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Pentadentate Copper Halide Complexes Have Higher Catalytic Activity in Atom Transfer Radical Polymerization of Methyl Acrylate Than Hexadentate Complexes

Lifen Zhang,[†,§,#] Huadong Tang,[†] Jianbin Tang,[‡] Youqing Shen,*[,†,‡] Lingzhi Meng,[§] Maciej Radosz,[†] and Navamoney Arulsamy[⊥]

[†]*Department of Chemical and Petroleum Engineering, University of Wyoming, Laramie, Wyoming 82071,* [‡]*State Key Lab of Chemical Engineering and Department of Chemical and Biochemical Engineering, Zhejiang University, Hangzhou, China 310027,* [§]*Department of Polymer Science, Wuhan University, Wuhan, China, and* [⊥]*Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071.* [#] *Visiting student from Wuhan University*

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ABSTRACT: Highly active catalysts mediating atom transfer radical polymerization (ATRP) at low concentrations, therefore requiring no postpolymerization catalyst removal, are highly desirable for wide commercial applications of ATRP. We previously reported that CuBr ligated by a hexadentate ligand, *N,N,N′,N′*-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN), was highly active in ATRP, but in solution the activator existed as a binuclear [Cu_2Br_2(TPEN)] complex and had to rearrange to form a more active mononuclear pentadentate active center for catalysis. Herein, we prepared *N,N,N′*-tris(2-pyridylmethyl)-*N′*-methylethylenediamine (TPMEN), a pentadentate ligand equivalent to a TPEN with one pyridyl group removed, and used it as a ligand for copper halides to understand the effect of the catalyst structure on its catalysis in ATRP. TPMEN formed mononuclear complexes with both copper(I) and copper(II) halides. Cyclic voltammograms (CV) results showed that Cu^{I}/TPMEN−Cu^{II}/TPMEN couples had a more negative redox potential than that of those ligated by TPEN. Cu^{I}Br (or Cl)/TPMEN indeed showed a higher catalytic activity at low temperatures in ATRP of MA than copper halide/TPEN. However, they could not polymerize MA well at room temperature or higher because of their high reactivity toward the initiator (persistent radical effect). In the presence of a reducing agent, the catalyst mediated well-controlled activator-regenerated electron transfer (ARGET) ATRP of MA at catalyst/initiator molar ratios of 0.003−0.01 (22−75 ppm). Self-extension and block copolymerization of PMA confirmed the livingness of the polymerization.

Introduction

Atom transfer radical polymerization (ATRP), a transition-metal-mediated living radical polymerization, is a controlled/"living" radical polymerization catalyzed by redox transition-metal complexes.[1−7] ATRP has been used extensively as a potent tool to synthesize macromolecules with precisely controlled structures of vinyl monomers[6] including block copolymers,[8−12] polymer brushes,[13−15] and hybrid materials[16−20] as well as various functionalities.[21]

A continuous effort to realize large-scale industrial applications of ATRP is to develop "greener" ATRP process[22−24]or catalysts,[25,26] either reusable[27−30] or highly active,[31−33] to reduce the catalyst residue concentration in the products, which is the main barrier to practical commercialization of ATRP.[25] Highly active catalysts that can catalyze the polymerization at very low concentrations are preferable since such catalysts can be safely and economically left in the products, avoiding the tedious separation process.

ATRP is based on an equilibrium between the activation reaction that generates radicals from the dormant chains for chain growth and the deactivation reaction that deactivates the radicals back to the dormant chains. The equilibrium constant, K_{ATRP}, which is the ratio of the rate constants of the activation (k_{act}) and the deactivation (k_{deact}), determines the polymerization reaction rate and its control, as shown in eqs 1 and 2.[3,4] A catalyst with a large K_{ATRP} leads to a fast polymerization and high catalytic activity.[34]

$$R_p = \frac{-dM}{dt} = \frac{k_p k_{act}[RX][M][CuX]}{k_{deact}[CuX_2]} \quad (1)$$

$$PDI = \frac{M_w}{M_n} = 1 + \left(\frac{k_p[RX]}{k_{deact}[CuX_2]}\right)\left(\frac{2}{p} - 1\right) \quad (2)$$

The catalyst activity of ATRP catalysts is determined by their ligands.[35−38] Copper halides ligated by multidentate nitrogen-based ligands, including picolylamine derivatives and branched tetradentate ligands such as tris[(2-pyridyl)methyl]amine (TPMA)[35,39] and tris[2-(dimethylamino)ethyl]amine (Me_6TREN),[40] have high catalytic activities. However, these catalysts alone still could not catalyze the polymerization to high yields at low concentrations, such as at 1 mol % of the initiator. Matyjaszewski et al. found that adding reducing agents greatly enhanced their activity and developed initiators for continuous activator regeneration (ICAR) and activator-regenerated electron transfer (ARGET) ATRP that could carry out the polymerization at the catalyst concentrations of tens of parts per million.[40−42] Percec et al. reported single-electron-transfer-mediated living radical polymerization (SET-LRP) of

*To whom correspondence should be addressed.

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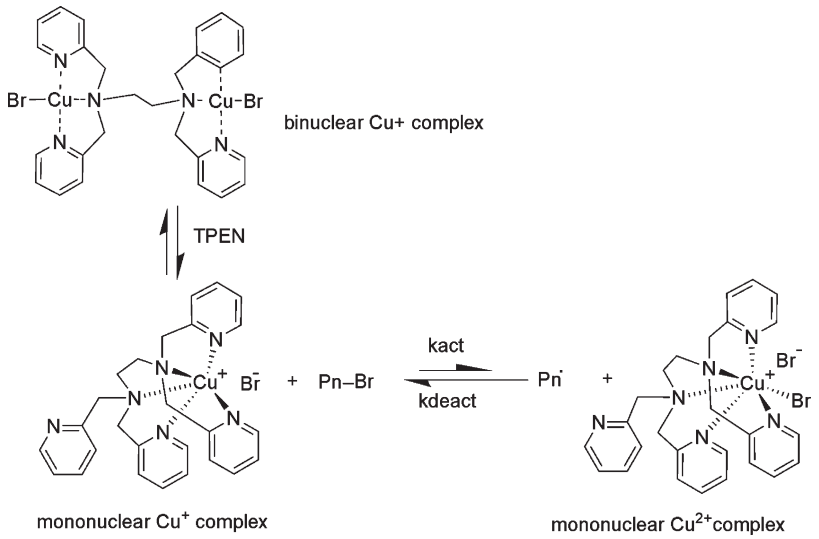
Scheme 1. Equilibrium between the Binuclear and Mononuclear Copper(I) Complexes of TPEN in Solution and Mediated ATRP Equilibrium



MA catalyzed by Cu(0)/Me_6TREN in DMSO. This SET-LRP process facilitated an ultrafast synthesis of ultrahigh-molecular-weight polymers.[31]

We recently reported that a hexadentate *N,N,N′,N′*-tetra[(2-pyridyl)methyl]ethylenediamine ligated CuBr (CuBr/TPEN) had a very high catalytic activity.[32] CuBr/TPEN alone mediated a well-controlled polymerization of MA at 0.5−1 mol % catalyst relative to initiator (tens of ppm of copper). In the presence of reducing agents such as trialkylamine, it could also polymerize MMA and styrene at these low catalyst concentrations.[32] Detailed study of the catalyst structures and mechanism showed that the activator in solution existed as binuclear tridentate [Cu_2Br_2 (TPEN)] and mononuclear pentadentate [CuBr(TPEN)] structures with a fast exchange equilibrium, while the deactivator $CuBr_2$/TPEN had a mononuclear [Cu(TPEN)Br]Br structure with one pyridyl nitrogen of the TPEN not coordinated with the Cu(II) (Scheme 1). We postulated that during the catalysis the binuclear [Cu_2Br_2 (TPEN)] had to rearrange to the mononuclear structure to catalyze the polymerization and thus not all the CuBr/TPEN acted as the catalytic species.

We thus further postulated that removing one pyridyl group from the TPEN ligand might force the resulting ligand to form mononuclear pentadentate complexes with both Cu(I) and Cu(II) halides. The Cu(I)/L complexes would need no structural rearrangement for catalysis and the catalyst would thus have even higher catalytic activity. Some pentadentate ligands were reported not to undergo structural change in their complexes with Cu(I) and Cu(II).[43] To prove this hypothesis, we prepared a corresponding pentadentate ligand *N,N,N′*-tris(2-pyridylmethyl)-*N′*-methylethylenediamine (TPMEN) and made its complexes with copper halides. The TPMEN complexes of Cu(I) and Cu(II) were indeed mononuclear. The Cu(I)Br (or Cl)/TPMEN complexes had higher activities in ATRP of MA than the corresponding complexes with TPEN at low temperatures.

Experimental Section

Materials. Methyl acrylate (MA, 99%, Aldrich) and styrene (St, 99%, Aldrich) were distilled under vacuum to remove the inhibitor. CuBr (99.99%, Aldrich) and CuCl (99.99%, Aldrich) were purified by washing with methanol. Ethyl 2-bromoisobutyrate (EBiB, 98%, Aldrich), methyl 2-bromopropionate (MBP), 2-picolyl chloride hydrochloride (98%, Aldrich), *N*-methylethylenediamine (97.0%, Aldrich), $CuBr_2$ (99%, Aldrich), $CuCl_2$ (99%, Aldrich), triethylamine (TEA, 98%, Aldrich), and sodium hydroxide (NaOH, 99.5%, Fisher Scientific) were used as received. TPEN was synthesized as previously reported.[32]

Synthesis of *N,N,N′*-Tris(2-pyridylmethyl)-*N′*-methylethylenediamine (TPMEN). 2-Picolyl chloride hydrochloride (6.0 g, 36.6 mmol) was dissolved in 10 N NaOH (45.8 mL, 366 mmol) aqueous solution. *N*-Methylethylenediamine (0.9 mL, 10.39 mmol) was added dropwise to the solution with stirring. After 3 days at room temperature, the upper oil layer was collected and dissolved in dichloromethane. The dichloromethane solution was washed with an excess of water and dried using anhydrous $MgSO_4$. After evaporation of dichloromethane, the crude sample was purified using a silicon column ($CHCl_3$: CH_3OH 10:1 (v/v)), yielding 2.7 g of light yellowish oil (TPMEN) (50%). ESI-MS: Calcd for $C_{21}H_{25}N_5$: 347.2; found M + 1: 348.2, M + Na^+: 370.3. ^{1}H NMR ($CDCl_3$): δ 8.49 (m, 3H, −py), 7.62 (m, 3H, −py), 7.52, 7.32 (m, 3H, −py), 7.1 (m, 3H, −py), 3.84 (s, 4H, $-N(-CH_2-py)_2$), 3.63 (s, 2H, $H_3C-N-CH_2-py$), 2.75−2.77 (d, 4H, $N-CH_2CH_2-N$), 2.21 (s, 3H, $N-CH_3$).

ATRP of MA. A general procedure of MA polymerization at a catalyst/initiator molar ratio of 0.1 is as follows: CuCl (1.08 mg, 0.011 mmol), TPMEN (3.818 mg, 0.011 mmol), and a stirring bar were charged into a Schlenk tube and sealed with a rubber septum. The tube was flushed with nitrogen for 5 min, and subsequently deoxygenated MA (1.0 mL, 11.0 mmol) was introduced into the tube and bubbled with N_2 for an additional 5 min. EBiB (16.17 μL, 0.11 mmol) was added with a degassed syringe, and the tube was immersed in an oil bath preheated to the desired temperature. At timed intervals, samples were withdrawn using a degassed syringe and stored in a freezer. Samples were analyzed by gel permeation chromatography (GPC) and ^{1}H NMR to follow the progress of the reaction.

ATRP of MA in the Presence of TEA. A typical polymerization procedure of MA at a MA/initiator/CuCl/TPMEN/TEA molar ratio of 100/1/0.01/0.01/0.25 is as follows. CuCl (1.08 mg, 0.011 mmol), TPMEN (3.818 mg, 0.011 mmol), and a stirring bar were added into a Schlenk tube and sealed with a rubber septum. The tube was flushed with nitrogen for 5 min, and subsequently deoxygenated MA (10.0 mL, 110 mmol) was introduced into the tube. EBiB (161.7 μL, 1.10 mmol) and TEA (38 μL, 0.27 mmol) were injected into the tube with a degassed syringe, and the tube was immersed in an oil bath preheated to the desired temperature. Samples were taken at timed intervals and analyzed by ^{1}H NMR and GPC to follow the progress of the reaction.

Preparation of PMA Macroinitiator. PMA macroinitiator was prepared using above procedure at a MA/EBiB/CuCl/

TPMEN/TEA ratio of 100/1/0.01/0.01/0.25. The polymers were purified by passing the THF solution through a column packed with silica to remove the catalyst, followed by precipitation into ether. Two PMA macroinitiators with M_n of 5100 (PDI, 1.22) and 6200 (PDI, 1.21) were prepared.

Self-Extension of PMA. PMA macroinitiator (M_n = 5100, PDI = 1.22, 0.36 g, 0.071 mmol), CuCl (1.08 mg, 0.011 mmol), and TPMEN (3.818 mg, 0.011 mmol) were charged into a Schlenk flask. The flask was sealed with a rubber septum and degassed. Degassed MA (1.0 mL, 11.0 mmol) and TEA (38 μL, 0.27 mmol) were added via a degassed gastight syringe, and the mixture was immersed in an oil bath at 70 °C. Samples were taken at timed intervals, and ^{1}H NMR and GPC were used to trace the progress of the polymerization.

Synthesis of block Copolymer PMA-*b*-PS. The purified PMA macroinitiator (M_n = 6200, PDI = 1.21, 0.67 g, 0.11 mmol), CuCl (1.08 mg, 0.011 mmol), and TPMEN (3.818 mg, 0.011 mmol) were introduced in a Schlenk flask and sealed with a rubber septum. Degassed St (1.25 mL, 11.0 mmol) and TEA (38 μL, 0.27 mmol) were added into the flask via a degassed gastight syringe. The reaction mixture was stirred at 100 °C for a predesignated time. The polymerization was traced using ^{1}H NMR and GPC.

Analysis. ^{1}H NMR spectra were obtained using a Bruker DRX-400 spectrometer using $CDCl_3$ as a solvent. The GPC measurements were carried out on a Waters SEC equipped with two 300 mm Waters Styragel solvent-saving columns (molecular weight ranges: 5×10^2–3×10^4; 5×10^3–6×10^5) and a Waters 2414 refractive index detector in THF at 30 °C at a flow rate of 0.3 mL min^{-1}. A series of polystyrene standards with molecular weights ranging from 1250 to 570 000 were employed to generate the universal calibration curves for PMA.[44]

The electrospray ionization mass spectrometry (ESI-MS) spectra were obtained on an electrospray ionization mass spectrometer (ESI-MS, Finnigan MAT LCQ mass spectrometer) operated in a positive-ion mode at the source temperature of 200 °C. The sample concentration was 100 μM in actonitrile. Elemental analysis of Cu(I) and Cu(II)/TPMEN complexes was performed by Midwest Microlab, LLC (Indianapolis, IN). The activator CuBr/TPMEN complex was obtained by precipitating the CuBr/TPMEN (1/1 molar ratio) actonitrile solution in ether under nitrogen. Anal. Calcd (%) for $C_{21}H_{25}BrCuN_5$ (CuBr/TPMEN 1/1 complex): C, 51.38; H, 5.13; N, 14.27. Found: C, 48.95; H, 4.69; N, 12.16. The deactivator $CuBr_2$/TPMEN complex was obtained from the blue precipitation produced during the polymerizations of MA at a catalyst/initiator ratio of 0.1. The blue precipitates were collected and washed with THF three times. Anal. Calcd (%) for $C_{21}H_{25}BrCuN_5$ ($CuBr_2$/TPMEN 1/1 complex): C, 44.19; H, 4.41; N, 12.27. Found: C, 42.32; H, 4.41; N, 11.08.

The reduction potential, $E_{p,c}$, oxidation potential, $E_{p,a}$, and redox potential, $E_{1/2}$, of the Cu(II)Br_2/TPMEN−Cu(I)Br/TPMEN and Cu(II)Cl_2/TPMEN−Cu(I)Cl/TPMEN couples were measured by cyclic voltammetry (CV) at room temperature with a Cypress Systems potentiostat (CS-1200) instrument. The solutions (1 mM) of Cu(II)Br_2/TPMEN and Cu(II)Cl_2/TPMEN were prepared in actonitrile containing 0.1 M Bu_4NBF_4 as the supporting electrolyte. Measurements were carried out under nitrogen at a scan rate of 100 mV/s using a glass−carbon disk as the working electrode, a platinum wire as the auxiliary electrode, and a saturated calomel reference electrode (SCE). The electrochemical properties of the Cu(II)Br_2/TPEN−Cu(I)Br/TPEN and Cu(II)Cl_2/TPEN−Cu(I)Cl/TPEN couples were measured under identical conditions.

Results and Discussion

Structures of Cu(I) and Cu(II)/TPMEN Complexes. Solid-state X-ray crystallography of single crystals is most accurate in determining the structures of complexes.[32,45] We previously obtained the single crystals of the CuBr/TPEN and $CuBr_2$/TPEN and determined their accurate structures using this method.[32] Unfortunately, all our efforts to grow single crystals of the halides of Cu(I) and Cu(II)/TPMEN complexes failed. Their structures were thus probed using electrospray ionization mass spectrometry (ESI-MS),[46,47] and their stoichiometric compositions were determined by elemental analysis.[32,48] Figure 1 shows the ESI-MS spectra of the isolated CuBr/TPMEN and $CuBr_2$/TPMEN complexes and the assignments of the major peaks. In the spectrum of the Cu(I) complex, the peaks resulting from the CuBr/TPMEN at the 1/1 ratio were present at 490.9 ($[CuBr/TPMEN + H]^+$), 410.2 ($[Cu/TPMEN]^+$), 317.1 ($[(CuBr/TPMEN)$-pyridylmethyl$)]^+$, and 205.1 ($[(TPMEN)Cu]^{2+}$). There was no trace resulting from CuBr/TPMEN at the 2/1 ratio, such as at 630.9 ($[2CuBr/TPMEN]^+$), 551.99 ($[(Cu + CuBr)/TPMEN]^+$), and 236.5 ($[2Cu/TPMEN]^{2+}$). The elemental analysis also confirmed that the complex was a 1/1 molar ratio of CuBr to TPMEN. This is in contrast to the CuBr/TPEN complex. CuBr/TPEN complex prepared at a 1/1 ratio existed as a binuclear [Cu_2Br_2(TPEN)] in solid form.[32] The major peaks in the spectrum of the $CuBr_2$/TPMEN complex are almost the same as those of the CuBr/TPMEN. This is due to the reduction of Cu(II) to Cu(I) during the electrospray ionization process.[49] The spectrum also indicates that the Cu(II)Br_2 complexed with TPMEN at the 1/1 molar ratio, which was again confirmed by elemental analysis. We thus concluded that both the CuBr and $CuBr_2$ complexes were mononuclear.

Neither spectra showed any trace of free TPMEN ($[TPMEN + H]^+$), suggesting high stability of the complexes and thus high catalytic activity in ATRP.[50] A ligand forming more stable Cu(II)/L complex will form a more reducing and thus more reactive Cu(I)/L complex as ATRP catalyst.[43,51]

Electrochemical Studies. The activity of the copper-based catalyst is directly related to the value of K_{ATRP}, which is proportional to the equilibrium constant K_{ET} of the electron transfer process from the Cu(I)/L complex to the Cu(II)/L complex,[52,53] or to the redox potential E of the couple Cu(II)/L/Cu(I)/L (eq 3). A more negative redox potential indicates a larger K_{ATRP} and thus a higher catalytic activity.[36,54,55] Thus, the redox potential of a complex is a measure of the activity of a catalyst (in terms of K_{ATRP})[36]

$$E \approx -\frac{RT}{F} \ln K_{ET} \quad (3)$$

where F is the Faraday constant, R is the gas constant, and T is the temperature in kelvin.

Ligands affect the redox potential of the complex through stabilization or destabilization of the complex's Cu(II) state. Greater stabilization of the Cu(II)/L relative to Cu(I)/L leads to a more negative redox potential of the couple.[51] The reduction potential, $E_{p,c}$, oxidation potential, $E_{p,a}$, and redox potential, $E_{1/2}$, of the $CuBr_2$/TPMEN−CuBr/TPMEN couple and those of the $CuBr_2$/TPEN−CuBr/TPEN couple were measured (Figure 2) and summarized in Table 1. The $E_{1/2}$ of $CuBr_2$/TPMEN was found to be 50 mV more negative than that of $CuBr_2$/TPEN, while that of the chloride analogue ($CuCl_2$/TPMEN) was 57 mV more negative than that of $CuCl_2$/TPEN. These results suggest that the ratio of the stability constants of Cu(II)/TPMEN to Cu(I)/TPMEN was higher than that of the TPEN complexes. On the basis of the electrochemical studies, the K_{ATRP} of CuBr/TPMEN would be about 6×10^{-6} calculated according to the plot reported

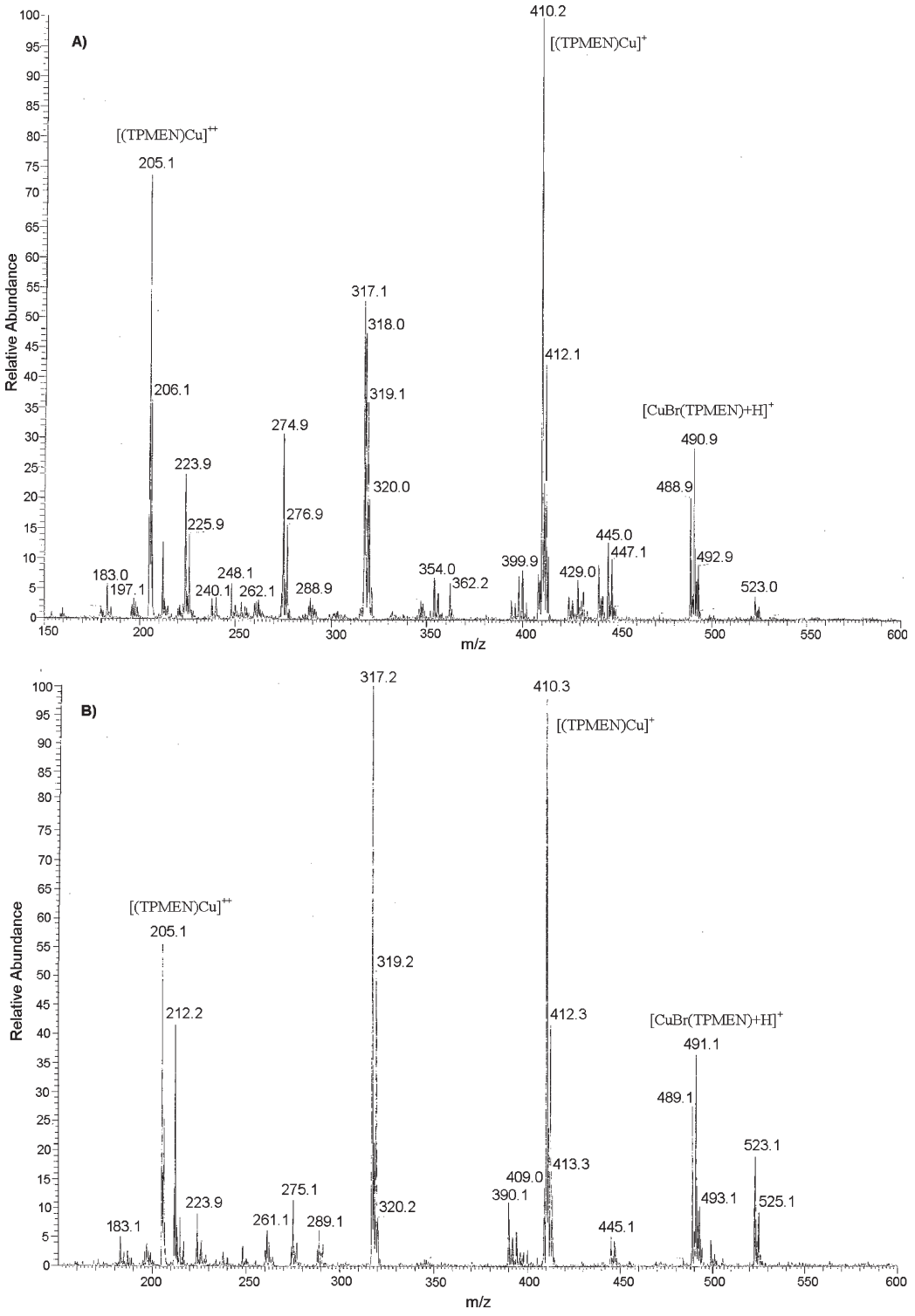


Figure 1. ESI-MS spectra of the CuBr (A) and $CuBr_2$ (B) complexes with TPMEN.

by Matyjaszewski et al.[36] compared to about 2×10^{-6} for CuBr/TPEN.

Comparison of the Catalytic Activities of CuBr/TPMEN and CuBr/TPEN. ATRP of MA was used to evaluate the catalytic activity of CuBr/TPMEN at a CuBr/initiator ratio (Cu/I) of 0.1 to compare it with that of CuBr/TPEN. When the initiator EBiB or MBP was added to the monomer solution of CuBr (or CuCl)/TPMEN at room temperature, some green-blue precipitate was produced. Much more precipitate was produced when the initiator was added at 70 °C, while little precipitates were formed when the initiator was added to the CuBr/TPEN solution. This suggests that the halide complexes of TPMEN reacted easily with the initiators and generated a large number of radicals at the early stages before the system reached equilibrium. The radicals terminated and thus caused accumulation of the ATRP deactivator (the Cu(II) complexes) (the persistent radical effect). The excess of deactivator Cu(II) complexes can slow and even stop the reaction.[56] Thus, under these conditions the measured polymerization kinetics do not reflect the real catalytic activity of the catalyst. To minimize the effects of the formed excess of Cu(II) complexes, the MA

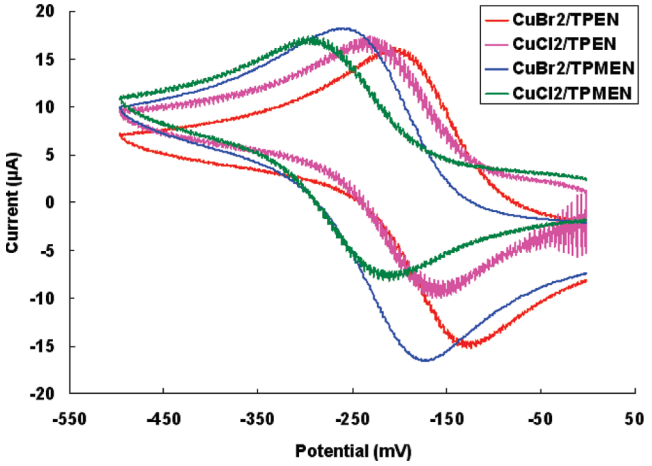


Figure 2. Cyclic voltammograms in CH_3CN of Cu^{II} halide complexes with TPEN or TPMEN (100 mV/s, 0.1 M Bu_4NBF_4 at room temperature).

Table 1. Redox Potentials of $CuBr_2$ and $CuCl_2$ Complexes of TPEN and TPMEN Measured by Cyclic Voltammetry at 100 mV/s in CH_3CN at Room Temperature

catalyst	$E_{p,a}$ (V)	$E_{p,c}$ (V)	ΔE_p (V)	$E_{1/2}{}^a$ (V)
$CuBr_2$/TPEN	−0.205	−0.126	0.079	−0.166
$CuCl_2$/TPEN	−0.230	−0.160	0.070	−0.195
$CuBr_2$/TPMEN	−0.261	−0.171	0.090	−0.216
$CuCl_2$/TPMEN	−0.292	−0.211	0.081	−0.252

[a] All potentials referred to SCE.

polymerization was conducted at low temperatures (0 and −15 °C). At these low temperatures, both the CuX/TPMEN and CuX/TPEN reacted with the initiator gently, and no precipitate formed.

Figure 3 shows the MA polymerization mediated by CuBr complexed with TPMEN or TPEN. Both $\ln([M]_0/[M])$ vs time plots were linear, implying that the radical concentration was constant during each polymerization. The apparent rate constants, $k_p[R^\bullet]$ ($\times 10^{-2}$ h^{-1}), estimated from $\ln([M]_0/[M]) = k_p[R^\bullet]t$ from the plots, catalyzed by CuBr/TPMEN and CuBr/TPEN were 2.4 and 1.6 at 0 °C and 1.45 and 0.97 at −15 °C, respectively. This comparison indicates that CuBr/TPMEN indeed exhibited relatively higher activity than CuBr/TPEN, in agreement with the CV and ESI-MS results.

The polymerization catalyzed by CuBr/TPMEN at 25 °C became faster than those at 0 and −15 °C but experienced an initial "jumping" and slowed down at the conversion of about 45% (Figure 4a). This is a typical persistent radical effect for highly active catalysts, in which the catalyst rapidly reacted with the initiator and produced a high concentration of radicals at the beginning of the polymerization.[32,56,57] The initial polymerization was thus very fast, but the high concentration of the radicals led to radical terminations and production of an excess of deactivator Cu(II) complexes, evidenced by the precipitation of the $CuBr_2$ complexes. The reduced living chain concentration and the increased deactivator concentration slowed the polymerization afterward. A halogen-exchange method using CuCl/TPMEN as the catalyst and EBiB as the initiator suppressed the initial jumping and had a slightly faster polymerization. Both polymerizations were living as evidenced by a linear increase of molecular weight with conversion and low polydispersity of the resulting PMA. The halogen-exchange method had better control over the PMA molecular weight (Figure 4b).

Interestingly, when the polymerizations were carried out at 70 °C, a large amount of green solids, analyzed as

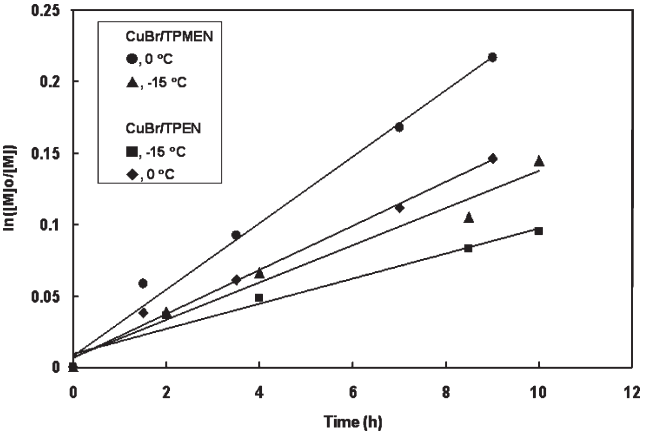


Figure 3. Kinetic plots of $\ln([M]_0/[M])$ vs time for ATRP of MA catalyzed by CuBr/TPMEN and CuBr/TPEN at 0 and −15 °C. [MA]/[CuBr]/[Ligand]/[EBiB] = 100/0.1/0.1/1.

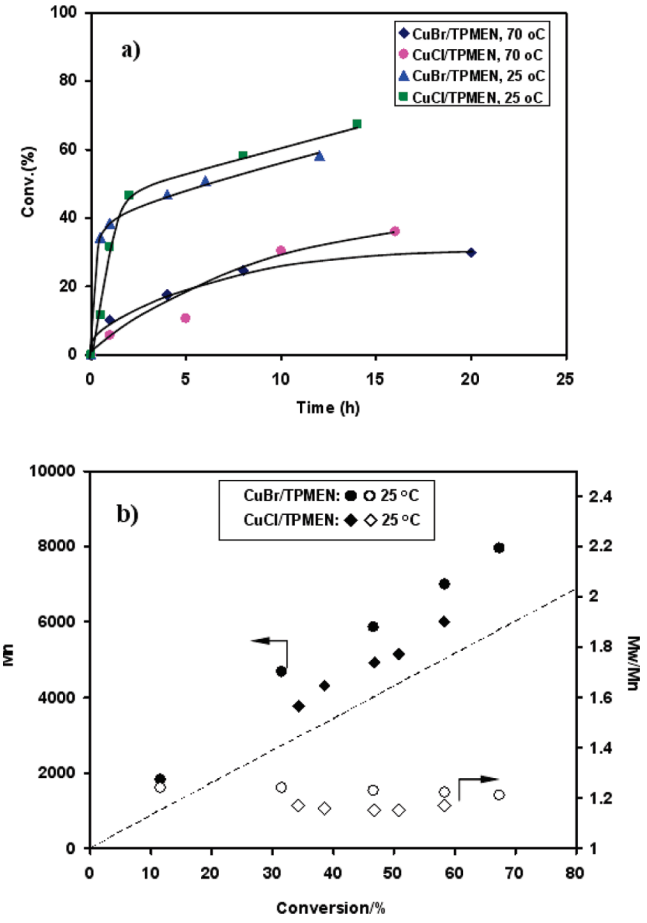


Figure 4. Plots of conversion as a function of time (a) and PMA molecular weight as a function of conversion (b) in ATRP of MA catalyzed by CuBr/TPMEN and CuCl/TPMEN. Conditions: [MA]/[Cu^I]/[TPMEN]/[EBiB] = 100/0.1/0.1/1.

$CuBr_2$/TPMEN complexes, precipitated out from the solution. The polymerization was even slower than that at 25 °C and leveled off at about 30% conversion (Figure 4a), suggesting that the initiator was almost completely consumed by the reaction with the CuBr/TPMEN. The halogen-exchange method using CuCl/TPMEN as catalyst did not improve this problem significantly. These results indicate that at this polymerization temperature copper halides complexed with TPMEN were too reactive toward the initiators.

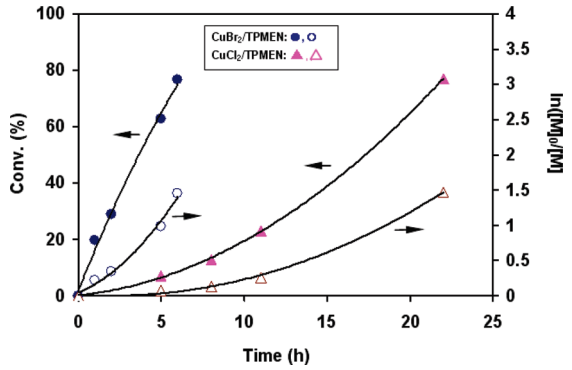


Figure 5. Conversion (solid symbols) and ln([M]$_0$/[M]) (open symbols) as a function of time in the reverse ATRP of MA catalyzed by $CuBr_2$ (or Cl_2)/TPMEN. Conditions: [MA]/[EBiB]/[Cu^{II}]/[TEA] = 100/1/0.01/1, [Cu^{II}]/[TPMEN] = 1/1, 70 °C.

Reverse and ARGET ATRP of MA. The above results indicate that TPMEN-complexed copper halides were highly active at low temperatures but showed low activity at elevated temperatures in the ATRP of MA due to their fast reaction consuming the initiator and producing an excess of copper(II) deactivators. One approach to activating catalysts is to use reducing agents to regenerate the produced Cu (II) deactivator to its activator Cu(I) complexes (ARGET ATRP).

Triethylamine (TEA) was used as a mild reducing agent as we previously reported due to its advantages of easy removal after polymerization and not over-reducing the Cu(II).[32,57] We first tested TEA reducing Cu(II)Br_2 (or Cl_2)/TPMEN to their corresponding Cu(I) activators using the reverse ATRP, in which Cu(II) deactivator is added to the system and the activator Cu(I) species is generated by in situ reduction of the Cu(II) deactivators.

In the presence of TEA (TEA/Cu = 100/1), $CuBr_2$ (or $CuCl_2$)/TPMEN could polymerize MA. The polymerization by $CuBr_2$/TPMEN was fast, but the polymerization by $CuCl_2$/TPMEN had an induction period and was slow (Figure 5). Both polymerizations had a self-acceleration as evidenced by the upward curves of the ln([M]$_0$/[M]) vs time plots, particularly that of $CuCl_2$/TPMEN. These results indicate that TEA can reduce the Cu(II) deactivator to its activator, but the reduction was relatively fast for $CuBr_2$/TPMEN to CuBr/TPMEN and slow for $CuCl_2$/TPMEN to CuCl/TPMEN. This is consistent with the CV result that the $CuCl_2$/TPMEN had a more negative redox potential and thus was more difficult to be reduced.

Subsequently, the ARGET ATRP of MA polymerization in the presence of TEA was examined. Because the halogen-exchange method showed a better control over the polymerization, CuCl/TPMEN was used as the catalyst and the bromine-based initiator EBiB was used as the initiator. The catalyst concentration was kept low, 1% of the initiator (Cu/I molar ratio of 0.01) or lower.

At this low catalyst concentration (Cu/I = 0.01), CuCl/TPMEN could not polymerize MA (< 10% conversion), which is similar to other catalysts.[57] In the presence of TEA (TEA/Cu molar ratio of 25:1) the polymerization became fast (Figure 6a). The conversion reached 90% in 24 h. The linear ln([M]$_0$/[M]) vs time plot suggests a constant radical concentration during the polymerization, which is consistent with a living-like process. The molecular weights of PMA increased linearly with MA conversions with a low PDI (PDI = 1.2) and were very close to the theoretical values (Figure 6b).

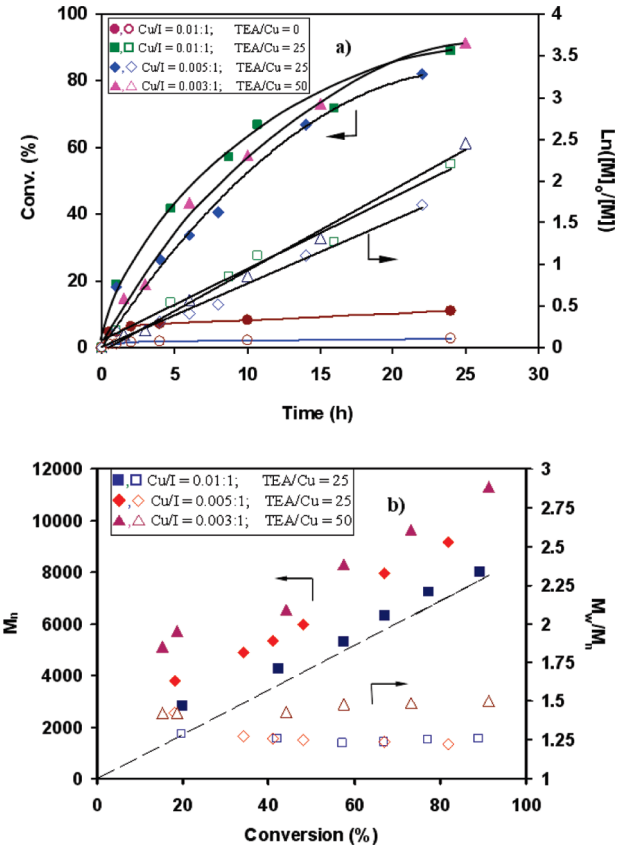


Figure 6. Polymerization kinetics (a) and the molecular weight and polydispersity as a function of conversion (b) in the ARGET ATRP of MA catalyzed by CuCl/TPMEN with TEA as a reducing agent. Conditions: [MA]/[EBiB]/[CuCl] = 100/1/(0.01−0.003), [CuCl]/[TPMEN] = 1/1, 70 °C.

When the catalyst concentration was decreased to a Cu/I ratio of 0.005 (37.2 ppm copper), the polymerization rate decreased slightly, but the ln[M]$_0$/[M] vs time plot was still linear. The molecular weights of the resulting PMA increased linearly with conversion and the polydispersity was still about 1.2, but the measured molecular weights were slightly higher than the theoretical values with an initiator efficiency of about 80%. The relatively low initiation efficiency may be attributed to chain irreversible terminations of the radicals due to insufficiently fast deactivation.

As the catalyst concentration was further decreased to a Cu/I ratio of 0.003 (24.8 ppm copper), the polymerization became very slow in the presence of the same amount of TEA (TEA/Cu = 25). The conversion was only 24% after a 9 h polymerization at 70 °C, and it leveled off afterward (data not shown). With the addition of more TEA, TEA/Cu = 50, the polymerization picked up the speed, but the molecular weights of the resulting PMA further deviated from their theoretical values with an initiator efficiency of about 65%. The polydispersity also became broader, around 1.5.

Chain Extension Catalyzed by ARGET ATRP at Low Catalyst Concentrations. Whether the resulting polymer from the ARGET ATRP at this low catalyst concentration had the terminal halogen (bromine here) capable of initiating the ATRP was demonstrated by the self-chain extension and block copolymerization of the PMA macromonomer. The PMA macroinitiators (PMA, M_n = 5100, PDI = 1.22) and (PMA, M_n = 6171, PDI = 1.21) were prepared by CuCl/TPMEN in the presence of TEA (conditions: MA/EBiB/CuCl/TEA = 100/1/0.01/0.25). After purification to remove the catalyst residue, they were used to initiate the

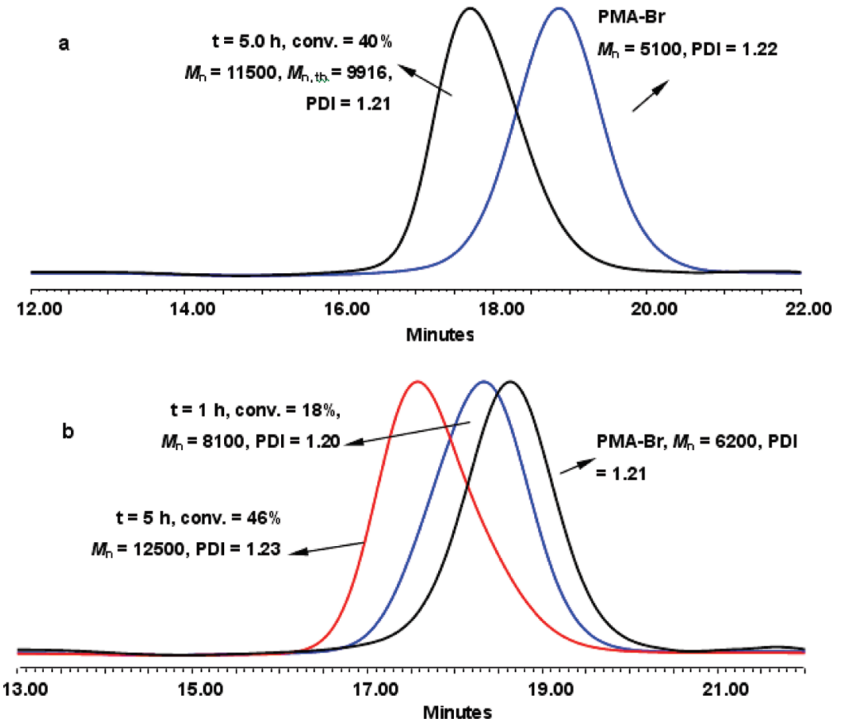


Figure 7. GPC traces of PMA-Br macroinitiator before and after chain extension with MA (a) or St (b). Conditions: MA/PMA-Br/CuCl/TPMEN = 155/1/0.155/0.155, TEA/Cu^I = 25, 70 °C (MA polymerization); St/PMA-Br/CuCl/TPMEN = 100/1/0.1/0.1,TEA/Cu^I = 25, 100 °C (for St polymerization).

polymerization of MA or St. Figure 7 shows the GPC traces before and after extension of PMA-Br with MA or St. The elution peak of the macroinitiator PMA (M_n = 5100) obviously shifted to a higher molecular weight of PMA-*b*-PMA (M_n = 11 500) very close to the theoretical value ($M_{n,th}$ = 9916) with a relatively low PDI (PDI = 1.21). The St polymerization using the PMA macroinitiator as catalyst also proved very efficient (M_n = 12 500, $M_{n,th}$ = 10 955, M_w/M_n = 1.23). These results demonstrated that the PMA resulting from the ARGET ATRP by CuCl/TPMEN/TEA retained the halogen group.

Conclusions

The pentadentate ligand TPMEN formed mononuclear complexes with Cu(I) and Cu(II) halides, and the Cu(I) complex showed higher activity than that complexed with the hexadentate ligand TPEN, proving our assumption. Compared to the needed structural rearrangement from the Cu(I)/TPEN to Cu(II)/TPEN requiring an additional ligand TPEN, the complexes of TPMEN with Cu(I) and Cu(II) have the same Cu/TPMEN ratio of 1/1, requiring no additional ligand during the structural rearrangement (if any). Therefore, the Cu(I)/TPMEN more easily reacts with the initiator to produce the corresponding Cu(II) complex and thus has a more negative redox potential and higher catalytic activity than that ligated by TPEN. The Cu(I) complexes of TPMEN, however, were too reactive toward the initiators, causing strong persistent radical effect at room temperature or higher and thus slowing the polymerization of MA. With TEA as a reducing agent, the catalyst mediated ARGET ATRP of MA at catalyst/initiator molar ratios of 0.003−0.01 and produced polymers with well-controlled molecular weights and low polydispersities. Self-extension and block copolymer PMA-*b*-PS of PMA proved that the PMA obtained from ARGET ATRP retained the terminal halide group.

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