A Dual Catalyst System for Atom Transfer Radical Polymerization Based on a Halogen-Free Neutral Cu(I) Complex

Yoshihisa Inoue and Krzysztof Matyjaszewski*

Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Received July 11, 2003; Revised Manuscript Received August 12, 2003

ABSTRACT: A neutral phenoxy−triamine copper(I) complex was synthesized, and its performance as a catalyst for the ATRP of *n*-butyl acrylate (BA) was investigated. This halogen-free neutral cuprous complex catalyzed BA polymerization, but while the polymerization rate was high there was poor control over polymerization. The level of control over the polymerization process was improved dramatically when a small amount of a suitable copper(II) complex was added as a deactivator. Several copper(II) complexes including $CuBr_2$, dNbpy/$CuBr_2$, PMDETA/$CuBr_2$, and Me_6TREN/$CuBr_2$ were investigated as deactivators. Among these deactivators, Me_6TREN/$CuBr_2$ was the most efficient at improving the level of control over the polymerization. When 3 mol % of Me_6TREN/$CuBr_2$ (versus the phenoxy−triamine copper complex) was added, the molecular weight increased linearly with conversion and agreed with theoretical values, and the polymer displayed a narrow molecular weight distribution ($M_w/M_n = 1.17$). The mechanism of the dual catalyst system might be similar to that proposed earlier for another binary catalyst system, the immobilized/soluble hybrid catalyst system. The high deactivation rate constant and high reducing power of Me_6TREN complex might be the key properties that allow successful control over the polymerization in this dual catalyst system.

Introduction

Controlled/living radical polymerization (CRP)[1−4] has been one of the most noteworthy research fields in polymer chemistry in the past decade, attracting increased academic and industrial interest. CRP provides access to materials with complex polymer architectures, some of which have never been synthesized before via conventional radical polymerization. Among the several CRP techniques examined, atom transfer radical polymerization (ATRP)[5−12] is one of the most promising synthetic methods that can be applied to the copolymerization of a variety of monomers and provides well-defined polymers with controlled topology and functionality. Several middle and late transition metal complexes have been investigated as ATRP catalysts; however, copper complexes are among most successful for ATRP due to their availability, versatility, and low cost.[5,13,14]

In ATRP, the activity of the catalyst, and the degree of control over the polymerization process, strongly correlate with the redox potentials and halogenophilicity of the metal center.[15] These primary properties of the catalyst are mostly determined by the ligands and counteranions present in the complexes. Therefore, the selections of ligands and counterions are key in conducting a successful ATRP reaction. In copper-mediated ATRP, highly active catalysts capable of conducting well-controlled polymerizations have been prepared using a broad spectrum of nitrogen-containing ligands, including pyridine derivatives (e.g., 4,4′-(di-5-nonyl)-2,2′-bipyridine (dNbpy)[16]), linear, branched, or cyclic aliphatic polyamines (e.g., *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA)[17] and tris(2-(dimethylamino)ethyl)amine (Me_6TREN)[18]),[19] imine derivatives,[20] picolylamine derivatives,[21] phenanthroline derivatives,[22] and terpyridine derivatives.[23] All of these suitable ligands possess a multidentate structure and neutral charge; therefore, counteranions must be present to neutralize the positive charge of the copper in complexes formed with these ligands. Halides such as chloride and bromide are the most common counterions for copper-mediated ATRP, though hexafluorophosphate (PF_6),[24] triflate (OTf),[25] tetraphenylborate (BPh_4),[26] carboxylate (e.g., OAc),[27] thiocyanate (SCN),[28,29] and cuprous dihalide (e.g., $[CuBr_2]^-$) have also been used as counteranions. Sometime (pseudo)halogens may bind directly to copper in certain neutral tridenate complexes, e.g., complexes formed with PMDETA.[30] Ligands/counterions may participate in exchange reactions with other components of the polymerization system. In some cases these exchange reactions are beneficial, e.g., a “halogen exchange” technique which significantly improves control and efficiency of block copolymer formation,[31] but sometimes, halogens may be displaced by other ligands, e.g., water, leading to reduced control over the polymerization. Thus, appropriate selection of the counteranion is critical for proper control in ATRP.

While many efficient copper-mediated catalyst systems have been identified, there are several reasons to continue the considerable effort that has been directed at the development of new catalysts for ATRP. These include development of highly active catalysts, less expensive catalysts, catalysts suitable for use in inorganic media including water, and catalysts that can polymerize monomers that are presently difficult to polymerize using existing ATRP catalysts.

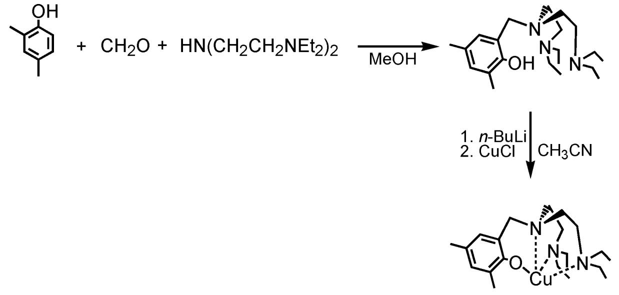
There have been only a few attempts to use negatively charged ligands, which should provide neutral Cu(I) complexes as ligands for ATRP. Such complexes should have higher stability due to a strong bond between the ligand and the metal center. This strong bond should also affect the ATRP equilibrium and could enhance the polymerization rate. Furthermore, charged ligands provide a counterion-free copper complex. Herein, we report the catalytic performance of a new neutral copper(I)

---

* Corresponding author. E-mail: km3b@andrew.cmu.edu.

10.1021/ma034979v CCC: $25.00

Scheme 1. Synthesis of the Phenoxy−Triamine Ligand and the Copper(I) Complex



complex bearing a phenoxy−triamine ligand (Scheme 1). We designed this complex as a potential catalyst since it has both strong copper−oxygen bond and branched triamine structure. One could anticipate high complex stabilities due to the covalent nature of the copper−oxygen bond and high catalytic activity due to the branched triamine structure of the ligand that is similar to the most active ATRP catalyst, $Me_6TREN/CuBr$.

This phenoxy−triamine copper complex does display high activity in the polymerization of *n*-butyl acrylate but, unfortunately, also provides poor control. However, control over the polymerization was dramatically improved by the addition of a small amount of a Cu(II) deactivator, especially $Me_6TREN/CuBr_2$. This dual catalyst system reminds us of a similar binary catalyst system discussed earlier, the immobilized/soluble hybrid catalyst system.[32,33] At that time we reported that high deactivation rate constant and high reducing power of $Me_6TREN/CuBr_2$ enhanced the level of control obtained with the immobilized/soluble hybrid catalyst system in a range of ATRP polymerization reactions. A similar mechanism might be expected to operate in the new dual catalyst system formed with the new neutral copper(I) complex bearing a phenoxy−triamine ligand as primary activator. The plausible mechanism for this dual catalyst system will be discussed.

Experimental Section

Characterization. ^1H NMR spectra of the ligand and the copper complex were collected using Bruker 300 MHz ^1H NMR with $CDCl_3$ and benzene-d_6 as solvents, respectively. Elemental analysis was performed by Midwest Microlab, LLC. Conversion of monomer was determined by gas chromatography using a Shimadzu GC 14-A gas chromatograph equipped with a FID detector and J&W Scientific 30 m DB WAX Megabore column. The molecular weight and molecular weight distribution of the polymers were determined by GPC using a PSS column (styrogel 10^5, 10^3, 10^2 Å) with RI detectors. GPC was performed using THF as an eluent at the flow rate of 1 mL/min. Linear polystyrene standards were used for calibration of poly(*n*-butyl acrylate). Theoretical molecular weights were calculated by following eq 1.

$$M_{n,th} = ([\text{monomer}]_0/[\text{initiator}]_0) \times \text{conversion} \times \text{MW(monomer)} + \text{MW(initiator)} \quad (1)$$

Materials. Copper(I) bromide,[34] copper(I) chloride,[34] tris(2-(dimethylamino)ethyl)amine (Me_6TREN),[35] and 4,4′-(di-5-nonyl)-2,2′-bipyridine (dNbpy)[34] were purified and prepared as detailed in previous reports. *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA) was purified by distillation under vacuum. *n*-Butyl acrylate (BA) was passed through a column filled with neutral alumina to remove stabilizer, dried over calcium hydride, and distilled under reduced pressure before use. Acetonitrile was distilled under nitrogen over calcium hydride prior to use. All other reagents and solvents were used as received.

Synthesis of 2,4-Dimethyl-6-bis(2-(diethylamino)ethyl)aminomethylphenol.[36] Paraformaldehyde (95% purity, 0.51 g, 16.1 mmol) and *N,N,N′,N′*-tetraethyldiethylenetriamine (90% purity, 3.87 g, 16.2 mmol) were added to a 50 mL round-bottom flask and stirred at 80 °C for 1 h. A solution of 2,4-dimethylphenol (2.0 g, 16.2 mmol) in methanol (10 mL) was then added to the resulting pale yellow oil, and this solution was stirred for 24 h under gentle reflux. After the reaction was complete, the methanol was removed through evaporation and the residual oil was purified by column chromatography with silica gel (CH_2Cl_2/methanol = 9/1 vol). After evaporation of the solvent, the desired compound was obtained as an yellow oil in 70% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 0.96 (t, 12 H), 2.16 (s, 3 H), 2.17 (s, 3 H), 2.47 (q, 8 H), 2.60 (m, 8 H), 3.67 (s, 2 H), 6.59 (s, 1 H), 6.81 (s, 1 H). Anal. Calcd for $C_{21}H_{39}N_3O$: C, 72.16; H, 11.24; N, 12.02. Found: C, 70.92; H, 11.43; N, 11.97.

Synthesis of 2,4-Dimethyl-6-bis(2-(diethylamino)ethyl)aminomethylphenoxycopper(I). Synthesis of the copper complex was performed using standard Schlenk techniques. 2,4-Dimethyl-6-bis(2-(diethylamino)ethyl)aminomethylphenol (1.06 g, 3.0 mmol) was added to a 50 mL Schlenk flask degassed under vacuum and placed under nitrogen. This phenol compound was dissolved in acetonitrile (15 mL), and then a solution of 2.5 N *n*-butyllithium in hexane (1.2 mL, 3.0 mmol) was added at 0 °C. After the addition of *n*-butyllithium, the reaction mixture was allowed to warm to room temperature and stirred for 2 h.

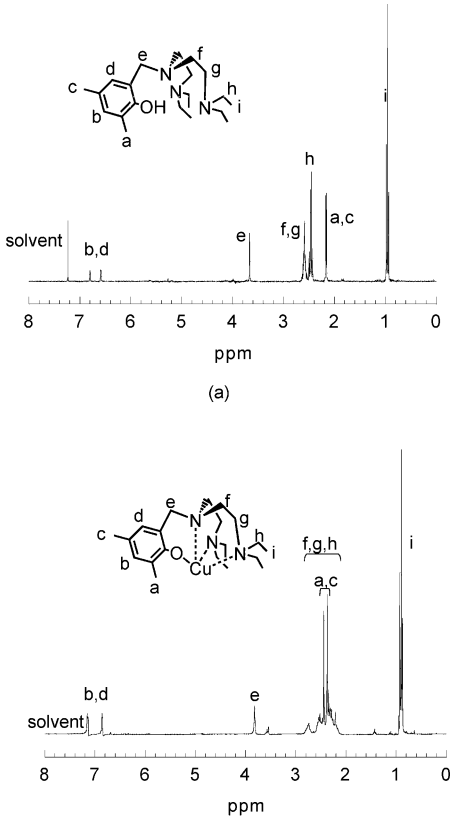
The resulting yellow solution was added to a suspension of CuCl (0.30 g, 3.0 mmol) in acetonitrile (10 mL) at 0 °C. A white solid was formed instantly, and the solution became light brown in color. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. After filtration, the filtrate was concentrated to ca. 15 mL and stored at −20 °C overnight, yielding a white powdery precipitate. This white powder was collected through decantation and recrystallized from acetonitrile to give the desired copper complex as colorless crystals in 56% yield. ^1H NMR (300 MHz, C_6D_6): δ 0.90 (t, 12 H), 2.1−2.9 (m, 16H), 2.38 (s, 3 H), 2.44 (s, 3 H), 3.82 (s, 2H), 6.86 (s, 1H), 7.14 (s, 1H). Anal. Calcd for $C_{21}H_{38}CuN_3O$: C, 61.21; H, 9.29; N, 10.20. Found: C, 60.80; H, 9.34; N, 10.13.

$CuBr_2$ Deactivator Stock Solution. $CuBr_2$ deactivator stock solution was prepared just prior to use. $CuBr_2$ (5.32 mg, 2.38×10^{-5} mol) was added to a 25 mL Schlenk flask, and then the flask was evacuated and backfilled with nitrogen three times. Acetone (10 mL) degassed by bubbling with nitrogen for 30 min and, optionally, Me_6TREN (6.28 μL, 2.38×10^{-5} mol), PMDETA (4.97 μL, 2.38×10^{-5} mol), or dNbpy (19.5 mg, 4.77×10^{-5} mol) were added to the flask, and the resulting solution was stirred for 10 min at room temperature. These solutions, containing Cu(II) (2.38×10^{-6} mol/mL) were used as stock $CuBr_2$ deactivator solutions.

ATRP of *n*-Butyl Acrylate (BA). A typical ATRP polymerization procedure was performed as follows. The phenoxy−triamine copper complex was placed in a 25 mL Schlenk flask, and then the flask was evacuated and backfilled with nitrogen three times. Toluene (1.4 mL), anisole (0.1 mL), and BA (1.5 mL, 1.05×10^{-2} mol) were successively added to the flask after degassing by bubbling with nitrogen for 30 min. The desired amount of $CuBr_2$ deactivator stock solution was added. Finally the initiator, ethyl 2-bromopropionate, was added. The resulting mixture was warmed to 70 °C to start the polymerization. Samples were taken periodically via a syringe to follow the kinetics of the polymerization process. The samples were diluted with tetrahydrofuran followed by filtration through a Gelman Acrodisc 0.2 μm PTFE filter prior to the analysis by gas chromatography (GC) and gel permeation chromatography (GPC).

Results and Discussion

Synthesis of Ligand and Copper Complex. The synthetic scheme for the preparation of the phenoxy−



(a)

(b)

Figure 1. 300 MHz ^{1}H NMR spectra of phenol–triamine in $CDCl_3$ (a) and phenoxy–triamine copper(I) complex in C_6D_6 (b).

triamine ligand and the resulting copper complex is summarized in Scheme 1. To avoid any reaction at the para position of phenol, which would result in the formation of a multisubstitution reaction product, 2,4-dimethylphenol was used as the starting material. 2,4-Dimethyl-6-bis(2-(diethylamino)ethyl)aminomethylphenol was synthesized through the reaction of *N,N,N′,N′*-tetraethyldiethylenetriamine, formaldehyde, and 2,4-dimethylphenol in methanol. After purification by passage through a silica column, the desired phenol–triamine compound was obtained as a yellow oil in 70% yield. Subsequently, the compound was reacted with *n*-butyllithium followed by CuCl in acetonitrile to give the desired neutral copper(I) complex. After recrystallization from acetonitrile, the complex was obtained as colorless crystals in 56% yield.

Figure 1 shows ^{1}H NMR spectra of the phenol–triamine compound and the phenoxy–triamine copper complex. Signals of aromatic protons and aromatic methyl protons (protons a, b, c and d) are shifted to a lower magnetic field, and the methylene protons (proton f, g, and h) show more complex signals due to the coordination to the copper metal center. Along with elemental analysis, these results support the proposed structure for the complex shown in Scheme 1. This neutral copper complex has good solubility in both polar and nonpolar organic solvents. The crystalline form of this copper complex was stable, at least for several hours, under ambient atmosphere; however, it decomposed easily in solution, forming a brown solution, probably due to oxidation of copper(I). An X-ray crystallography study of the structure of this copper complex is underway.

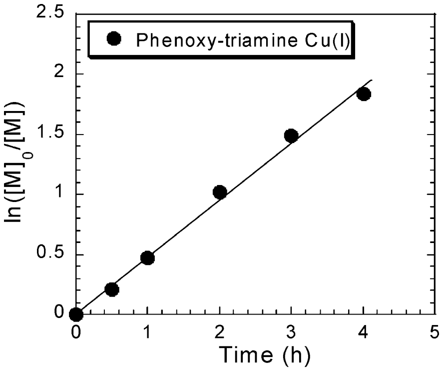


Figure 2. Kinetics plots for the polymerization of BA using phenoxy–triamine Cu(I) complex. See Table 1 for polymerization conditions.

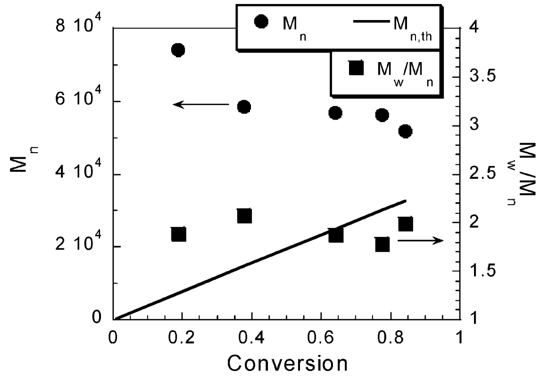


Figure 3. Evolution of M_n and M_w/M_n vs conversion for the polymerization of BA using phenoxy–triamine Cu(I) complex. See Table 1 for polymerization conditions.

BA Polymerization in the Absence and Presence of $CuBr_2$ Deactivators. The phenoxy–triamine copper complex was used for the polymerization of BA in 50% toluene at 70 °C. The ratio of $[BA]_0/[I]_0/[Cu(I)\ complex]_0$ was set at 300/1/1 for all experiments. Under these conditions, the phenoxy–triamine catalyst promoted a relatively fast polymerization reaction. As shown in Figure 2, semilogarithmic kinetic plots showed linearity vs polymerization time and monomer conversion reached 84% in 4 h. However, this phenoxy–triamine catalyst did not control the polymerization reaction very well. As shown in Figure 3, the molecular weight jumped to 74 000 at 19% monomer conversion, approximately 10 times higher than the value expected for quantitative initiation. Although molecular weight was decreasing with increasing conversion, it was still considerably higher than theoretical molecular weight throughout the polymerization. The molecular weight distribution was broad with PDI values around 2, also indicating poor control. These facts indicate that the phenoxy–triamine catalyst could promote relatively fast activation of the dormant species but slow deactivation of growing radicals. Therefore, this catalyst system leads to inefficient initiation, higher molecular weight polymers, and broad molecular weight distribution.

To increase the rate of deactivation and improve control over the polymerizations, we decided to add a small amount of an additional Cu(II) deactivator complexed with various ligands. Fast activation by phenoxy–triamine catalyst and fast deactivation by an additional deactivator was anticipated. Thus, 3 mol % (versus phenoxy–triamine complex) of $CuBr_2$, dNbpy/$CuBr_2$, PMDETA/$CuBr_2$, or $Me_6TREN/CuBr_2$ was added

Table 1. Conditions and Results for ATRP of BA Using Phenoxy−Triamine Cu(I) Complex in the Absence and Presence of Cu(II) Deactivator[a]

expt	Cu(II) complex	$[Cu(I)]_0/[Cu(II)]_0$	t (h)	conv (%)	M_n ($\times 10^{-4}$)	$M_{n,theo}$ ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	M_w/M_n
1			4	84.1	5.20	3.25	10.3	1.99
2	$Me_6TREN/CuBr_2$	1/0.03	5	66.5	2.11	2.58	2.47	1.17
3	$PMDETA/CuBr_2$	1/0.03	8	72.5	2.89	2.81	5.00	1.73
4	$dNbpy/CuBr_2$	1/0.03	9	65.6	2.62	2.54	5.96	2.28
5	$CuBr_2$	1/0.03	8.5	67.4	2.26	2.61	3.88	1.71

[a] Polymerization conditions: initiator = ethyl 2-bromopropionate, temperature = 70 °C, Cu(II) complexes were added as a stock solutions in acetone. Concentration of Cu(II) in stock solution was 2.38 mM ($CuBr_2/Me_6TREN = CuBr_2/PMDETA = 1/1$ mol/mol, $CuBr_2/dNbpy = 1/2$ mol/mol in stock solution); for expt 1, $[BA]_0 = 3.49$ M, $[BA]_0/[I]_0/[Cu(I)\ complex]_0 = 300/1/1$, BA/toluene = 1/1 v/v; for expt 2−5, $[BA]_0 = 3.05$ M, $[BA]_0/[I]_0/[Cu(I)\ complex]_0/[Cu(II)\ complex]_0 = 300/1/1/0.03$, BA/toluene/acetone = 1/1/0.29 v/v/v.

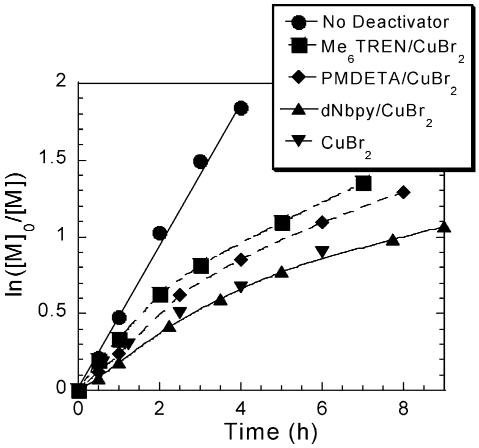


Figure 4. Kinetics plots for the polymerization of BA using phenoxy−triamine Cu(I) complex in the presence of variable Cu(II) deactivators. See Table 1 for polymerization conditions.

to the polymerization system as a deactivator. The results of these polymerizations using the various dual catalyst systems are summarized in Table 1, along with the result of ATRP using the phenoxy−triamine complex alone. Polymerization rates decreased in the presence of deactivators due to higher concentration of Cu(II) species. The overall polymerization rate depended on the structure of deactivator, and the order of decreasing rate was $Me_6TREN/CuBr_2 > PMDETA/CuBr_2 > dNbpy/CuBr_2 \sim CuBr_2$ (Figure 4). The order of polymerization rates correlates with the order of activation rate constant and equilibrium constants for Me_6TREN, PMDETA, and dNbpy.[37] As mentioned later, some amount of Cu(I) complex can be generated from the added deactivator through halogen migration reaction, and it might have some contribution to the activation process. Thus, the smaller rate reduction in the presence of the Me_6TREN and PMDETA complex, when compared to dNbpy and $CuBr_2$ alone, could be due to the contribution of $Me_6TREN/CuBr$ and PMDETA/CuBr to the activation process.

In the presence of $CuBr_2$, $dNbpy/CuBr_2$, or $PMDETA/CuBr_2$, the level of control over the polymerization was improved, but it was still insufficient (Figures 6−8). Molecular weights increased with conversion; however, some deviations from predicted values were observed, and molecular weight distributions were still quite broad ($M_w/M_n > 1.6$). However, ATRP in the presence of $Me_6TREN/CuBr_2$ was surprisingly well-controlled.

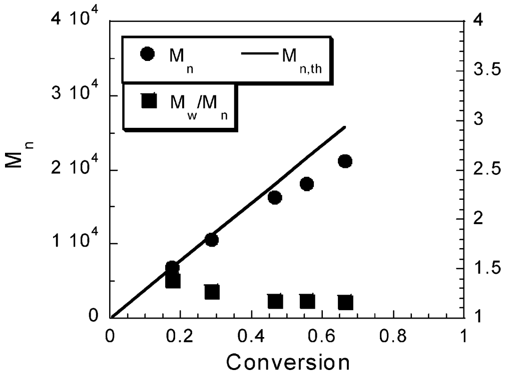


Figure 5. Evolution of M_n and M_w/M_n vs conversion for the polymerization of BA using phenoxy−triamine Cu(I) complex in the presence of 3 mol % of $Me_6TREN/CuBr_2$. See Table 1 for polymerization conditions.

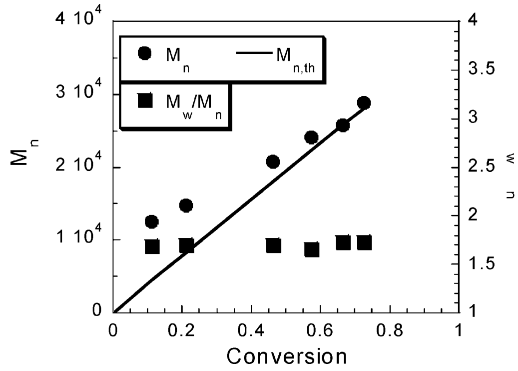


Figure 6. Evolution of M_n and M_w/M_n vs conversion for the polymerization of BA using phenoxy−triamine Cu(I) complex in the presence of 3 mol % of $PMDETA/CuBr_2$. See Table 1 for polymerization conditions.

Molecular weights increased linearly with conversion and agreed with predicted values. PDI values decreased during the polymerization and eventually reached $M_w/M_n = 1.17$ (Figure 5). Some deviation of molecular weight from predicted value was observed at high conversion, plausibly due to the contribution of chain transfer reactions with an excess ligand (Figure 1b).[38,39]

Thus, a small amount of the proper deactivator enhanced the deactivation step and promoted a well-controlled polymerization, while the polymerization rate was slightly reduced. These results remind of a similar binary catalyst system, the immobilized/soluble hybrid catalyst system.[32,33,40,41]

BA Polymerization in the Presence of $Me_6TREN/CuBr_2$. To determine the minimum amount of the additional deactivator required for preparation of an efficient dual catalyst system, the polymerization was conducted in the presence of 0.5, 1, and 2 mol % of $Me_6TREN/CuBr_2$. The results are summarized in Table 2. As shown in Figure 9, polymerization rates correlate with the amount of deactivator; with less deactivator leading to higher polymerization rates. Regarding the level of control over the polymerization process, the

Table 2. Conditions and Results for ATRP of BA Using Phenoxy−Triamine Cu(I) Complex in the Presence of Variable Amount of $Me_6TREN/CuBr_2$[a]

expt	catalyst	$[I]_0/[Cu(I)]_0/[Cu(II)]_0$	t (h)	conv (%)	M_n ($\times10^{-4}$)	$M_{n,theo}$ ($\times10^{-4}$)	M_w ($\times10^{-4}$)	M_w/M_n
1	phenoxy−triamine	1/1/0	4	84.1	5.20	3.25	10.3	1.99
2	phenoxy−triamine	1/1/0.005	4	84.4	2.60	3.26	4.23	1.63
3	phenoxy−triamine	1/1/0.01	5	80.3	2.65	3.11	3.69	1.39
4	phenoxy−triamine	1/1/0.02	5	72.9	2.30	2.82	2.86	1.24
5	phenoxy−triamine	1/1/0.03	5	66.5	2.11	2.58	2.47	1.17
6	$Me_6TREN/CuBr$	1/0.01/0	6	32.6	1.39	1.27	2.39	1.72

[a] Polymerization conditions: initiator = ethyl 2-bromopropionate, temperature = 70 °C, $Me_6TREN/CuBr_2$ was added as a stock solutions in acetone. Concentration of $Me_6TREN/CuBr_2$ in stock solution was 2.38 mM ($CuBr_2/Me_6TREN$ = 1/1 mol/mol in stock solution); for expt 1, $[BA]_0 = 3.49$ M, $[BA]_0/[I]_0/[Cu(I)\ complex]_0 = 300/1/1$, BA/toluene = 1/1 v/v; for expt 2, $[BA]_0 = 3.40$ M, $[BA]_0/[I]_0/[Cu(I)\ complex]_0/[Me_6TREN/CuBr_2]_0 = 300/1/1/0.005$, BA/toluene/acetone = 1/1/0.05 v/v/v; for expt 3, $[BA]_0 = 3.32$ M, $[BA]_0/[I]_0/[Cu(I)\ complex]_0/[Me_6TREN/CuBr_2]_0 = 300/1/1/0.01$, BA/toluene/acetone = 1/1/0.10 v/v/v; for expt 4, $[BA]_0 = 3.18$ M, $[BA]_0/[I]_0/[Cu(I)\ complex]_0/[Me_6TREN/CuBr_2]_0 = 300/1/1/0.02$, BA/toluene/acetone = 1/1/0.19 v/v/v; for expt 5, $[BA]_0 = 3.05$ M, $[BA]_0/[I]_0/[Cu(I)\ complex]_0/[Me_6TREN/CuBr_2]_0 = 300/1/1/0.03$, BA/toluene/acetone = 1/1/0.29 v/v/v; for expt 6, $[BA]_0 = 3.49$ M, $[BA]_0/[I]_0/[CuBr]_0/[Me_6TREN]_0 = 300/1/1/0.01/0.01$, BA/toluene = 1/1 v/v.

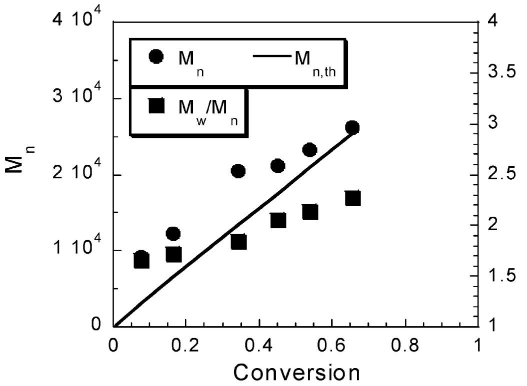


Figure 7. Evolution of M_n and M_w/M_n vs conversion for the polymerization of BA using phenoxy−triamine Cu(I) complex in the presence of 3 mol % of $dNbpy/CuBr_2$. See Table 1 for polymerization conditions.

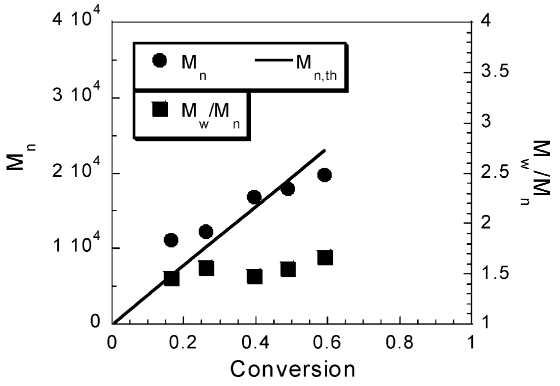


Figure 8. Evolution of M_n and M_w/M_n vs conversion for the polymerization of BA using phenoxy−triamine Cu(I) complex in the presence of 3 mol % of $CuBr_2$. See Table 1 for polymerization conditions.

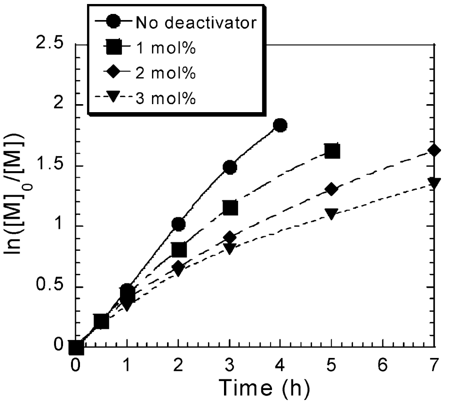


Figure 9. Kinetics plots for the polymerization of BA using phenoxy−triamine Cu(I) complex in the presence of variable amounts of $Me_6TREN/CuBr_2$. See Table 2 for polymerization conditions.

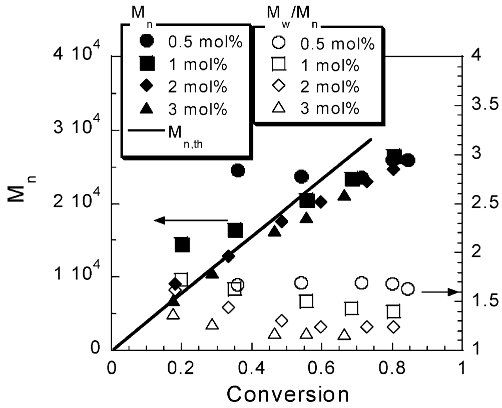


Figure 10. Evolution of M_n and M_w/M_n vs conversion for the polymerization of BA using phenoxy−triamine Cu(I) complex in the presence of variable amounts of $Me_6TREN/CuBr_2$. See Table 2 for polymerization conditions.

polymerization was still controlled even in the presence of 1 or 2 mol % deactivator, though the degree of control was reduced gradually with decreasing amount of deactivator. For instance, in the presence of 1 mol % $Me_6TREN/CuBr_2$, some deviation of molecular weight at low conversion and relatively high PDI values ($M_w/M_n \sim 1.4$) were observed. When the amount of deactivator was decreased to 0.5 mol %, the level of control attained in the polymerization was poor. Molecular weight stayed at constant values, around 25 000, and PDI values were higher than 1.6 throughout the polymerization. Therefore, at least 1 mol % of $Me_6TREN/CuBr_2$ deactivator is necessary to control the polymerization. This amount corresponds to ~30 ppm vs BA monomer (molar basis). It is surprising that such a small amount of additional Cu(II) species provides an efficient control over polymerization.

As indicated above and described later, some $Me_6TREN/CuBr$ should exist in this polymerization system due to the halogen migration reaction between the phenoxy−triamine copper(I) complex and $Me_6TREN/CuBr_2$. $Me_6TREN/CuBr$ is the most active ATRP catalyst for BA polymerization and promotes well-controlled polymerization using a significantly lower amount of catalyst.[35] Therefore, we conducted polymerization of BA in the presence of only $Me_6TREN/CuBr$ with $[BA]_0/[I]_0/[Me_6TREN/CuBr]_0 = 300/1/0.01$ in

Scheme 2. Halogen Migration Reaction between the Phenoxy−Triamine Copper Complex and the Additional Deactivators

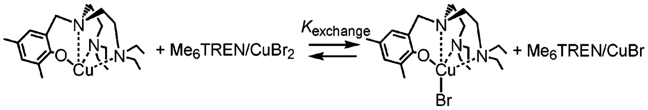


Table 3. Equilibrium Constant of ATRP (K_{eq}) and Deactivation Rate Constant (k_d) for a Variety of Catalyst Systems

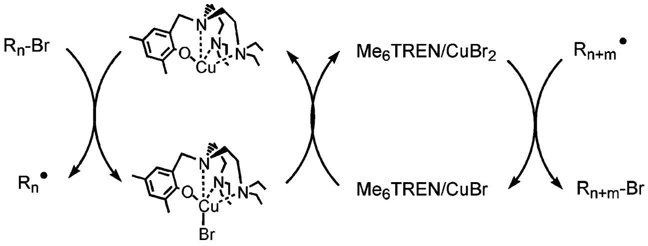
catalyst system	K_{eq}[a]	k_d[b] (L mol^{-1} s^{-1})
Me$_6$TREN/Cu$^{I/II}$	10^{-6}	1.4×10^7
PMDETA/Cu$^{I/II}$	10^{-8}	6.1×10^6
dNbpy/Cu$^{I/II}$	10^{-9}	2.5×10^7

[a] Equilibrium constant of ATRP for methyl acrylate measured at 90 °C for Me$_6$TREN and PMDETA and at 100 °C for dNbpy. [b] Deactivation rate constant measured at 75 °C in acetonitrile with 1-phenylethyl radical.

order to confirm the contribution of Me$_6$TREN/CuBr-mediated polymerization in the dual catalyst system. The result is shown in experiment 6 in Table 2. Slower rate of polymerization and limited control over polymerization were observed when compared to the polymerization catalyzed by the dual catalyst system using the same amount of Me$_6$TREN/CuBr$_2$. Although molecular weights were properly controlled (fast initiation), polydispersities were relatively high (too low deactivator concentration). Therefore, high activity and well-controlled polymerization behavior are achieved by mutual contribution of both the phenoxy−triamine catalyst and Me$_6$TREN/CuBr$_2$.

Proposed Mechanism for the Dual Catalyst System. When polymerization was conducted using the phenoxy−triamine catalyst alone, relatively fast polymerization was demonstrated; however, poor control of polymerization was attained, i.e., low initiation efficiency resulting in high molecular weight and high polydispersity. This suggests that although the phenoxy−triamine Cu(I) complex could activate the dormant species sufficiently fast, the corresponding Cu(II) complex deactivates too slow. Thus, the rate of deactivation (R_d) should be increased to improve control over the polymerization process. The addition of a small amount of a strong Cu(II) deactivator can increase overall R_d in ATRP, as demonstrated for the immobilized/soluble hybrid catalyst system.

Scheme 3. Proposed Mechanism for the Dual Catalyst System



Me$_6$TREN/CuBr$_2$, PMDETA/CuBr$_2$, and dNbpy/CuBr$_2$ were investigated as deactivators for this dual catalyst system. When these Cu(II) species are added to a solution the Cu(I) complex, halogen migration reaction between the phenoxy−triamine complex and these additional deactivators could occur to yield a mixture of phenoxy−triamine Cu$^{I/II}$ complexes and additional Cu$^{I/II}$ ligand species (Scheme 2). There are two important factors to consider in the desire to increase overall R_d by an addition of Cu(II) deactivator: one is a high deactivation rate constant of the additional deactivator but another, perhaps even more important, is the presence of a sufficient concentration of this deactivator. The latter depends on the relative values of the equilibrium constants. Values for the deactivation rate constants (k_d)[37] and equilibrium constants ($K_{eq} = k_a/k_d$)[35] for the Me$_6$TREN/Cu, PMDETA/Cu, and dNbpy/Cu systems are listed in Table 3 to allow a comparison of these properties. All these systems possess similar and relatively high deactivation rate constants ($k_d \sim 10^7$), while they have quite different K_{eq}. The Me$_6$TREN/Cu system has the highest K_{eq}, and this indicates that the Me$_6$TREN complex prefers to be in the higher oxidation state as compared to PMDETA and dNbpy complexes. This was confirmed earlier by the measurement of halogen migration equilibrium constants between Me$_6$TREN and dNbpy complexes and between PMDETA and dNbpy complexes.[33] This high reducing power forces the Me$_6$TREN complex to stay in the higher oxidation state in the dual catalyst system, and the resulting Me$_6$TREN/CuBr$_2$ deactivates the growing radical efficiently. The resulting Me$_6$TREN/CuBr should then reduce the phenoxy−triamine Cu(II) complex to its lower oxidation state and return again to the Cu(II) state. Higher concentration of a deactivator having high k_d should decrease the polydispersity index as the latter is inversely proportional to the deactivation rate constant and deactivator concentration (eq 2). This proposed "shuttling" mechanism is again similar to the mechanism for the immobilized/soluble hybrid catalyst system (Scheme 3).[32,33]

$$M_w/M_n = 1 + (k_p[I]_0/k_d[\text{deactivator}])(2/p - 1) \quad (2)$$

Addition of CuBr$_2$ without ligand was also investigated. CuBr$_2$ should increase the concentration of phenoxy−triamine Cu(II) complex through halogen migration reaction. However, control over polymerization did not improve significantly. This again indicates that the phenoxy−triamine Cu(II) complex is not a good deactivator, and it is necessary to increase both deactivator concentration and overall k_d in order to improve the level of control over polymerization.

The Me$_6$TREN complex is perhaps the best deactivator for this dual catalyst system because of its high reducing power and high deactivation rate constant.

Conclusions

A phenoxy−triamine copper complex promotes relatively fast polymerization of BA; however, this complex does not control the polymerization well. Analysis of the kinetics of the polymerization indicates that this is due to a slow deactivation step, indicating the phenoxy−triamine Cu(II) complex is a poor deactivator. When a small amount of an efficient deactivator was added, the level of control over the polymerization process was improved. Especially, the Me$_6$TREN/CuBr$_2$ system improved the control dramatically, and the addition of only ∼30 ppm of the deactivator vs BA monomer was effective in improving the control to the desired degree. Both the high deactivation rate constant and the high reducing power of the Me$_6$TREN complex are responsible for the success of Me$_6$TREN/CuBr$_2$ in the preparation of this dual catalyst system. The Me$_6$TREN/Cu complex might act as "shuttling" agent and in addition to assisting the deactivation process may also reduce the phenoxy–triamine Cu(II) complex. This proposed mechanism is similar to that proposed for the immobilized/soluble hybrid catalyst system where $Me_6TREN/CuBr_2$ overcomes slow deactivation due to diffusion limitation in the immobilized/soluble hybrid catalyst system. This study demonstrates that addition of small amounts of good deactivators can overcome the slow deactivation step due to low deactivation rate constant of the major catalyst. This result indicates the some catalyst systems inherently providing poorly controlled ATRP could be improved by the addition of a small amount of Cu(II) deactivator even in a homogeneous system.

Acknowledgment. We greatly appreciate the financial support from Mitsui Chemicals, the National Science Foundation (DMR-0090409), and CRP Consortium at Carnegie Mellon University.

References and Notes

(1) Matyjaszewski, K., Ed.; *Controlled Radical Polymerization;* ACS Symposium Series Vol. 685; American Chemical Society: Washington, DC, 1998.
(2) Matyjaszewski, K., Ed.; *Controlled/Living Radical Polymerization. Progress in ATRP, NMP, and RAFT;* ACS Symposium Series Vol. 768; American Chemical Society: Washington, DC, 2000.
(3) Matyjaszewski, K., Ed.; *Advances in Controlled/Living Radical Polymerization;* ACS Symposium Series Vol. 854; American Chemical Society: Washington, DC, 2003.
(4) Matyjaszewski, K., Davis, T. P., Eds.; *Handbook of Radical Polymerization*; Wiley-Interscience: Hoboken, 2002.
(5) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921.
(6) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689.
(7) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901.
(8) Patten, T. E.; Matyjaszewski, K. *Acc. Chem. Res.* **1999**, *32*, 895.
(9) Davis, K. A.; Matyjaszewski, K. *Adv. Polym. Sci.* **2002**, *159*, 2.
(10) Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 337.
(11) Pyun, J.; Matyjaszewski, K. *Chem. Mater.* **2001**, *13*, 3436.
(12) Matyjaszewski, K. *Chem.—Eur. J.* **1999**, *5*, 3095.
(13) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(14) Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901.
(15) Pintauer, T.; McKenzie, B.; Matyjaszewski, K. In *Advances in Controlled/Living Radical Polymerization;* ACS Symposium Series Vol. 854; Matyjaszewski, K., Ed.; American Chemical Society: Washington, DC, 2003; p 130.
(16) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866.
(17) Xia, J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7697.
(18) Xia, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 5958.
(19) Xia, J.; Zhang, X.; Matyjaszewski, K. In *Transition Metal Catalysis in Macromolecular Design*; ACS Symposium Series Vol. 760; Boffa, L. S., Novak, B. M., Eds.; American Chemical Society: Washington, DC, 2000; p 207.
(20) Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. *Macromolecules* **1997**, *30*, 2190.
(21) Xia, J.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 2434.
(22) Destarac, M.; Bessiere, J. M.; Boutevin, B. *Macromol. Rapid Commun.* **1997**, *18*, 967.
(23) Kickelbick, G.; Matyjaszewski, K. *Macromol. Rapid Commun.* **1999**, *20*, 341.
(24) Davis, K. A.; Paik, H.-j.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 1767.
(25) Woodworth, B. E.; Metzner, Z.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 7999.
(26) Johnson, R. M.; Ng, C.; Samson, C. C. M.; Fraser, C. L. *Macromolecules* **2000**, *33*, 8618.
(27) Matyjaszewski, K.; Wei, M.; Xia, J.; Gaynor, S. G. *Macromol. Chem. Phys.* **1998**, *199*, 2289.
(28) Singha, N. K.; Klumperman, B. *Macromol. Rapid Commun.* **2000**, *21*, 1116.
(29) Davis, K.; O'Malley, J.; Paik, H.-J.; Matyjaszewski, K. *Polym. Prepr.* **1997**, *38*, 687.
(30) Pintauer, T.; Reinoehl, U.; Feth, M.; Bertagnolli, H.; Matyjaszewski, K. *Eur. J. Inorg. Chem.* **2003**, 2082.
(31) Matyjaszewski, K.; Shipp, D. A.; Wang, J.-L.; Grimaud, T.; Patten, T. E. *Macromolecules* **1998**, *31*, 6836.
(32) Hong, S. C.; Paik, H.-J.; Matyjaszewski, K. *Macromolecules* **2001**, *34*, 5099.
(33) Hong, S. C.; Matyjaszewski, K. *Macromolecules* **2002**, *35*, 7592.
(34) Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674.
(35) Queffelec, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 8629.
(36) Lubben, M.; Hage, R.; Meetsma, A.; Byma, K.; Feringa, B. L. *Inorg. Chem.* **1995**, *34*, 2217.
(37) Matyjaszewski, K.; Paik, H.-j.; Zhou, P.; Diamanti, S. J. *Macromolecules* **2001**, *34*, 5125.
(38) Bednarek, M.; Biedron, T.; Kubisa, P. *Macromol. Chem. Phys.* **2000**, *201*, 58.
(39) Schoen, F.; Hartenstein, M.; Mueller, A. H. E. *Macromolecules* **2001**, *34*, 5394.
(40) Hong, S. C.; Neugebauer, D.; Inoue, Y.; Lutz, J.-F.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 27.
(41) Hong, S. C.; Lutz, J.-F.; Inoue, Y.; Strissel, C.; Nuyken, O.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 1075.

MA034979V