension, and analyzed the end groups and stereoregularity of the PMMA obtained using different ligands. In this paper, we focus on optimizing the experimental conditions of the ARGET ATRP of MMA initiated by EBrP.



Scheme 1: Mechanism of ARGET ATRP.

2. EXPERIMENTAL

2.1. Materials

Methyl methacrylate (MMA, CP), cyclohexanone (analytical reagent, AR), methanol (AR), ethylene glycol (EG, AR), tetrahydrofuran (THF, AR), and $CuCl_2{\cdot}2H_2O$ (AR) were all purchased from the Xilong Chemical Plant in Shantou, Guangdong Province (China). Tris(2-(dimethylamino)ethyl)amine (Me_6TREN, 99%) was provided by Alfa Aesar (Tianjin) Chemical Co. Ltd. (China). 2,2'-bipyridine (bpy, AR, 99%), ethyl 2-bromoisobutyrate (EBiB，98%)，ethyl 2-bromopropionate (EBrP, 98%), ascorbic acid (AsAc, AR,>99%), N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA, 99%), 1,1,4,7,10,10-Hexamethyltriethyl-enetetramine (HMTETA, 98%), tin(II) 2-ethylhexanoate ($Sn(EH)_2$, 95%), glucose (AR) were all purchased from Aladdin Industrial Corporation (Shanghai, China). Ethanol absolute (AR) was purchased from Guangdong Guanghua Sci-Tech Co., Ltd. (Shantou China). MMA was washed with 10% NaOH and deionized water, and vacuum distilled it before use. $CuCl_2{\cdot}2H_2O$ was dehydrated via dissolution and evaporation in ethanol before use. All other chemicals were used as received without further purification.

2.2. Synthesis of PMMA by ARGET ATRP

We used the following typical polymerization procedure: we added 5 mL of cyclohexanone and 5 mL of a premixed solution (molar ratio of MMA/EBrP/$CuCl_2$/PMDETA/glucose = 500/1/0.1/1/2), to a 100 mL well-dried round-bottomed flask. We then stirred the mixture, degassed it under vacuum conditions, and bubbled it with nitrogen for 15 min. Then, the sealed flask was placed in an oil bath at 80 °C for several hours. After the reaction, THF was added to dissolve the polymer, and then the mixture was precipitated into excess methanol, and the solids were filtered and dried under vacuum at 60 °C for 24 h.

2.3. Extension of PMMA Macroinitiator with MMA by ARGET ATRP

A PMMA macroinitiator (M_n = 22 600, M_w/M_n = 1.22, 0.0229 g) prepared by ARGET ATRP was dissolved in a MMA monomer (5 mL, 4.72 g), along with the mixture solutions (molar ratio of MMA/$CuCl_2$/PMDETA/glucose = 500/0.01/0.1/1.5) were added to a 100 mL well-dried round-bottomed flask. The resulting mixture was stirred and degassed under vacuum and bubbled with nitrogen for 15 min. Then, the sealed flask was placed in a thermostatic oil bath at 80 °C for several hours. After the reaction, THF was added to dissolve the polymer, and then the mixture was precipitated into excess methanol, and the solids were filtered and dried under vacuum at 60 °C for 24 h.

2.4. Analysis

The molecular weights and dispersities (M_w/M_n) of the resulting polymers were measured by gel permeation chromatography (GPC) with a Malvern Model 270 equipped with a refractive index detector, a viscosity detector and a light scattering detector, and T6000 microstyragel columns. THF was used as the

eluent at a flow rate of 1.0 mL/min and operated at 35 °C. Hydrogen nuclear magnetic resonance (^{1}H-NMR) spectra were obtained on an Avance 500 MHz spectrometer (Bruker, Switzerland) using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. The monomer conversions were calculated gravimetrically. Theoretical molecular weights ($M_{n,theo}$) of the resulting PMMA was calculated by the following equation:

$$M_{n,theo}=([M]_0/[I]_0)*Conv(\%)*M_{MMA}+M_{EBrP}.$$

Where $[M]_0$ and $[I]_0$ stand for the initial concentrations of monomer and initiator, respectively. Conv(%) stands for the monomer conversion, M_{MMA} and M_{EBrP} indicate the molecular weights of MMA and EBrP, respectively.

3. RESULTS AND DISCUSSION

3.1. Comparison of EBiB and EBrP

We carried out the ARGET ATRP of MMA using EBiB and EBrP as initiators under the same polymerization conditions. As shown in Figure **1**, EBrP was a high-efficiency initiator in this initiating/catalytic system. The semi-logarithmic plot of ln([M]$_0$/[M]) versus the polymerization time was linear when MMA was initiated by EBrP/$CuCl_2$/PMDETA. Moreover, the molecular weight of PMMA obtained while using EBrP was closer to the theoretical value than that of using EBiB. Both products had a relatively low M_w/M_n value (< 1.40). These results demonstrate that EBrP is a better initiator for the ARGET ATRP of MMA in this system and may be contribute to the effect of the initiator structure on the selectivity of the $CuCl_2$/PMDETA system.

3.2. Kinetics of the ARGET ATRP of MMA

In general, the most important features in living radical polymerization are the pseudo first-order kinetics of polymerization, a well-controlled molecular weight, the low M_w/M_n, linear evolution of molecular weight with monomer conversion, and perfect or near-perfect chain-end functionalities [32]. The reaction conditions and experimental results for the ARGET ATRP of MMA are shown in Table **1** and Figure **2**.

As shown in Figure **2a**, the semi-logarithmic plot of ln([M]$_0$/[M]) versus polymerization time was linear, with a pseudo-first order rate constant (k_{app}) of 2.55 × 10^{-4} s^{-1}. Moreover, as shown in Figure **2c**, the monomer conversion displayed a rapid increase within the first 2 h. For example, for the ARGET ATRP of MMA, 85.1% of the monomer conversion was reached after only 2 h. Subsequently, the rate of polymerization began to decrease, and the monomer conversion curve tended to level off. This is possibly due to the increasing viscosity of the system. Figures **2b** and **2d** show that $M_{n,GPC}$ increased linearly with the monomer conversion and maintained a low M_w/M_n value ($M_w/M_n \leqslant 1.30$), indicating that good control over the molecular weights and a low M_w/M_n in the EBrP/$CuCl_2$/PMDETA system were achieved. From the above results, it is clear that the polymerization exhibited characteristics of living polymerization. Furthermore, the monomer conversion reached 97% in 4 h, which represents a great improvement compared with the aforementioned literature [9, 32], in which an EBiB/$CuCl_2$/TMEDA system [9] or an EBrP/CuBr/bpy system [32] had been used. This finding suggests that when the appropriate reducing agent and ligand are used, EBrP exhibits a higher initiation efficiency than EBiB for the ARGET ATRP of MMA.

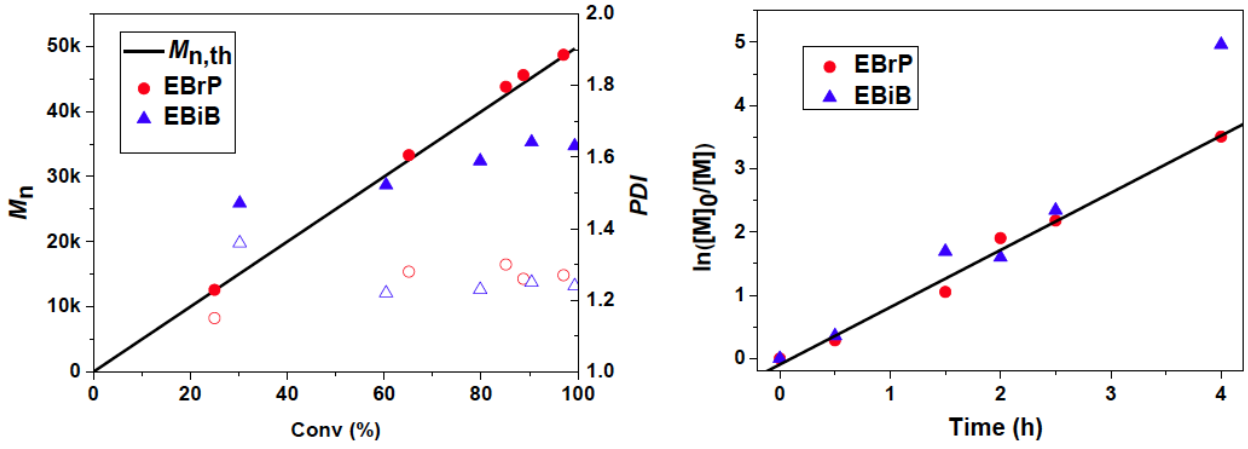


Figure 1: ARGET ATRP of MMA Initiated by EBiB and EBrP. Polymerization condition: MMA/Initiator/$CuCl_2$/PMDETA/Glucose = 500/1/0.1/1/1.5. T = 80 °C, MMA/solvent = 1:1 (v/v).

Table 1: Experimental Conditions and Properties of PMMA Prepared by ARGET ATRP

Entry	Reducing agent	[Reducing agent]$_0$/[Cu]$_0$	Time (h)	Conv (%)	$M_{n,theo}$ /×10^4	$M_{n,GPC}$ /×10^4	M_w/M_n
1[a]	EG	20	4	98.8	4.94	4.24	1.50
2[a]	$Sn(EH)_2$	20	4	96.8	4.84	3.50	1.48
3[a]	AsAc	20	16	19.0	0.95	5.04	1.31
4[a]	glucose	20	4	91.2	4.56	4.51	1.41
5[a]	glucose	15	4	82.6	4.13	4.95	1.50
6[a]	glucose	10	4	74.4	3.72	4.60	1.49
7[a]	glucose	5	4	70.1	3.51	4.17	1.57
8[b]	glucose	15	0.5	25.0	1.25	1.26	1.15
9[b]	glucose	15	1	47.5	2.38	2.14	1.26
10[b]	glucose	15	1.5	65.1	3.26	3.33	1.28
11[b]	glucose	15	2	85.1	4.26	4.38	1.30
12[b]	glucose	15	2.5	88.7	4.43	4.56	1.26
13[b]	glucose	15	3	89.4	4.47	4.15	1.25
14[b]	glucose	15	4	97.0	4.85	4.87	1.27

[a]bpy as ligand, MMA/EBrP/$CuCl_2$/bpy = 500/1/0.1/1. [b]PMDETA as ligand, MMA/EBrP/$CuCl_2$/PMDETA = 500/1/0.1/1. T = 80 °C, MMA/solvent = 1:1 (v/v).

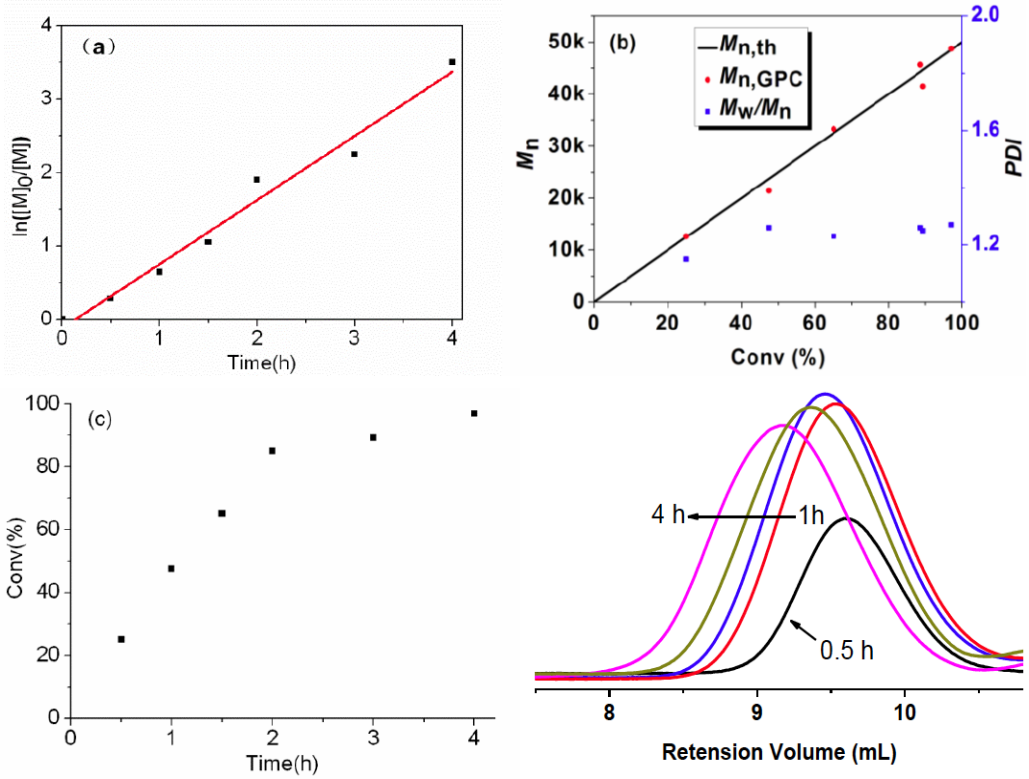


Figure 2: Ln([M]$_0$/[M]) as a function of time (**a**) and average-number molecular weight (M_n) and molecular weight distribution (M_w/M_n) versus the conversion (**b**) and conversion versus time (**c**) and GPC traces of PMMA by different polymerization time (**d**) for ARGET ATRP of MMA. Polymerization condition: as shown in Table **1** (Entry 8[b]~14[b]).

3.3. Effect of Reducing Agents on the ARGET ATRP of MMA

We also conducted the ARGET ATRP of MMA using EG, $Sn(EH)_2$, AsAc, and glucose as reducing agents. Table **1** (entries 1[a]–4[a]) shows the corresponding experimental conditions and results. As shown in Table **1**, the reaction rate of polymerization was very fast when using either EG, $Sn(EH)_2$ or

glucose as a reducing agent, and in these three cases, the monomer conversion surpassed 90% after a reaction period of only 4 h. In contrast, the monomer conversion reached only 19% even after a reaction period of 16 h when using AsAc as the reducing agent. This is possibly because AsAc is a relatively weak reducing agent in this system and cannot convert enough Cu(II) species to the Cu(I) state. With glucose as the reducing agent, we observed good control over the molecular weights in the ARGET ATRP of MMA, which produced a PMMA with $M_{n,GPC}$ = 45 100 ($M_{n,theo}$ = 45 600) and M_w/M_n = 1.41. However, the M_w/M_n value is a little high, which was probably caused by the use of bpy as the ligand. Therefore, further investigation the effect of ligand types on the ARGET ATRP of MMA is necessary. In addition, as a reducing agent, glucose is inexpensive, readily available, non-toxic, and biocompatible. Thus, we chose glucose as our reaction reducing agent in subsequent experiments.

3.4. Effect of the Amount of Glucose on the ARGET ATRP of MMA

The amount of reducing agent plays a crucial role in ARGET ATRP. In order to determine the optimal amount of glucose for use in ARGET ATRP, we performed a series of experiments at 80 ^{o}C. The results are listed in Table **1** (Entry 4^a~7^a). As shown in Table **1** (Entry 4^a~7^a), the monomer conversion decreased from 91.2% to 70.1% with a decrease in the amount of the reducing agent, which indicates that the polymerization rate increased with an increase in the amount of glucose, due to the increased concentration of Cu(I) species. However, when we used only a tiny amount of glucose, the M_w/M_n of the polymer broadened (M_w/M_n = 1.57, Entry 7^a).

3.5. Effect of Ligand Types on the ARGET ATRP of MMA

Next, we investigated the effect of ligand types on MMA polymerization by ARGET ATRP. We maintained the molar ratio of $[MMA]_0/[EBrP]_0/[CuCl_2]_0/[Ligand]_0/[glucose]_0$ at 500/1/0.1/1/2 and fixed the polymerization temperature at 80 ^{o}C. Table **2** shows the monomer conversion, molecular weight, and M_w/M_n results with different ligands. As seen in Table **2**, the polymerizations of MMA were well controlled when using bpy, PMDETA and HMTETA as the ligand. However, no PMMA formed after polymerization for 4 h and 22 h when using Me_6TREN as the ligand, which suggests that Me_6TREN maybe not be an efficient ligand for this system. It is possible that the equilibrium of Cu(Me_6TREN)Cl/Cu(Me_6TREN)Cl_2 favors Cu(Me_6TREN)Cl_2 too much, such that glucose is not strong enough to reduce Cu(Me_6TREN)Cl_2 to Cu(Me_6TREN)Cl. In addition, we found PMDETA to be a better ligand than either HMTETA or bpy, as the measured molecular weight of the PMMA prepared by PMDETA was closer to the theoretical values, while also maintaining a low M_w/M_n value. Compared with HMTETA and bpy, the polymerization rate was also fastest when using PMDETA as the ligand. Moreover, PMDETA is cheap and readily available. Hence, we chose PMDETA as the ligand in the following experiments.

3.6. Effect of the Amount of Catalyst on the ARGET ATRP of MMA

We varied the amount of catalyst from a "high concentration" of 200 ppm to 20 ppm *vs* the monomer. Table **3** shows the reaction conditions and results of these polymerizations. As shown in Table **3**, the polymerization rate decreased slightly with a reduction in the concentration of the copper species. In ATRP, the ratio of Cu (I) to Cu (II) determines the polymerization rate, while the absolute Cu (II) concentration influences the M_w/M_n [34]. Therefore, it is important to determine the minimal amount of Cu needed to control the polymerization while still achieving an acceptable reaction rate. As shown in Table **3**, both 100 ppm and 200 ppm of catalyst provided acceptable reaction rates and low M_w/M_n in the product, whereas 20 ppm and 50 ppm of the

Table 2: Effects of Ligand Type on ARGET ATRP of MMA

Entry	Ligands	Time(h)	Conv(%)	$M_{n,theo}/\times 10^4$	$M_{n,GPC}/\times 10^4$	M_w/M_n
1	Bpy	4	91.2	4.56	4.51	1.41
2	PMDETA	4	93.5	4.67	4.65	1.37
3	HMTETA	4	75.0	3.75	3.80	1.26
4	Me6TREN	4	0	-	-	-
5	Me6TREN	22	0	-	-	-

Table 3: Effects of the Amount of Catalyst on ARGET ATRP of MMA

Entry	R	Cu (ppm)	Time (h)	Conv (%)	$M_{n,theo}$ / × 10^4	$M_{n,GPC}$ / × 10^4	M_w/M_n
1	500/1/0.1/1/1.5	200	4	97.0	4.85	4.87	1.27
2	500/1/0.05/1/1.5	100	4	93.5	4.68	4.35	1.41
3	500/1/0.025/1/1.5	50	4	92.9	4.65	5.55	1.45
4	500/1/0.01/1/1.5	20	4	91.8	4.59	5.59	1.45

R= n(MMA)/n(EBrP)/n($CuCl_2$)/n(PMDETA)/n(Glucose), T = 80 °C.

catalyst were somewhat low for the ARGET ATRP of MMA in this system.

3.7. Effect of Reaction Temperature on the ARGET ATRP of MMA

Normally, increasing the temperature in an ATRP system accelerates the polymerization process due to the increase of both the radical propagation rate constant and the atom transfer equilibrium constant. Next, we investigated the effect of temperature on the ARGET ATRP of MMA. We maintained the molar ratio of $[MMA]_0/[EBrP]_0/[CuCl_2]_0/[PMDETA]_0/[glucose]_0$ at 500/1/0.1/1/1.5, and results are listed in Table **4**.

As seen in Table **4**, the polymerization rates were very fast at 70 and 80 °C, and increased with increasing reaction temperatures from 60 to 80 °C. As further evidenced by the apparent rate constant (k_{app}), the k_{app} values for polymerizations at 60 °C, 70 °C and 80 °C were 8.13×10^{-6}, 2.35×10^{-4} and 2.55×10^{-4} s^{-1}, respectively. We calculated k_{app} by the slope of the kinetic plot (Figure **3**), Rp = −d[M]/dt = kp*[Pn]*[M] = k_p^{app}*[M]. Obviously, the polymerization temperature favorably influenced the polymerization rate. As shown in Figure **3**, the first-order kinetic plots are linear for the three reaction temperatures which imply a constant number of active species throughout the polymerizations. We note that the molecular weights deviated significantly from the theoretical values, while the M_w/M_n remained low at 60 °C, which may have contributed to the very low Cu (I) concentration and thus the low initiation efficiency. Although the M_w/M_n changed slightly with an increasing polymerization temperature, the M_w/M_n still remained low (< 1.40).

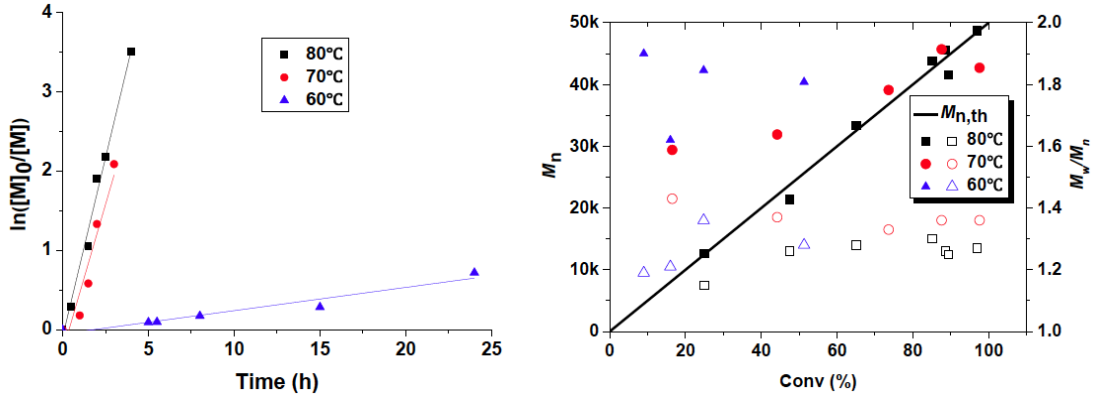


Figure 3: Kinetic plot for MMA polymerization at different temperatures.

Table 4: Effects of Temperature on ARGET ATRP of MMA

Entry	Temp (°C)	Time (h)	Cu (ppm)	Conv (%)	$M_{n,theo}$ /×10^4	$M_{n,GPC}$ /×10^4	M_w/M_n	k_{app} (s^{-1})
1	80	1.5	200	65.1	3.26	3.52	1.23	2.55×10^{-4}
2	70	1.5	200	44.2	2.21	3.19	1.37	2.35×10^{-4}
3	60	1.5	200	-	-	-	-	-
4	60	4	200	-	-	-	-	-
5	60	24	200	51.3	2.57	4.04	1.28	8.13×10^{-6}

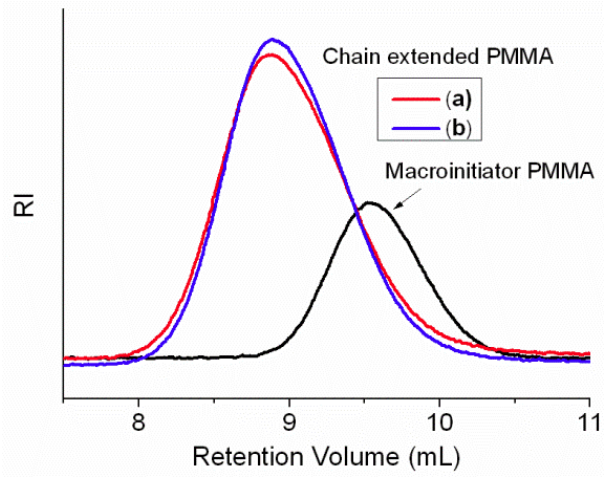


Figure 4: GPC traces of PMMA macroinitiator before and after chain extension. Experimental condition for chain extension: $[MMA]_0/[PMMA]_0/[CuCl_2]_0/[PMDETA]_0/[Glucose]_0$ = 500/0.01/0.1/1/1.5 (a), 500/0.005/0.1/1/1.5 (b), at 80 °C, reaction time = 4 h.

3.8. Chain Extension of PMMA

To verify the living characteristics of the ARGET ATRP of MMA, we performed further polymerization to examine the chain extension reaction. We used the obtained PMMA as a macroinitiator to carry out the chain extension experiment. Figure **4** shows the GPC curves of the macroinitiator and the chain-extended PMMA. Obviously, the GPC curves indicate a shift from a macroinitiator PMMA ($M_{n,GPC}$ = 22 600, M_w/M_n =1.22) to a chain-extended PMMA ($M_{n,GPC}$ = 72 600, M_w/M_n = 1.36) (Figure **4a**). The narrow molecular weight distribution and the unimodal shape of the GPC trace of the chain-extended polymer demonstrate the success of the chain extension and the chain-end functionality of the macroinitiator PMMA. Nevertheless, termination occurs in all reversible-deactivation radical polymerizations, and it is important to know how many chains lost functionality and could not be further extended. However, when using the chain-extended PMMA (Figure **4a**) as a macroinitiator to carry out the chain extension reaction again, the molecular weight of the PMMA no longer increased (as shown in Figure **4b**). This suggests that when the molecular weight reached to a certain point, the macromolecular chain is so long that the chain-end functionality is decreased.

3.9. End-Group and Stereoregularity Analysis

We used ^{1}H-NMR spectroscopy to characterize the obtained PMMA via the ARGET ATRP of MMA with bpy, HMTETA, and PMDETA as ligands. As shown in Figure **5**, the chemical shift at 7.27 ppm was attributed to the solvent–deuterated chloroform, in which the peak

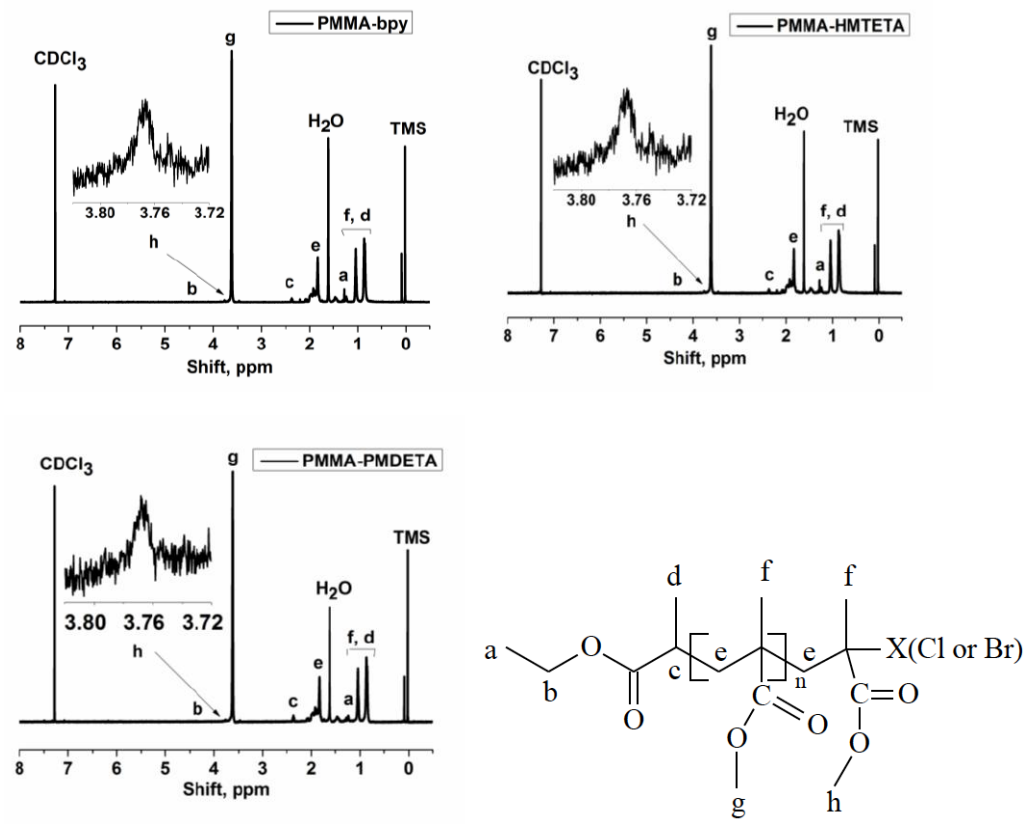


Figure 5: ^{1}H-NMR spectra of PMMA obtained with different ligands (bpy, HMTETA and PMDETA).

h at 3.76 ppm corresponds to the methoxy group adjacent to the bromine atom at the ω-end. This result obviously deviates from the peak *g* at 3.62 ppm of the methoxy groups in the PMMA backbone due to the electron attraction function of the ω-Br atom. The chemical shift at around 4.2 ppm was assigned to the protons of the methylene of EBrP. This result is consistent with previous literature.[34] The peaks at 0.80–1.30 ppm were assigned to the protons of the methyl groups of -CH_3, the peaks at 1.43 and 1.81 ppm were attributed to the methylene group of -CH_2-. The areas of the three signals at 0.80–1.30 ppm of -CH_3 represented the syndiotactic, atactic, and isotactic PMMA, respectively, with increasing shift value. If the peak areas were expressed as α, β, and γ, the ratio of the isotactic configuration was γ / (α+β+γ). We calculated the syndiotactic values for PMMA-bpy, PMMA-HMTETA, and PMMA-PMDETA to be 62.1%, 61.3%, and 62.5%, respectively, which illustrate that the stereoregularity of the polymer had given priority over a syndiotactic architecture, and the effect of ligand types on the stereoregularity was very slight.

4. CONCLUSIONS

In this study, we successfully initiated copper (II)-mediated ARGET ATRP of MMA by EBrP, and we found EBrP to be an efficient initiator of the ARGET ATRP of MMA. Our results show the monomer conversion increase with increased of polymerization temperature, and the amounts of reducing agent and catalyst. Compared with EG, $Sn(EH)_2$, and AsAc, glucose proved to be the best reducing agent in this system. And we found PMDETA to be a better ligand than either HMTETA or bpy. We confirmed the “living” characteristics of the polymerization by the resulting first- order kinetics. The molecular weights increased linearly with monomer conversion and were consistent with the theoretical values. We further confirmed the “living” feature by the chain extension of the obtained PMMA macroinitiator and end-group analysis results. Moreover, ^{1}H-NMR analysis results indicate that the stereoregularity of the polymer has given priority over a syndiotactic architecture. The effect of ligand types on the stereoregularity was very slight.

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