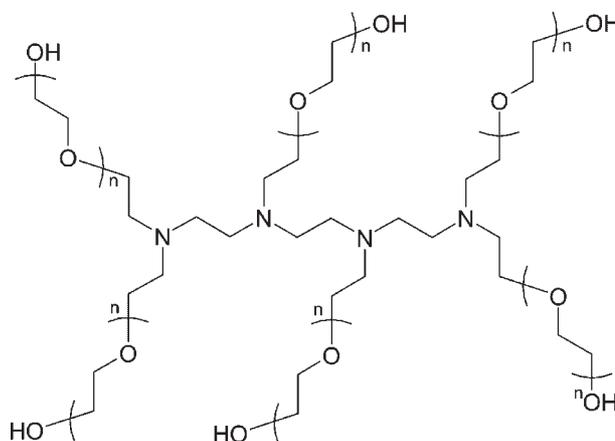


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# Cu(II)-Mediated ATRP of MMA by Using a Novel Tetradentate Amine Ligand with Oligo(ethylene glycol) Pendant Groups

Caglar Remzi Becer, Richard Hoogenboom, David Fournier, Ulrich S. Schubert\*

A novel tetradentate amine ligand namely *N,N,N',N'',N''',N'''*-hexaoligo(ethylene glycol) triethylenetetramine (HOEGTETA) was employed in the homogenous ATRP of MMA in anisole using CuBr and CuBr<sub>2</sub> as the catalyst and ethyl 2-bromoisobutyrate (EBiB) as an initiator. The effect of the polymerization temperature and the various ratios of Cu(I) to Cu(II) were investigated in detail. Moreover, we demonstrated the ATRP of MMA by using only Cu(II) in the absence of any free radical initiator, reducing agent, or air. The ATRP of MMA with the use of only Cu(II) and HOEGTETA or *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) resulted in well-defined PMMA.



## Introduction

Atom transfer radical polymerization (ATRP)<sup>[1]</sup> is one of the most widely used controlled/“living” radical polymerization techniques that has attracted great attention during recent years. The synthesis of well-defined polymers with desired compositions, architectures, and functionalities is possible using controlled/“living” radical polymerization methods. In addition, these techniques are more tolerant to functional groups and impurities compared to other living polymerization mechanisms, i.e., anionic, cationic, and ring-opening polymerizations.

In general, the ATRP technique comprises a halide functionalized initiator, a transition metal ion, and a

ligand which forms a complex with the metal ion. The transition metal complex plays a crucial role in the occurrence of a fast and reversible halogen transfer between the active radical and the dormant species. The amount of catalyst required for ATRP ranges from 0.1 to 1 mol-% with respect to the monomer which has to be removed from the final polymer. The most important challenge that stimulated the investigation of new ATRP systems was the elimination or reduction of the required amount of metal content. Several studies were also conducted on removing and recycling the catalyst efficiently by using different methods, i.e., extraction, immobilization, precipitation, and biphasic systems.<sup>[2]</sup>

Several different techniques, i.e. reverse ATRP,<sup>[3]</sup> simultaneous reverse and normal initiation (SR&NI) ATRP,<sup>[4]</sup> activators generated by electron transfer (AGET),<sup>[5]</sup> activators regenerated by electron transfer (ARGET),<sup>[6]</sup> single electron transfer living radical polymerization (SET-LRP)<sup>[7]</sup> were successfully developed by the groups of Matyjaszewski and Percec mostly with the aim of reducing the

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initial catalyst concentration, using air-stable catalysts at their higher oxidation state, or for synthesizing high molar mass polymers at an ambient temperature. All of these systems are based on metal-mediated LRP, whereby different initiation mechanisms have been examined in detail by changing the polymerization parameters,<sup>[8]</sup> i.e., initiator, transition metal ion, and ligand.<sup>[9]</sup>

It is possible to reduce the required concentration of metal ion and ligand complex to as low as a few ppm by using the ARGET process. However, the use of an appropriate ligand is still of major importance to provide an efficient halogen-exchange reaction between the dormant and the active species.<sup>[10]</sup> Most of the research that was conducted on ATRP has been focused on the synthesis and investigation of nitrogen-based ligands<sup>[11]</sup> since sulfur, oxygen, or phosphorus ligands<sup>[12]</sup> are often more expensive and less effective due to inappropriate electronic effects or unfavorable binding constants.

In this study, we investigated the effect of a novel tetradentate amine ligand bearing *N,N,N',N'',N''',N''''*-hexaoligo(ethylene glycol) triethylenetetramine (HOEGTETA) pendant groups, on the ATRP of methyl methacrylate (MMA). The ATRP of MMA was conducted at three different polymerization temperatures in order to determine the most effective temperature. Subsequently, the effect of the Cu(I) to Cu(II) ratio on the control over the polymerization was investigated and comparison reactions were done by using *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) as the ligand. Since, the higher oxidation state of the metal ion is less expensive and also air stable, a special attention was given to the ATRP system which was conducted by the use of only Cu(II) in the absence of any reducing agent or free radical initiator.

## Experimental Part

### Materials

MMA (99%, Aldrich) and anisole (99.0%, Fluka) were passed through neutral alumina oxide column, prior to use. CuBr (99.999%, Aldrich), Cu(II)Br<sub>2</sub> (99.999%, Aldrich), ethyl 2-bromoisobutyrate (EBiB) (98%, Aldrich), PMDETA (99%, Aldrich), and poly(ethylene glycol) ( $\bar{M}_n = 300 \text{ g} \cdot \text{mol}^{-1}$ , Aldrich) were used as received. HOEGTETA ( $\bar{M}_{n,\text{NMR}} = 2790 \text{ g} \cdot \text{mol}^{-1}$ ) was kindly provided by the BASF AG and precipitated into diethyl ether and dried under vacuum. All the other solvents such as diethyl ether, chloroform, *N,N*-dimethylacetamide, and methanol were purchased from Biosolve and used without further purification.

### Instrumentation

Monomer conversion was determined by <sup>1</sup>H NMR spectroscopy, which was recorded on a Varian Mercury 400 NMR in deuterated

chloroform. The chemical shifts were calibrated to tetramethylsilane (TMS). Gel permeation chromatography (GPC) was measured on a Shimadzu system equipped with an SCL-10A system controller, an LC-10AD pump, an RID-10A refractive index detector, an SPD-10A UV detector, and both a PSS Gram30 and a PSS Gram1000 column in series, whereby *N,N*-dimethylacetamide with 5 mmol LiCl was used as an eluent at 1 mL · min<sup>-1</sup> flow rate and the column oven was set to 60 °C. The molecular weight and the molecular weight distribution of the prepared polymers were calculated by using poly(methyl methacrylate) standards.

## Polymerizations

A typical polymerization procedure of MMA using Cu(I)Br was as follows: CuBr (36 mg, 2.5 mmol), HOEGTETA (697.5 mg, 2.5 mmol), and a stirring bar were added into a Schlenk tube and sealed with a rubber septum. The tube was flushed with argon for 15 min and subsequently deoxygenated anisole (5.35 mL, 50 vol.-% with respect to MMA) and MMA (5.35 mL, 50 mmol) were introduced into the tube and bubbled for an additional 15 min with argon. EBiB (36.5 μL, 2.5 mmol) was added with a degassed syringe and the tube was immersed into an oil bath that was preheated to the desired temperature. At different time intervals, samples were withdrawn with a degassed syringe and each sample was divided into two portions. The first portion was diluted with deuterated chloroform for the determination of conversion by measuring <sup>1</sup>H NMR spectroscopy. The second portion was precipitated into methanol to remove the catalyst prior to the injection to GPC for the determination of molecular weight and polydispersity index. All the polymerizations and sample preparations were conducted with the same procedure unless otherwise indicated.

## Results and Discussion

The ATRP of MMA was performed in anisole at three different temperatures (60, 80, and 90 °C) by using EBiB as an initiator. CuBr and HOEGTETA were used as a homogeneous catalyst in the polymerization medium and the ratio of MMA/EBiB/CuBr/HOEGTETA was 200:1:1:1. As depicted in Figure 1, a linear increase in the semilogarithmic kinetic plot was observed for all the three reaction temperatures and higher apparent rate constants were obtained at elevated temperatures, as expected. The calculated apparent rate constants, which are listed in Table 1 (entry 1, 2, and 3) were found as  $4.4 \times 10^{-5}$ ,  $1.20 \times 10^{-4}$ , and  $2.42 \times 10^{-4} \text{ (s}^{-1}\text{)}$  for the polymerization temperatures of 60, 80, and 90 °C, respectively.

The molecular weight distributions of the synthesized polymers were found to be rather broad (Table 1, entries 1, 2, and 3), which is an evidence of an inadequate control over the polymerization process. In addition, the observed molecular weights were higher than the theoretical values, in particular at the beginning of the reaction. One reason for the poor control over the molecular weight increase might be a steric hindrance of the bulky pendant groups

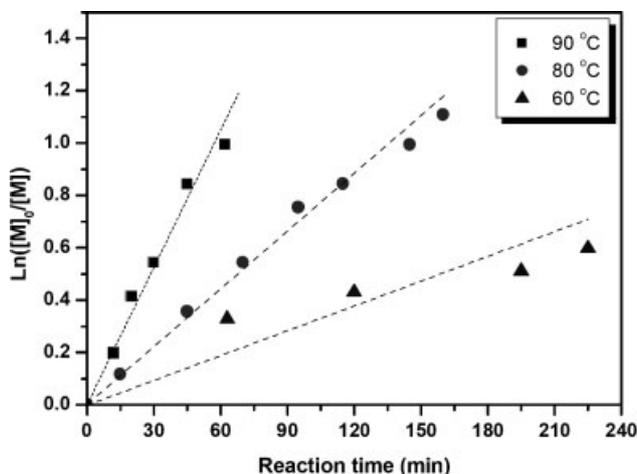


Figure 1. Kinetic plots for the ATRP of MMA at (▲) 60 °C, (●) 80 °C, and (■) 90 °C.  $[MMA]_0 = 2.0 \text{ M}$ ,  $[EBiB]_0 = [CuBr]_0 = [HOEGTETA]_0 = 1.0 \times 10^{-2} \text{ M}$ . Anisole was used as a solvent (50 vol.-%).

which limit the accessibility of the amine core. Although these pendant groups provide the formation of a homogenous metal–ligand complex in the polymerization medium, they also reduce the accessibility of the copper ions and, thus, the efficiency of the halogen exchange equilibrium. Another reason for the loss of control that should be considered is the low amount of deactivator ( $CuBr_2$ ) at the initial state of the polymerization. Therefore, the activation reaction is fast but the radical deactivation reaction is slow at the early stage of the polymerization, which results in a high radical concentration. As a result of these effects, irreversible radical terminations can more

frequently occur at the beginning of the polymerization, which cause a decrease in initiation efficiency and polymerization rate.

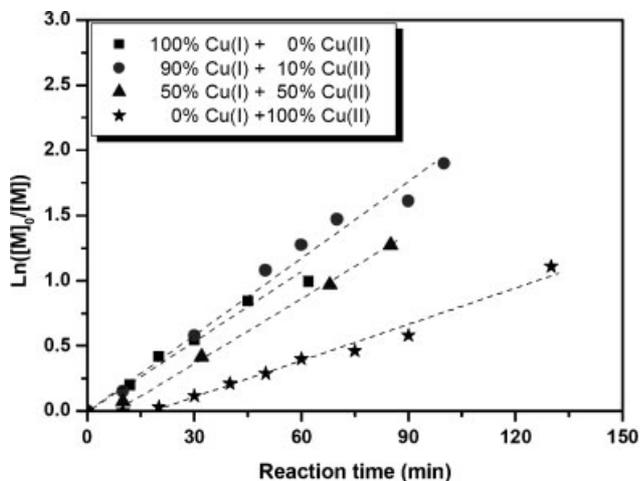
To analyze the effect of the amount of the deactivator in the ATRP of MMA, different amounts of Cu(II) were added to the polymerization medium. For the first attempt, the ratio of  $[Cu(I)]/[Cu(II)]$  was changed from 1:0 to 0.9:0.1 (Table 1, entry 1 and 4) and a very slow propagation was expected. Surprisingly, the apparent rate of polymerization was found to be higher when 10% Cu(II) (with respect to the total amount of copper species) was added to the system, and at the same range when 50% Cu(II) was present, as shown in Figure 2. Besides this, the polydispersity indices of the resulting polymers were decreased and an improved control over the molecular weights was achieved. In order to better understand this effect, the ratio of Cu(I) to Cu(II) was altered from 0.9:0.1 to 0.5:0.5 and to 0:1.0. The apparent rates of polymerization decreased when the amount of Cu(II) was increased. Although there is a difference between the theoretical molecular weights and the obtained molecular weights, monomer conversions of more than 70% were achieved with polydispersity indices around 1.3, as listed in Table 1 (entry 4, 5, and 6). However, the results obtained for the polymerization of MMA starting from 100% Cu(II) lead us to consider possible reducing agents or radical sources. According to the normal ATRP procedure, this reaction should never initiate the polymerization without any reducing agent or radical source.

When considering the reverse ATRP or AGET mechanism, a free radical source or a reducing agent is required to generate the lower oxidation state of the transition metal complex, respectively. Since there is no free radical

Table 1. Polymerization of MMA under different conditions. All the reactions were performed in anisole (50 vol.-%).

Entry	Temperature	Reaction time	Conversion	$\bar{M}_{n,theo}$	$\bar{M}_{n,GPC}$	PDI ( $\bar{M}_w/\bar{M}_n$ )	$k_{app}$
	°C			min	%		$g \cdot mol^{-1}$
1 <sup>a)</sup>	90	62	63	12 800	15 000	1.46	2.88
2 <sup>a)</sup>	80	160	67	13 600	15 000	1.63	1.20
3 <sup>a)</sup>	60	275	47	9 600	13 600	1.44	0.44
4 <sup>b)</sup>	90	100	85	17 200	26 000	1.34	3.25
5 <sup>c)</sup>	90	85	72	14 600	22 100	1.27	2.47
6 <sup>d)</sup>	90	190	86	17 400	27 100	1.32	1.66
7 <sup>e)</sup>	90	125	44	9 000	11 000	1.15	0.77
8 <sup>f)</sup>	90	125	46	9 400	10 800	1.15	0.75

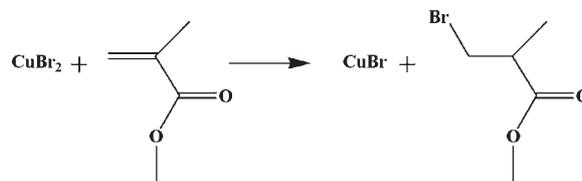
<sup>a)</sup> $[MMA]/[EBiB]/[Cu(I)]/[Cu(II)]/[HOEGTETA] = 200:1:1:-:1$ ; <sup>b)</sup> $[MMA]/[EBiB]/[Cu(I)]/[Cu(II)]/[HOEGTETA] = 200:1:0.9:0.1:1$ ; <sup>c)</sup> $[MMA]/[EBiB]/[Cu(I)]/[Cu(II)]/[HOEGTETA] = 200:1:0.5:0.5:1$ ; <sup>d)</sup> $[MMA]/[EBiB]/[Cu(I)]/[Cu(II)]/[HOEGTETA] = 200:1:-:1:1$ ; <sup>e)</sup> $[MMA]/[EBiB]/[Cu(I)]/[Cu(II)]/[PMDTA] = 200:1:-:1:1$ ; <sup>f)</sup> $[MMA]/[EBiB]/[Cu(I)]/[Cu(II)]/[PMDTA]/[PEG_{300}] = 200:1:-:1:1:1$ .



**Figure 2.** Kinetic plots for the polymerization of MMA at 90 °C with different concentrations of Cu(I) and Cu(II).  $[MMA]_0 = 2.0$  M,  $[EBiB]_0 = [HOEGTETA]_0 = 1.0 \times 10^{-2}$  M, (★)  $[Cu(II)]_0 = 1.0 \times 10^{-2}$  M, (●)  $[Cu(II)]_0 = 0.9 \times 10^{-2}$  M and  $[Cu(I)]_0 = 0.1 \times 10^{-2}$  M, (▲)  $[Cu(II)]_0 = 0.5 \times 10^{-2}$  M and  $[Cu(I)]_0 = 0.5 \times 10^{-2}$  M, (■)  $[Cu(I)]_0 = 1.0 \times 10^{-2}$  M. Anisole was used as a solvent (50 vol.-%).

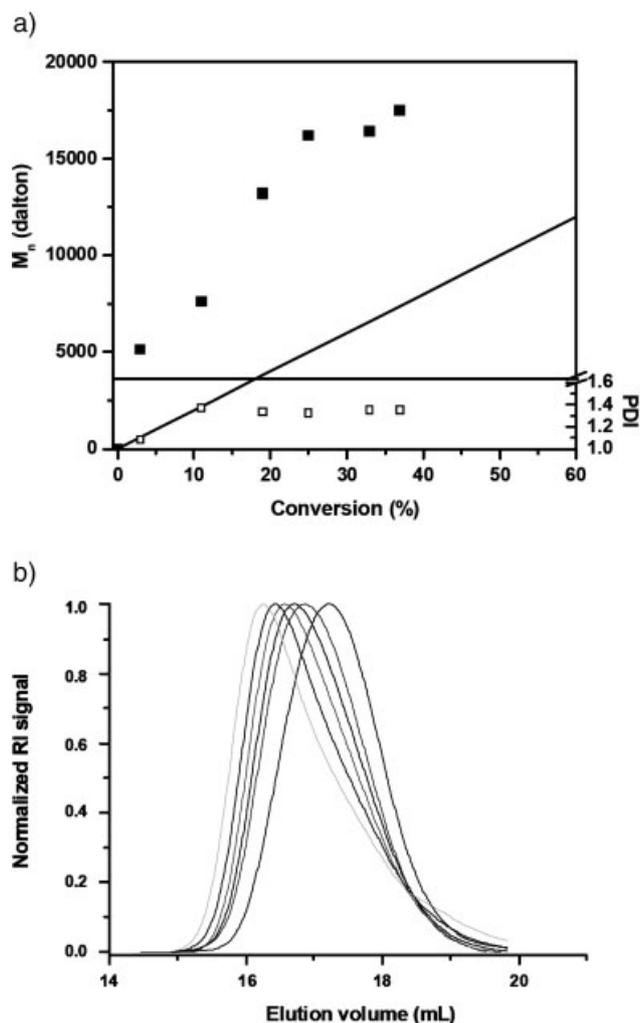
initiator in the present system, we searched for possible reducing agents. Different reducing agents such as phenols,<sup>[13]</sup> thiophenols,<sup>[14]</sup> monosaccharides,<sup>[15]</sup> triethylamine,<sup>[16]</sup> and ascorbic acid<sup>[17]</sup> were examined in detail by various research groups and they successfully conducted reverse ATRP or AGET by the use of these compounds. However, the present optimization reactions reported in this study were carried out in the absence of any of these reducing agents.

Mathias et al. reported a study on an air-induced ATRP of methacrylates in the absence of an initiator and using  $CuCl_2/PMDETA$  as a catalyst complex.<sup>[18]</sup> They showed the possibility of synthesizing polymers with low polydispersity indices by using a transition metal ion at its higher oxidation state. On the other hand, the polymerization conditions did not allow the quantification of the effects of individual components such as the ratio of monomer to initiator. Moreover, the molecular weights of the resulting polymers were unpredictable. However, when we performed the polymerization of MMA in the absence of initiator, we did not observe any polymer formation which shows that there is no air-induced initiation in our system. Matyjaszewski et al. provided a deeper insight into the oxygen-initiated mechanism by performing kinetic studies on the synthesis of high molecular weight polymers.<sup>[19]</sup> Furthermore, the authors investigated the addition reaction of  $CuBr_2$  and MMA that resulted in a reduction of Cu(II) to Cu(I) and the formation of 1,2-dibromoisobutyrate. This indirect generation of Cu(I) species allows a halogen-exchange mechanism, possibly combined with an induction period at the beginning of the polymerization. We also observed an induction period as



**Scheme 1.** Addition reaction between MMA and  $CuBr_2$ .

seen in Figure 2, especially when more Cu(II) was used in comparison to Cu(I). Therefore, we propose that the polymerization with Cu(II) observed here proceeds via a kind of AGET mechanism, whereby the MMA reduces the Cu(II) ion to Cu(I) by an addition reaction<sup>[19]</sup> which is shown in Scheme 1. It should also be considered that the



**Figure 3.** Dependence of the  $\bar{M}_{n,SEC}$  and the PDI of PMMA on monomer conversion (a) at a polymerization temperature of 90 °C and  $[MMA]_0 = 2.0$  M,  $[EBiB]_0 = [HOEGTETA]_0 = [Cu(II)]_0 = 1.0 \times 10^{-2}$  M. GPC traces of the prepared polymers (b).

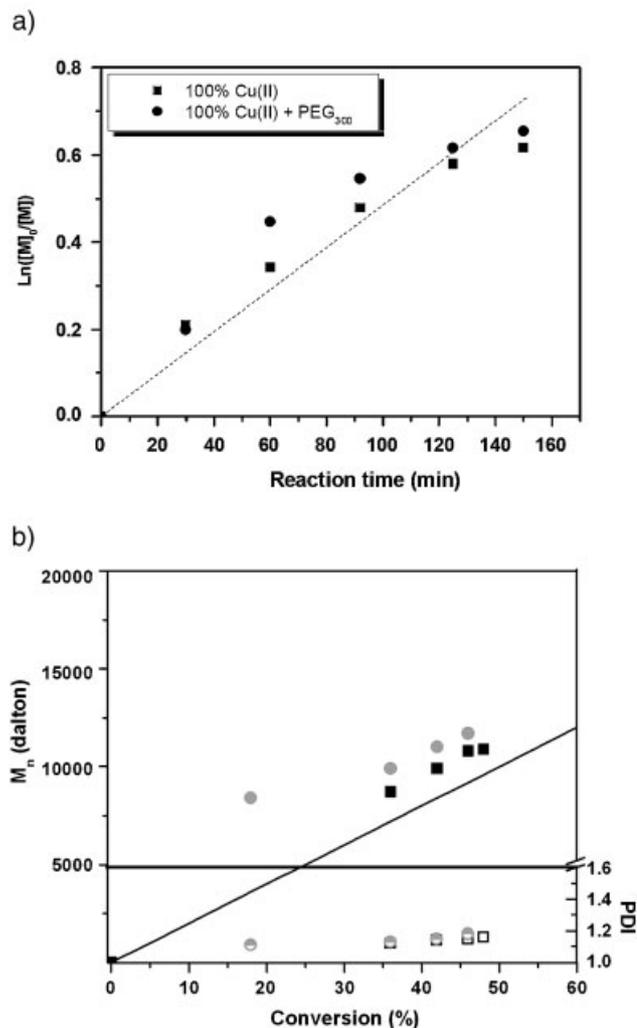
amine core of the ligand is capable of reducing Cu(II) ions to Cu(I).

Figure 3 shows the GPC results of the MMA polymerization when there is only Cu(II) added at the beginning of the reaction. The molecular weights of the obtained PMMA increased and the polydispersity indices remained relatively low as the MMA conversion progressed. In addition, the GPC traces of the resulting polymers shifted to high molecular weights as illustrated in Figure 3b as well. The reason for the difference between the measured molecular weights and the theoretical values can be found in slow exchange reactions which result in low initiation efficiencies.

The ATRP of MMA in the presence of only Cu(II) was also conducted by using PMDETA as a ligand in order to compare the rate of polymerization obtained with HOEGTETA with a known ligand. PMMA was synthesized with low polydispersity indices and the experimental molecular weights were found to be close to the theoretical values (Figure 4). The apparent rate of the polymerization was found to be lower with PMDETA compared to HOEGTETA as a ligand (Table 1, entry 6 and 8). There can be two possible reasons for this. The difference in the number of dentates of ligands affects the polymerization rate. It is known that ATRP conducted by using tetradentate amine ligands in comparison to tridentate amine ligands exhibits faster apparent rate constants.<sup>[20]</sup> Secondly, HOEGTETA forms a homogenous complex with the metal ion, whereas PMDETA dissolves the metal ion only partially. It should be taken into account that the differences in the solubility of the copper ions in the polymerization medium have a great effect on the rate of polymerization.

Haddleton et al. reported the effect of water on the copper mediated LRP and it was found that increase in the polarity of the medium provides an enhanced polymerization rate.<sup>[21]</sup> To study the effect of the PEG chains of HOEGTETA on the ATRP of MMA, we also investigated the effect of free PEG units in the polymerization mixture. The ATRP of MMA was conducted with Cu(II), PMDETA, and one equivalent of PEG<sub>300</sub> (regarding to the ratio of PMDETA). As depicted in Figure 4, there is no significant effect of PEG<sub>300</sub> on the polymerization rate of MMA and also on the molecular weight distribution (Table 1, entry 7 and 8).

Besides the addition reaction between CuBr<sub>2</sub> and MMA as the reducing agent, it is also reported that some radicals may react with metal centers, reversibly forming organometallic species.<sup>[22]</sup> It should also be noted that in case of generation of any radicals by autoinitiation or any other ways, this reaction may occur with either Cu(I) or Cu(II) species leading to R-Cu(II) and R-Cu(III) species, respectively. These radicals are capable of subsequently generating new radicals which may also have an effect on the control of the polymerization.



**Figure 4.** Semilogarithmic kinetic plot (a) at a polymerization temperature of 90 °C with and without additional PEG<sub>300</sub>, dependence of the  $\bar{M}_{n,SEC}$  and the PDI of PMMA on monomer conversion (b).  $[MMA]_0 = 2.0$  M,  $[EB/B]_0 = [PMDETA]_0 = [Cu(II)]_0 = 1.0 \times 10^{-2}$  M, (●)  $[PEG_{300}]_0 = 0$ , (■)  $[PEG_{300}]_0 = 1.0 \times 10^{-2}$  M, open symbols correspond to PDI. Anisole was used as a solvent (50 vol.-%).

## Conclusion

In this communication, we have demonstrated for the first time, the polymerization of MMA by using a linear tetramine bearing oligo(ethylene glycol) pendant groups. The effect of polymerization temperature and Cu(I) to Cu(II) ratio on the polymerization process was investigated in detail. It was found that a controlled polymerization of MMA could be conducted by using the transition metal ion at its higher oxidation state in the absence of any reducing agent. According to the results obtained in this study, Cu(I) species were presumably generated by an addition reaction of CuBr<sub>2</sub> and MMA. This generation of lower

oxidation state metal species resulted in an initiation of the ATRP of MMA. Excess of Cu(II) provided a better control over the polymerization and prevented the loss of control at the early stage of the polymerization. These conditions were also employed for the polymerization of MMA by using PMDETA, demonstrating the controlled radical polymerization with only Cu(II) species. It was also shown that the catalytic amount of PEG<sub>300</sub> had no significant effect on the polymerization of MMA by using PMDETA. The HOEGTETA polymeric ligand will be further investigated to study its ability to remove the metal–ligand complex from the polymerization medium by selective precipitation. In addition, the ATRP of other monomers will be investigated with HOEGTETA, whereby special attention will be given to the homogenous aqueous ATRP.

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