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Comparative study of a variety of ATRP systems with high oxidation state metal catalyst system

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ABSTRACT

MMA (methyl methacrylate) was polymerized in different ATRP systems using the different ligands of HMTETA (1, 1, 4, 7, 10, 10, hexamethyltriethylenetetraamine), TMEDA (N,N,N′,N′-Tetramethylethylenediamine) with copper salts ($CuBr/CuBr_2$) and EBriB was used as an initiator in toluene at a reaction temperature of 80 °C. Both conventional and a low catalyst to initiator ratios ranging from 1/1 to 0.01/1 were compared in this study. All four of the ATRP methods, such as normal, reverse, AGET and ATRP using a high oxidation state metal complex without any additives, were evaluated at different conditions. The ATRP using a high oxidation state metal system in the absence of a conventional radical initiator like AIBN, which is used in reverse ATRP, or reducing agents such as $Sn(EH)_2$ in AGET ATRP was a better controlled system in terms of both the catalytic activity and controllability (PDI ~ 1.2).

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1. Introduction

Atom transfer radical polymerization (ATRP) is one of the most robust and widely used controlled radical polymerization (CRP) techniques in the field of polymer science since 1995 [1,2]. This technique became a momentous tool in the synthesis of a wide range of materials with a definite structure and a composition having a predetermined molecular weight and narrow PDI [3–6]. Control over the molecular weight and molecular weight distribution in all of the CRP techniques is established through a dynamic equilibrium between the dormant species and the propagating radicals. The properties of the catalyst play a crucial role in the ATRP technique. Matyjaszewski, Sawamoto, and other scientists have made a great efforts towards clarifying the influence that the properties of transition metal compounds exert on ATRP through systematic experiments with a variety of metal complexes, such as copper [7–14], iron [15–22], ruthenium [23–29] and other metals [30–36].

However, some drawbacks have also been discovered in ATRP due to the use of low oxidation state metals which require special handling procedures as well as air and moisture free storage. Recently, several methods, such as reverse ATRP (rATRP) [37–39], activators generated by electron transfer (AGET) [40,41], activators regenerated by electron transfer (ARGET) [11], and initiators for continuous initiator regeneration (ICAR) [42], have been explored in an attempt to employ high oxidation state metal complexes directly to the reaction instead of the air and moisture sensitive low oxidation state metals in order to overcome these limitations. One of the common features of these methods is the introduction of a higher oxidation state metal compound with either a radical initiator or reducing agent for *in situ* generation of activators, which are the lower oxidation metal compound. In addition to the increased stability and convenience, these routes, particularly ICAR and ARGET, provide the additional advantage using an extremely small amount of the metal compound, which may be good for polymerization. Interest has grown in the utilization of high oxidation state metal catalysts for transition metal catalyzed radical polymerization because of their advantages.

In 2008, activators were generated using monomer addition (GAMA) ATRP in a previous report [18]. GAMA (generation of activator via monomer addition) is similar to the abovementioned methods from the standpoint of using a high oxidation state metal compound. However there is a definite difference between GAMA and the other methods since absolutely no additives, such as radical initiators and reducing agents, are used for *in situ* generation of the activators in GAMA [16,18]. One remarkable thing about GAMA is that polymerization can be better controlled compared to ATRP in spite of the lack of any additive. Schubert et al. [43] also reported that ATRP of MMA with high oxidation state copper (II) resulted in a well defined PMMA with low initiation efficiencies and controllability. This suggests that a good combination of all of the elements of ATRP is required to establish a well controlled radical

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polymerization. In a continuous effort to extend GAMA to other applications, the comparison studies among GAMA and the other known controlled radical systems, including ATRP and its derivatives, were explored in this study for the polymerization of several monomers.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA; Aldrich; 99%), styrene (Aldrich; 99%), and n-Butyl methacrylate (BMA, 99% Aldrich) were passed through a column filled with neutral alumina, dried over CaH_2, distilled under reduced pressure, and stored in a freezer under nitrogen. Tetrahydrofuran (THF; Fisher; HPLC grade) and toluene (Fisher; certified grade) were freshly distilled from Na/K alloy with benzophenone (Aldrich; 99%) and stored under nitrogen, $CuBr_2$ (Aldrich; 98%), CuBr (Aldrich; 98%), ethyl-2-bromoisobutyrate (EBriB; Aldrich; 99%), Sn $(EH)_2$TinEthylhexanoate(Sigma; 95%), HMTETA (1,1,4,7,10,10,hexa methyltriethylenetetraamine) (Aldrich; 97%), TMEDA, tetramethylethylenediamine (Aldrich; 99%), AIBN (azoisobutylnitrile) are used as received. Anisole (Aldrich; 99%), and other solvents were used after distillation. The monomers and solvents were purged by bubbling with dry nitrogen for 30 min immediately before polymerization.

2.2. Polymerization

ATRP of MMA was carried out using the following procedure; A schlenk flask (50 ml) was charged with CuBr (0.0286 g, 0.2 mM) or $CuBr_2$ (0.0446 g, 0.2 mM) and HMTETA (0.0921 g or 0.109 ml, 0.4 mM) or TMEDA (0.062 g, 0.4 mM) in a glove box. The flask with a magnetic stirring bar was sealed with a rubber septum and recycled three times between a vacuum and a nitrogen atmosphere to remove oxygen from the system. The degassed MMA (4.28 ml, 40 mM) and a solvent (50% by volume of the monomer) including internal standard (anisole) were added to the flask using a degassed syringe, and the solution was stirred for 20–30 min at room temperature. After that, the flask was sealed with a new rubber septum and degassed using three freeze–pump thaw cycles to remove oxygen. Finally the desired amount of initiator (EBriB – 30 μl, 0.2 mM) was added to the system after defreezing. The flask was immersed in an oil bath thermostat at 80 °C, and samples were withdrawn at different time intervals from the flask with a degassed syringe. The samples were diluted with THF and filtered through the column filled with neutral alumina to remove the copper catalyst. A sample withdrawn at a given time interval was divided into two parts. One part was used for gas chromatography (GC) measurements to determine the monomer conversion. The other part was of PMMA was precipitated using an excess of n-hexane, and then the polymers were dried under vacuum for 24 h in preparation for the gel permeation chromatography (GPC) measurements that were used to determine the molecular weights and molecular weight distributions of the obtained polymers. The polymerizations of n-BMA and styrene were carried out in the same way.

2.3. Characterization

The monomer conversion in the THF solvent with anisole as an internal standard was determined using HP 6890 gas chromatography equipped with a FID detector and J&WScientific 30 m DB WAX Mega bore column. The injector and detector temperatures were kept at 250 °C. The analysis was run isothermally at 40 °C for 1 min, and then the temperature was increased to 120 °C at a heating rate of 20 °C/min. The number average molecular weight (Mn) and molecular weight distribution (Mw/Mn) were determined by GPC using Waters columns (Styragel, HR 5E) equipped with a Water 515 pump and a Waters 2410 differential refractometer using diphenyl ether as the internal standard. THF was used as the eluent at the flow rate of 1 mL/min. Linear polystyrene standard was used for the calibration.

3. Results and discussion

3.1. Effect of ligand

In previous reports, the polymerization of MMA using GAMA with a FeX_3/DPPP system was explored without the use of any additives [17,18]. PMMA formed using GAMA possessed a narrower PDI than the PDI obtained from normal ATRP. Additionally, the polymerization process of GAMA exhibited a better controlled living system despite the lack of any additives. The reaction between $FeBr_3$ and the MMA monomer formed 1, 2-dibromoisobutyrate, which confirmed that $FeBr_2$ was generated *in situ* fashion to initiate CRP [44]. Here, a comparison study was carried out among ATRP, rATRP, AGET and GAMA with high oxidation copper and two nitrogen containing ligands (HMTETA and TMEDA) for the polymerization of MMA, n-BMA, and styrene. AIBN and Sn $(EH)_2$ were used for the radical initiator of rATRP and the reducing agent of AGET respectively.

The four types of controlled radical polymerization of MMA led to the first-order kinetics with respect to the monomer in Figs. 1(a) and 2(a). In terms of linearity, both rATRP and ATRP exhibited significant curvature suggesting the existence of considerable termination, whereas AGET and GAMA exhibited pretty well defined linear kinetic lines. The polymerization rate among the four different polymerization processes increased in the order of GAMA < ATRP < AGET < rATRP. Regardless of the ligand structure, GAMA formed PMMA with the lowest PDI, which indicated that GAMA had the best controllability and living characteristics followed by AGET. Although the basic reaction characteristics of the two ligands were similar in some points as mentioned above, some dissimilar points should also be noted. First, the rates of polymerization were faster with HMTETA than with TMEDA in every case. The use of TMEDA created a significant initiation delay with GAMA and ATRP because of the slow rate of polymerization, Fig. 2(a). Second, the molecular weights of PMMA from the HMTETA ligand were below the theoretical molecular weight line, Fig. 1(b), which meant that the non-negligible occurrence of chain transfer took place during the polymerization. Particularly the polymers from AGET and rATRP showed this trend most. On the other hand, the use of TMEDA seemingly was effective in leveling off the differences among polymerization methods. Fig. 2(b) shows that the molecular weights increased according to the conversion, and above 50% conversion, any visible distinction between the four polymerization methods was difficult to observe. It should be pointed out that most of the molecular weights of the prepared polymers were actually slightly larger than the theoretical ones, which was another definite difference between two ligands. Third, interestingly enough, the PDI trend opposite to the molecular weight trend. All of the PMMA made with HMTETA possessed very low PDIs, which represented excellent living characteristics and controllability of polymerization. However, the PDI difference among the polymers formed using the four polymerization routes became bigger for TMEDA ligand implication. As a result, the use of HMTETA induced a big difference between the experimental and theoretical molecular weights, but only a small difference in the PDI among the polymerization procedures. On the contrary, TMEDA ligand exhibited the opposite trends among the

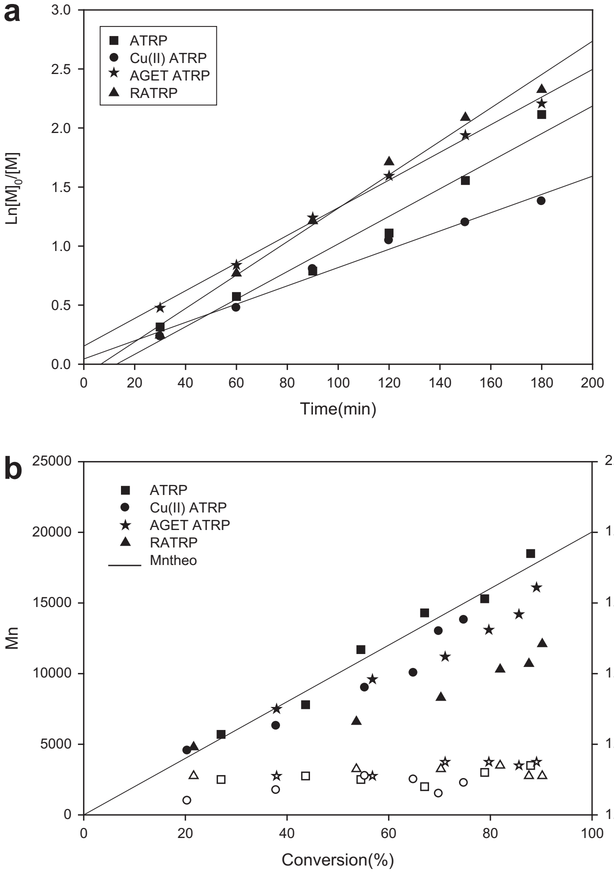


Fig. 1. (a) Semi-logarithmic kinetic plot for the ATRP of MMA in different ATRP systems at 80 °C in toluene (50% by volume) using following [MMA]/[EBriB]/[CuBr]/[HMTETA] = 200/1/1/2 in ATRP; [MMA]/[AIBN]/[$CuBr_2$]/[HMTETA] = 200/1/1/2 in rATRP; [MMA]/[EBriB]/[$CuBr_2$]/[HMTETA] = 200/1/1/2 in Cu(II) ATRP [MMA]/[EBriB]/[$CuBr_2$]/[HMTETA]/[Sn $(EH)_2$] = 200/1/1/2/1 in AGET ATRP, Sn $(EH)_2$ is used as reducing agent and AIBN is used as initiator in AGET ATRP and reverse ATRP respectively. (b) Dependence of molecular weights, Mn (filled symbols), and molecular weight distributions, Mw/Mn (empty symbols), on monomer conversion for ATRP of MMA in different ATRP systems in toluene (50% by volume) at 80 °C. [MMA]/[EBriB]/[CuBr]/[HMTETA] = 200/1/1/2 in ATRP; [MMA]/[AIBN]/[$CuBr_2$]/[HMTETA] = 200/1/1/2 in rATRP; [MMA]/[EBriB]/[$CuBr_2$]/[HMTETA] = 200/1/1/2 in Cu(II) ATRP; [MMA]/[EBriB]/[$CuBr_2$]/[HMTETA]/[Sn $(EH)_2$] = 200/1/1/2/1 in AGET ATRP, Sn $(EH)_2$ is used as reducing agent and AIBN is used as initiator in AGET ATRP and reverse ATRP respectively.

four polymerization methods. In summary, the comparison of the four methods of ATRP resulted in a considerable distinction in not only polymerization kinetics but also the properties of polymers. Particularly, one very important feature that should be mentioned was that GAMA demonstrated a very impressive and competitive performance in terms of the living characteristics of the polymerization compared to the other three methods using high oxidation state metal compounds.

3.2. Solvent effect

The choice of solvent is also important for the ATRP. To know the effect of solvent, polymerization of MMA initiated by EBriB and catalyzed by CuBr or $CuBr_2$/HMTETA, two solvents one polar (anisole) and other non-polar (toluene) at 80 °C were investigated; the rate of polymerization is almost similar in both the solvents for all ATRP systems as shown in Figs. 1(a) and 3(a), which correspond to the kinetic plots in toluene and anisole respectively. Figs. 1(b) and 3(b) indicate the molecular weight and its distribution in which we can see the Mn experimental is close to the Mn theoretical in case of

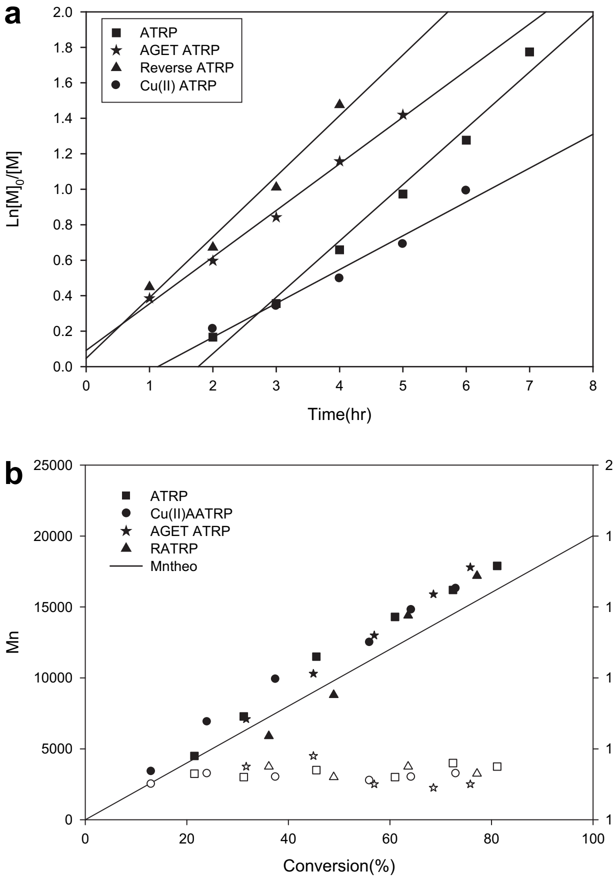


Fig. 2. (a) Semi-logarithmic kinetic plot for the ATRP of MMA in different ATRP systems at 80 °C in toluene (50% by vol.). [MMA]/[EBriB]/[CuBr]/[TMEDA] = 200/1/1/2 in ATRP; [MMA]/[AIBN]/[$CuBr_2$]/[TMEDA] = 200/1/1/2 in rATRP; [MMA]/[EBriB]/[$CuBr_2$]/[TMEDA] = 200/1/1/2 in Cu(II) ATRP; [MMA]/[EBriB]/[$CuBr_2$]/[TMEDA]/[Sn $(EH)_2$] = 200/1/1/2/1 in AGET ATRP, Sn $(EH)_2$ is used as reducing agent and AIBN is used as initiator in AGET ATRP and reverse ATRP respectively. (b) Dependence of molecular weights, Mn (filled symbols), and molecular weight distributions, Mw/Mn (empty symbols), on monomer conversion for ATRP of MMA in different ATRP systems in toluene (50% by volume) at 80 °C. [MMA]/[EBriB]/[CuBr]/[TMEDA] = 200/1/1/2 in ATRP; [MMA]/[AIBN]/[$CuBr_2$]/[TMEDA] = 200/1/1/2 in rATRP; [MMA]/[EBriB]/[$CuBr_2$]/[TMEDA] = 200/1/1/2 in Cu(II) ATRP; [MMA]/[EBriB]/[$CuBr_2$]/[TMEDA]/[Sn $(EH)_2$] = 200/1/1/2/1 in AGET ATRP, Sn $(EH)_2$ is used as reducing agent and AIBN is used as initiator in AGET ATRP and reverse ATRP respectively.

toluene than that of anisole but in both the cases, $CuBr_2$/HMTETA have shown the most closest points to the theoretical line compared with another ATRP systems and molecular weight distribution is less than 1.2. Therefore, we can infer that toluene is better solvent in terms of controllability, cost and availability. So for the further study, we used toluene as solvent and HMTETA as ligand to know the effect of metal salt concentration having different amount of catalyst to ligand.

3.3. Polymerization using different monomers by different ATRP methods

Various monomers were successfully polymerized using the four controlled radical polymerization methods, and the results are displayed in Table 1, where the selected examples were picked conveniently in order to observe the different features of four procedures. The results according to the different monomer and different polymerization procedures were very consistent as well. Regardless of the employed monomer, GAMA exhibited an advantage over the other polymerization techniques. In Table 1, the

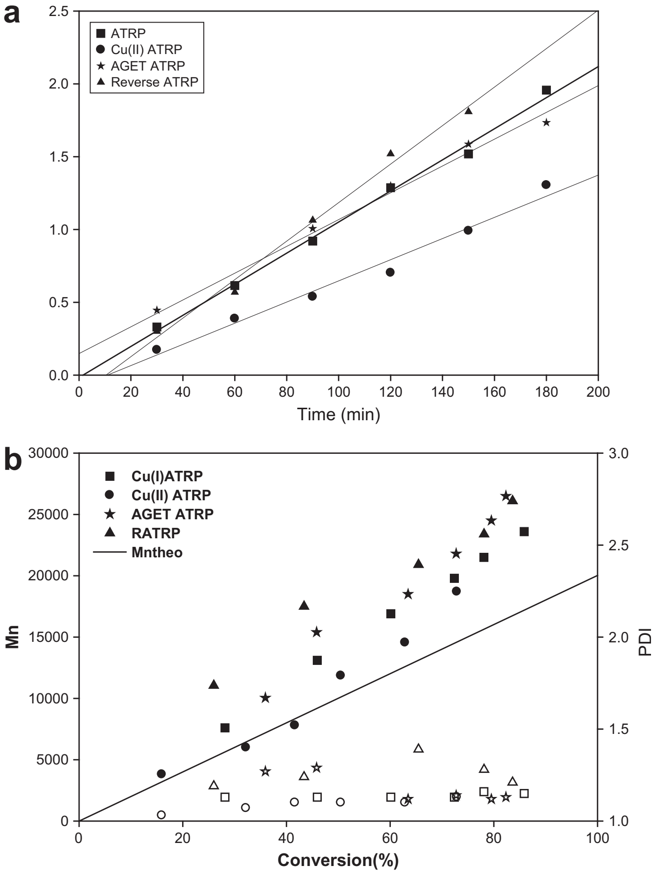


Fig. 3. (a) Semi-logarithmic kinetic plot for the ATRP of MMA in different ATRP systems at 80 °C in anisole (50% by volume). [MMA]/[EBriB]/[CuBr]/[HMTETA] = 200/1/1/2 in ATRP; [MMA]/[AIBN]/[$CuBr_2$]/[HMTETA] = 200/1/1/2 in rATRP; [MMA]/[EBriB]/[$CuBr_2$]/[HMTETA] = 200/1/1/2 in Cu(II) ATRP; [MMA]/[EBriB]/[$CuBr_2$]/[HMTETA]/[Sn $(EH)_2$] = 200/1/1/2/1 in AGET ATRP, Sn $(EH)_2$ is used as reducing agent and AIBN is used as initiator in AGET ATRP and reverse ATRP respectively. (b) Dependence of molecular weights, Mn (filled symbols), and molecular weight distributions, Mw/Mn (empty symbols), on monomer conversion for ATRP of MMA in different ATRP systems in Anisole (50% by volume) at 80 °C. [MMA]/[EBriB]/[CuBr]/[HMTETA] = 200/1/1/2 in ATRP; [MMA]/[AIBN]/[$CuBr_2$]/[HMTETA] = 200/1/1/2 in rATRP; [MMA]/[EBriB]/[$CuBr_2$]/[HMTETA] = 200/1/1/2 in Cu(II) ATRP; [MMA]/[EBriB]/[$CuBr_2$]/[HMTETA]/[Sn $(EH)_2$] = 200/1/1/2/1 in AGET ATRP, Sn $(EH)_2$ is used as reducing agent and AIBN is used as initiator in AGET ATRP and reverse ATRP respectively.

GAMA PDI values of the polymers formed using three monomers were all below 1.20. On the other hand, the polymers formed using ATRP, AGET, and rATRP were as high as 1.24 (entry 3, Table 1), 1.56 (entry 10, Table 1), and 1.56 (entry 7, Table 1), respectively. The fact that AGET and rATRP using a high oxidation state metal complex actually displayed a worse controllability than ATRP was particularly interesting because it indicated that these methods may not be extensively available in spite of the merit of the oxidation proof. This shortcoming was more serious in the case of styrene polymerization. Regardless of the polymerization method, MMA polymerization was better controlled than the other monomers PDIs in the range of 1.06 (entry 11, GAMA) and 1.15 (entry 5, rATRP). The polymerization of BMA was controlled reasonably well (entry 3 and 13). However, the progress of the styrene polymerization seemed to be considerably affected by the polymerization route employed. These outcomes corresponded to a balance between the polymerization method and the monomer that was a significant element in establishing a well controlled living system. Remarkably, the GAMA system was superior to the other living polymerization methods for the polymerization of a variety of monomers.

Table 1

Entry	ATRP methods	Monomers	Time (min)	Yield (%)	Mn,theo (g/mol)	Mngpc (g/mol)	Mw/Mn (PDI)	*f*
1	Normal	MMA	180	88	16,000	15,300	1.14	0.95
2	ATRP	MMA*	360	63	12,800	13,500	1.09	0.94
3		n-BMA	360	91	26,000	29,800	1.24	0.87
4		St	120	85	9000	11,700	1.21	0.77
5	Reverse	MMA	180	90	9000	12,100	1.15	0.74
6	ATRP#	MMA*	240	77	7700	17,200	1.11	0.45
7		St	90	80	8500	12,100	1.56	0.70
8	AGET	MMA	180	89	18,000	16,100	1.11	1.22
9	ATRP$	MMA*	300	76	15,400	17,800	1.10	0.87
10		St	60	79	8400	16,200	1.56	0.52
11	GAMA	MMA	180	75	15,000	13,800	1.06	1.08
12	ATRP	MMA*	300	62	12,600	12,500	1.13	1.00
13		n-BMA	360	68	19,400	21,200	1.15	0.91
14		St	120	74	7900	8,900	1.19	0.89

Polymerizations of MMA, n-BMA and styrene were performed using HMTETA as ligand in toluene at 80, 90, 110 °C, respectively; [Monomer]:[copper salt]:[ligand]:[EBriB] = 200/1/2/1; [MMA] = 4.67 M; [n-BMA] = 3.15 M; [Styrene] = 8.72 M; [St]:[copper salt]:[HMTETA]:[PEBr] = 100/1/2/1. No solvent for styrene polymerization. *Ligand = TMEDA, # initiator = AIBN, $ [Sn $(EH)_2$] was used as reducing agent. n-BMA = butyl methacrylate, TMEDA = N,N,N′,N′-tetramethylethylenediamine, PEBr = 1-phenylethylbromide, Sn $(EH)_2$ = tin(II) 2-ethylhexanoate, EBiBr = Ethyl-2-bromoisobutyrate, *f* = Mnteho/Mnex. (initiator efficiency).

3.4. *Effect of low metal salt concentration*

Recently, researchers have faced a great struggle in reducing the amount of catalyst in the ATRP products. However, many methods of the catalyst residue removal methods are problematic because of their high cost and lack of control over the polymerization. Using a minute amount of catalyst may be the simplest method for reducing the catalyst residue in the ATRP products [42,45–47]. The GAMA system using a high oxidation state transition metal without any additive was tested with a reduced amount of catalyst in polymerization. The reaction conditions and results of these polymerizations are shown in Fig. 4 and Table 2. Fig. 4(a) and (b) shows the kinetic plots of $\ln[M]_0/[M]$ versus time and Mn and Mw/Mn against the monomer conversion, respectively. The polymerization was determined to be approximately first order with respect to the monomer concentration from the linearity of these plots. According to the results in Fig. 4(a), the rate of polymerization was dependent on both the amount of catalyst and the ratio of catalyst to ligand (Cu/L). Basically, the polymerization rate decreased with the reduction of the copper species concentration. However, the rates of polymerization for the Cu/L ratios of 0.05/0.25 and 0.01/0.1 were faster than the 0.1/0.1 and 0.05/0.1 ratios, respectively. This clearly indicated that the delivery of a greater amount of ligand compared to the corresponding catalyst effectively sped up the polymerization. At the Cu/L ratios of 0.1 and 0.05, the conversion reached 77% in 7 and 12 h, respectively. Even at the Cu/L ratio of 0.01, $CuBr_2$/HMTETA still catalyzed the polymerization of MMA, producing PMMA with a very low PDI (Fig. 4(b)). However, the polymerization stopped at a conversion of ~38% after 32 h possibly because of the unstable or less stable copper complexes, even though they had a very high K_{ATRP} and k_{act}, that may have dissociated at the low catalyst concentration or changed their structure in the coordinated solvents/monomers that in turn reduced their catalytic activity [45]. The effect of catalyst to ligand ratio likely played an important role in the generation of the stable active species. The reaction took 18 h to reach a monomer conversion of 81% when the reaction was performed by reducing 10-fold of catalyst with 1/1 catalyst/ligand ratio. On the other hand, the same reaction took just 7 h to reach a 77% conversion by changing the catalyst/ligand ratio to 1/2 even with the better controllability. This result repeatedly

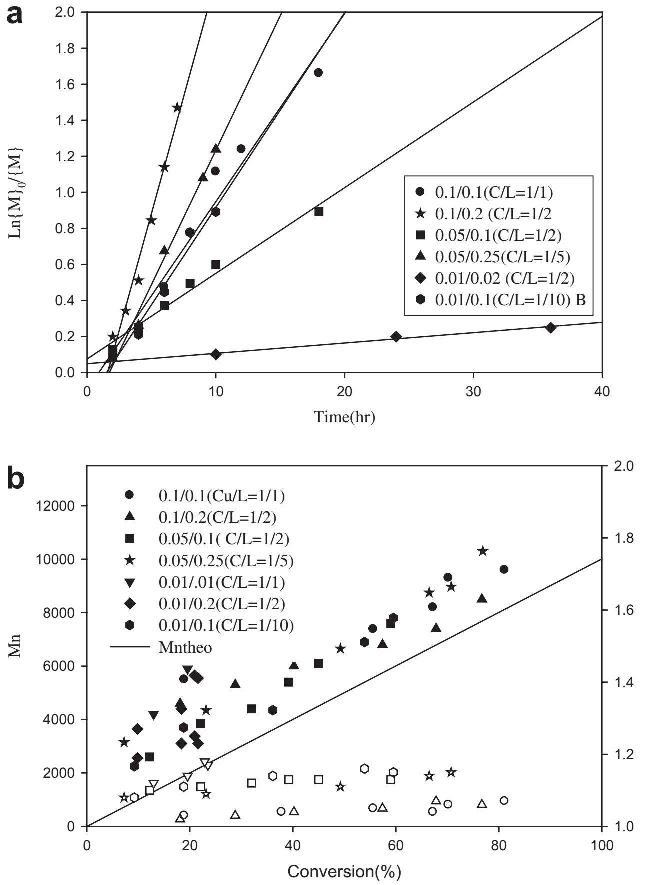


Fig. 4. (a) Kinetic plot of Ln$[M]_0$/[M] versus time for ATRP of MMA catalyzed by Cu(II)/HMTETA in toluene at 80 °C (C/L is catalyst/ligand). At the Cu/I ratio of 0.01/0.1, no solvent was used when 10-fold excess ligand was used. [MMM] = 4.67 M; [MMA]/EBriB] = 100/1, B = Bulk. (b) Dependence of molecular weight Mn, and molecular weight distribution, Mw/Mn, on monomer conversion for Cu(II)-catalyzed ATRP of MMA in toluene with $CuBr_2$/HMTETA complex using different catalyst to ligand concentrations at 80 °C. [MMA] = 4.67; [MMA]/EBriB] = 100/1. At the C/I = 0.01/0.1, no solvent was used when 10-fold excess of ligand was used.

displays that using the excess amount of HMTETA efficiently promoted the rate of polymerization partially due to its reducing ability since HMTETA is known to act as a reducing agent as well as a ligand when it is excessively used [48]. A good correlation was achieved between the experimental and theoretical Mn values for the different catalyst concentrations, indicating that the molecular weights of PMMA were still well controlled even with a very little amount of the copper catalysts in the reaction medium. The PDIs of the obtained PMMA remained narrow (less than 1.2). The molecular weights were still well controlled for PMMA with narrow molecular weight distributions (Mw/Mn = 1.05–1.15) when an excess ligand was used. The polymerization of MMA was also examined for the different reaction methods catalyzed with a low concentration of copper complexes (Table 2). Remarkably, among the four methods, the best polymerization controllability was observed in the GAMA system catalyzed with $CuBr_2$/HMTETA (Table 2, entries 10–15). Throughout, the whole range of metal catalyst concentrations the best controlled polymerization results were provided by GAMA (PDI = 1.07–1.21). The ranges of PDI for PMMA formed via ATRP and AGET under the same reaction conditions as GAMA were 1.10–1.33 and 1.20–2.02, respectively. Pretty surprising, AGET exhibited the worst controllability because the decrease in the catalyst concentration likely led to the broadening of the molecular weight distribution (Table 2 – entries 6–9). In the case of 1 and 5% catalyst concentrations, the experimental molecular weights were very far from the theoretical ones with broad molecular weight distributions (PDI > 1.4, entries 7, 8). All of these results indicate one very clear and significant message that GAMA was advantageous to the other routes under any circumstances even with the very low concentrations.

Table 2
Results of ATRP of MMA catalyzed by the low concentration of copper complexes in different ATRP system.

Entry	ATR methods	Cu^*/L/I/R	Time (h)	Yield (%)	Mn,theo (g/mol)	Mngpc (g/mol)	M_w/M_n
1	Normal	0.01/0.01/1/0($)	30	22	2400	7600	1.33
2	ATRP	0.01/0.02/1/0($)	24	38	4000	7400	1.30
3		0.05/0.1/1/0	10	64	6600	7900	1.23
4		0.1/0.2/1/0	6.5	80	8200	9300	1.10
5		1/2/1/0	1.5	77	7900	9200	1.31
6	AGET	0.01/0.01/1/0.1($)	10	74	7600	21,500	2.02
7	ATRP	0.01/0.02/1/0.1($)	5	70	7200	17,500	1.46
8		0.05/0.1/1/0.1	5	61	6300	9300	1.41
9		0.1/0.2/1/0.1	7	83	8500	12,400	1.20
10	GAMA	0.01/0.02/1/0($)	32	38	4000	7600	1.21
11	ATRP	0.05/0.1/1/0	10	45	4700	6000	1.13
12		0.05/0.25/1/0	10	77	7300	8500	1.15
13		0.1/0.2/1/0	7	77	7900	8500	1.07
14		1/1/1/0	2.5	81	8300	8600	1.16
15		1/2/1 ($)	2.5	82	8400	8700	1.20

Polymerization of MMA was performed using HMTETA ligand in toluene (50%, v/v) at 80 °C; [MMA]/[EBiBr] = 100/1; [MMA] = 4.67 M. *Cu = copper salt (CuBr/$CuBr_2$); L = Ligand (HMTETA); I = Initiator (EBiBr). $ Toluene (33%, v/v), R = Reducing agent [Sn $(EH)_2$].

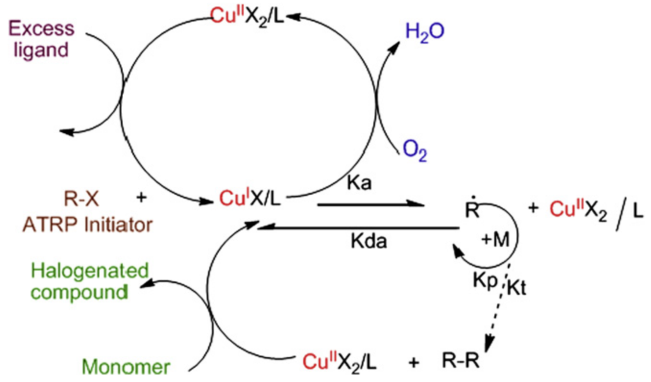
3.5. *Effect of limited amount of oxygen in reaction media*

The ATRP system is sensitive to oxygen because oxygen can inhibit polymerization not only through the formation of unreactive peroxy radicals but also through the irreversible oxidation of transition metal catalysts [49]. So new ATRP techniques, such as reverse ATRP [37–39], AGET ATRP [40,41], ARGET ATRP [11] and ICAR ATRP [42], that used high oxidations state metal catalysts were invented to overcome the problems associated with the low oxidation state metal catalysts. The polymerization of MMA was carried out using AGET ATRP, normal ATRP and high oxidation state ATRP in order to examine the effects of using a limited amount of oxygen along a monomer and solvent without that were not distilled. No external reducing agent was added to reduce the higher oxidized transition metal to a low oxidized activating species (Table 3, entries 2, 4, 6). Scheme 1 shows the plausible mechanism which was similar to a previous study with the addition of the monomer to $CuBr_2$ [50]. In this mechanism, the monomer acted as reducing agent similar to the mechanism of ARGET ATRP

Table 3

Entry	ATRP methods	Monomers	Time (min)	Yield (%)	Mn,theo g/mol	Mn,exp g/mol	Mw/Mn PDI	*f*
1	Normal	MMA*	360	69	14,100	17,650	1.36	0.79
2	ATRP	MMA§	240	82	16,700	21,300	1.34	0.78
3	AGET	MMA*	360	83	16,800	18,200	2.86	0.92
4	ATRP #	MMA§	180	73	14,800	17,500	2.64	0.84
5	GAMA	MMA*	360	84	17,000	20,300	1.32	0.84
6	ATRP	MMA§	240	72	14,600	17,500	1.13	0.83

All reactions are performed in toluene (50%, by volume) at 80 °C; [MMA]/[EBiBr]/[Copper salt]/[HMTETA] = 200/1/1/2; [MMA] = 4.67 M. MMA* = Monomer and solvent used without distillation and monomer is passed through the alumina column to remove inhibitors. # = Reducing agent as 1/1 ratio of $CuBr_2$/[Sn $(EH)_2$], *f* = Mntheo/Mnexp (initiator efficiency), § = reaction is performed in presence of limited amount of O_2 (5 ml).



Scheme 1. Representing the probable mechanism of GAMA ATRP.

with an excess amount of reducing agent that reduced the high oxidation state metal to a low oxidation so that normal ATRP could proceed. For convenient use in industry, the polymerization was also carried out using MMA without distillation after passing it through an alumina powder with an impure solvent as it was received from the company (JUNSEI) (Table 3 (entries 1, 3, 5)). The polymers formed by this system were more controlled (Table 3, entries 5, 6) than the other system. However, the rate of polymerization of impure MMA was slower than the purified MMA possibly due to presence of some inhibitors.

4. Conclusions

In an attempt to use ATRP as a commercial method on the industrial scale, different ATRP systems were evaluated with a new copper based system in which a high oxidation state transition metal was used in absence of any additive, using either a $CuBr_2$ or CuBr/HMTETA complex in toluene at 80 °C and EBriB as an initiator with methacrylate and styrene as the monomers. All of the systems were compared using a monomer and solvent without distillation, with addition of a limited amount of air and using a low catalyst to initiator ratio from the conventional ratio to 0.01/1. The system using a high oxidation transition metal was better controlled compared to the normal, reverse and AGET ATRP methods in terms of the catalytic activity and controllability. Even with a low amount of catalyst, the PDIs were <1.2. The use of the oxidatively stable catalysts overcame the air sensitive problems of lower oxidation state metals and made the preparation and storage of the ATRP catalyst system more sophisticated. Therefore, further research using high oxidation state metals is still in progress to implement the new ATRP techniques on a large scale using different monomers and ligands, etc.

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