

# Effect of Ferrocene Moieties on the Copper-Based Atom Transfer Radical Polymerization of Methyl Methacrylate

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**ABSTRACT:** The atom transfer radical polymerization (ATRP) of methyl methacrylate catalyzed by copper–tripodal complexes with ferrocene moieties (CuX/TRENFcImine, where X is Br or Cl, and TRENFcImine is tris-[2-(ferrocenyl-methyleneimino)ethyl]amine) was investigated to understand the effect of redox active moieties on the performance of ATRP catalysts. The CuBr/TRENFcImine system was highly active, with 82% conversion in 2 h. However, the polymerization became slower at higher molar ratios of monomer to catalyst. The polydispersity index was broad, and the initiation efficiency was relatively low. On the basis of the conformational analysis, the highly active and less controlled polymerization was probably caused by the electronic effect rather than the steric effect on the ferrocene moieties, which led to

the higher and lower values in the activation and deactivation steps, respectively. The polydispersity index was improved by the addition of CuBr<sub>2</sub>, but this led to slower rates of polymerization. The effect of halide groups on ATRP caused a faster rate in the CuBr/TRENFcImine polymerization system than in the CuCl/TRENFcImine system. The higher molar ratio of monomer to catalyst had no significant effect on the CuCl/TRENFcImine system. Nonetheless, the trace of water in the CuCl<sub>2</sub>·2H<sub>2</sub>O system accelerated the rate of propagation, which led to a higher molecular weight. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3766–3773, 2009

**Key words:** atom transfer radical polymerization (ATRP); catalysts; conformational analysis

## INTRODUCTION

Atom transfer radical polymerization (ATRP)<sup>1,2</sup> is one of the controlled/living radical polymerization processes that has grown rapidly in the past decade because of its successful polymerization with controlled molecular weight, well-defined compositions, architectures, and functionalities of polymers.<sup>3–10</sup> In the general process of ATRP (Scheme 1), a radical (R·) and a metal complex at the higher oxidation state (X–M<sub>t</sub><sup>n+1</sup>) were generated by the transfer of halogen (X) from an alkyl halide initiator (R–X) to the lower oxidation state of the metal complex (M<sub>t</sub><sup>n</sup>). Then, the radical is propagated with the consumption of monomers [with the rate constant of propagation ( $k_p$ )], and it is somehow deactivated by reacting with the oxidized complex, transforming into the original active catalyst and an oligomeric

alkyl halide. This process repeats itself [with the rate constants of activation ( $k_{act}$ ) and deactivation ( $k_{deact}$ )], and the molecular weights of the polymers are controlled in this process to obtain high molecular weights and narrow molecular weight distributions. The ATRP process is involved in the chemical exchange between the metal catalyst active species and the oxidized metal complex deactivated species; therefore, the catalyst (transition metals and ligands) in ATRP plays a crucial role in the catalytic pathway. A successful ATRP requires a fast activation/deactivation equilibrium with a small  $k_{act}$  and large  $k_{deact}$  to control the polymerization process. A wide variety of transition metal complexes used in ATRP systems, such as copper,<sup>11</sup> iron,<sup>12</sup> nickel,<sup>13</sup> ruthenium,<sup>14</sup> rhenium,<sup>15</sup> molybdenum,<sup>16</sup> and osmium,<sup>17</sup> with suitable ligands, such as multidentate amines, has been reported.

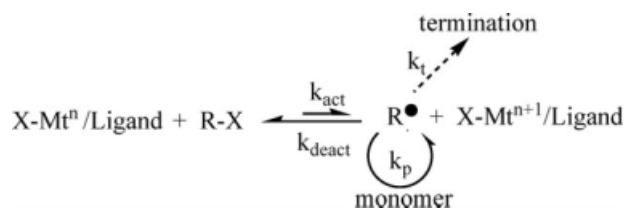
Ligands play a major role in ATRP by tuning the activity of the metal center and solubilizing the metal salts. Examples of highly active ATRP catalysts are a copper(I) bromide system with tetradentate ligands, such as CuBr/*tris*-[2-(*N,N*-dimethylamino)ethyl]amine (Me<sub>6</sub>TREN)<sup>18</sup> and CuBr/*tris*-(2-pyridylmethyl)amine,<sup>19</sup> which are much more active than the original CuBr/bipyridine system. The ligand structure greatly influences the effectiveness of the catalyst. A linear correlation between the

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**Scheme 1** Transition-metal-catalyzed ATRP.

redox potential of copper complexes and the logarithm of the apparent rate constant of propagation has been reported for ATRP in aqueous media.<sup>20</sup> The performance of more active and stable ATRP catalysts is based on the electron transfer processes.<sup>21</sup> Nevertheless, the redox potential of the metal complex is an important parameter to be considered in the design of new catalysts.

The objective of this study was to modulate the redox potential of the metal center of the ATRP catalyst on the basis of the redox properties of ferrocene moieties to obtain a high reactivity and dynamics for the atom transfer process due to the fast electron transfer process. Tripodals with ferrocene moieties were well characterized in the study of electron communication among ferrocene centers.<sup>22,23</sup> In this study, we studied the effect of the ferrocene moieties on the reactivities of ATRP catalyzed by copper-tripodal complexes.

## EXPERIMENTAL

### Materials and equipment

Methyl methacrylate (MMA; 99%, Fluka, Steinheim, Germany) was vacuum-distilled before use. (1-Bromoethyl)benzene (97%, Acros, Geel, Belgium), (1-chloroethyl)benzene (97%, Acros, Geel, Belgium), CuBr (97%, Riedel-de Haën, Seelz, Germany), CuBr<sub>2</sub> (99%, J. T. Baker Chemical Co., Phillipsburg, NJ), CuCl (98%, Merck, Hohenbrunn, Germany), CuCl<sub>2</sub>·2H<sub>2</sub>O (97%, Fluka), acetonitrile (ACN; analytical-reagent-grade, Lab Scan, Bangkok, Thailand), tetrahydrofuran (THF; analytical-reagent-grade, Lab Scan, Bangkok, Thai-

land), and diethyl ether (analytical-reagent-grade, Lab Scan, Bangkok, Thailand) were used without purification. The starting materials for the tripodal ligand were as follows: ferrocenecarboxaldehyde (98%, Aldrich, Steinheim, Germany) and *tris*-(2-aminoethyl)-amine (TREN; 98%, Fluka). <sup>1</sup>HNMR spectra were collected on a 300-MHz Bruker Avance spectrometer (Rheinstetten, Germany). Electrospray ionization mass spectra were recorded on a Bruker Daltonics Data Analysis 3.3 Esquire-LC mass spectrometer, which was equipped with an electrospray source.

### Synthesis of *tris*-(2-(ferrocenyl methylene amino)ethyl)amine (TRENFcImine)

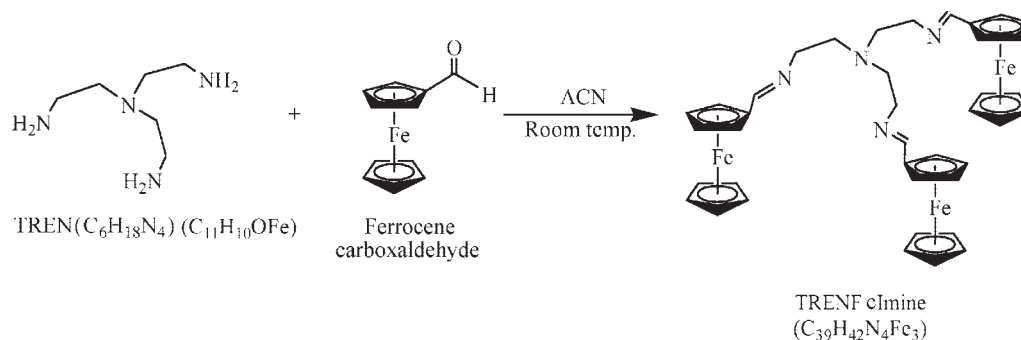
TRENFcImine was prepared as shown in Scheme 2 with a moderate yield. The synthesis was performed under ambient conditions at room temperature.

The synthetic method was modified from the literature.<sup>22,23</sup> A mixture of TREN (1.00 g, 6.86 mmol) and ferrocenecarboxaldehyde (4.07 g, 19.01 mmol) with a small amount of ACN was mixed and stirred overnight at room temperature. The obtained orange precipitate was filtered, then washed with ACN and then diethyl ether several times to remove impurities, and dried under reduced pressure to yield the tripodal *tris*-imine ligand (3.93 g, 5.35 mmol, 78%).

<sup>1</sup>HNMR (300 MHz, CD<sub>3</sub>OD,  $\delta$ , ppm): 8.02 [s, 3(HC=N), 3H], 4.54 [m, 3(C<sub>5</sub>H<sub>4</sub>), 6H], 4.36 [m, 3(C<sub>5</sub>H<sub>4</sub>), 6H], 4.09 [s, 3(C<sub>5</sub>H<sub>5</sub>), 15H], 3.49 [t, 3(N-CH<sub>2</sub>CH<sub>2</sub>-), 6H], 2.78 [t, 3(N-CH<sub>2</sub>CH<sub>2</sub>-), 6H]. Electrospray ionization mass spectrometry (m/z): 735.3 [M+H]<sup>+</sup> (calcd for C<sub>39</sub>H<sub>42</sub>N<sub>4</sub>Fe<sub>3</sub>: 734.1).

### Polymerization

The polymerization of MMA was carried out under dry argon in a dried Schlenk flask equipped with a magnetic stirring bar. The Schlenk flask was charged with the required amount of ligand and metal halide catalyst, sealed with a rubber septum, and then evacuated and backfilled with argon gas three times. After the MMA monomer was added via a syringe, three freeze-pump-thaw cycles were performed to



**Scheme 2** Synthesis of the tripodal ligand with ferrocene moieties (TRENFcImine).

remove oxygen, and then, degassed solvents were added with an argon-purged syringe. The solution mixture was stirred for 10–15 min at room temperature before we continued to preheat the mixture at the desired temperature with an oil bath and continually stirred it for 10 min; then, an initiator was added to initiate polymerization. After a given time, the reaction was quenched with THF and cooled to room temperature. The obtained polymer solution was passed over an alumina column to remove the remaining catalysts. The polymer product and remaining ligands with THF were removed by evaporation and then washed with an excess amount of methanol. Finally, the final polymer product was dried *in vacuo* and further used for the kinetic studies.

### Polymer characterization

We determined the yield percentage of the polymerization gravimetrically by weighing the dried polymer products. The molecular weight and polydispersity index (PDI) values of the polymer products (relative to polystyrene standard calibration) were measured with a Waters 150-CV gel permeation chromatograph (Milford, MA) equipped with PLgel 10- $\mu\text{m}$  mixed B2 columns (molecular weight resolving range = 500–10,000,000) and a refractive-index detector with THF as an eluent at 30°C with a flow rate of 1.0 mL/min.

### Conformer search

The model structures of Cu(I)–TRENFc(*cis*-Imine) and Cu(I)–TRENFc(*trans*-Imine) were generated by the Conformer Search Module of CERIU<sup>2</sup> (version 4.9, Accelrys, San Diego, CA) with the universal force field.<sup>24</sup> The starting structure of each model was randomly generated and minimized by CERIU<sup>2</sup>. The free-rotation torsion angles of each model were randomly varied over 360° in the conformer searching. A total of 200 minimized conformers for each model were obtained and then overlaid on the minimized conformers by CERIU<sup>2</sup>.

## RESULTS AND DISCUSSION

### Polymerizations of MMA with the tripodal ligand/CuBr catalyst

Multidentate nitrogen-based ligands are the most effective ligands in copper-based ATRP, and Me<sub>6</sub>TREN is the best active ATRP ligand among the tripodal ligand architecture.<sup>25</sup> A sterically hindered ligand usually promotes a much slower and less controlled polymerization.<sup>18</sup> Although a ferrocene moiety is bulkier than a methyl group, the redox active properties of ferrocene moieties are expected to facilitate the electron transfer process in ATRP and also to enhance the catalytic activities. The polymerization of MMA catalyzed by CuBr/Me<sub>6</sub>TREN in

toluene was not very successful with less than 10% initiation,<sup>25</sup> even though controlled polymerization was achieved in a highly polar solvent.<sup>26</sup> In this study, the CuBr/TRENFcImine system was tested in toluene, a common nonpolar solvent for polymerization, for the ATRP of MMA with 1-bromoethyl benzene (PEBr) as an initiator at 90°C (Table I, entries 1–5). No significant amount of polymer was obtained after polymerization with the ligand or CuBr/TRENFcImine system for 35 min at 90°C. Figure 1 shows a kinetic plot of the percentage conversion versus time. The monomer conversion increased with time, and the rate of the reaction was relatively fast (82% conversion within 2 h); this indicated that this catalytic system was highly active. The slower rate of polymerization due to the sterically hindered ligand could be overcome with the facilitation of electron transfer from ferrocene moieties. Figure 2 shows a plot of  $\ln([M]_0/[M]_t)$  (where  $[M]_0$  is the initial monomer concentration and  $[M]_t$  is the monomer concentration at time  $t$ ) versus time for the homogeneous ATRP of MMA in 60% (v/v) toluene. The linearity of  $\ln([M]_0/[M]_t)$  versus time was observed with an observed rate constant ( $k_{\text{obs}}$ ) value of  $2.3 \times 10^{-4} \text{ s}^{-1}$  [Fig. 2(A)]; this suggested that the polymerization was first-order with respect to the monomer, and the concentration of growing radicals remained constant throughout the reaction.<sup>27</sup> The number-average molecular weight ( $M_n$ ) from gel permeation chromatography was not observed with a linear increase in  $M_n$  versus monomer conversion (as required for living polymerization). This was possibly due to an inefficiency of the initiation step, which was influenced by several factors, including the bond dissociation ability of the R–X initiator, the bond formation ability between the metal catalyst and halide group from the initiator, the bond dissociation ability of the M–X of Cu(II)X/ligand complex, and the solubility of the metal catalyst in the reaction solvent, which leads to the production of active radicals for the growing chains of polymers. The rate of initiation and rate of propagation are usually dependent on the bond dissociation energy of R–X and P<sub>n</sub>–X, respectively. If the structures of the initiator and monomer are not similar, a rate of propagation higher than that of initiation might be observed. Therefore, the initiation efficiency might be improved with the use of an initiator with a structure similar to the growing chain of the polymer. All of the  $M_n$  results in Table I (entries 1–5) show that  $M_n$  increased with monomer conversion and reaction time. A broad molecular weight distribution [weight-average molecular weight/number-average molecular weight ( $M_w/M_n$ ) = 1.63–2.11] was obtained in the polymerizations of MMA with the condition of  $[\text{Monomer}]/[\text{Initiator}]/[\text{Metal catalyst}]/[\text{Ligand}] = 100 : 1 : 1 : 1$  at 90°C.

TABLE I  
ATRP of MMA Catalyzed by CuBr/TRENFcImine

Entry	Time (h)	Yield (%)	$M_w/M_n$	$M_n$ (theo) <sup>d</sup>	$M_n$ (exp)	Initiation efficiency <sup>e</sup>
1 <sup>a</sup>	0.33	30.4	2.11	3,231	10,575	0.3
2 <sup>a</sup>	1	72.2	1.86	7,418	9,721	0.8
3 <sup>a</sup>	2	81.7	1.71	8,369	11,877	0.7
4 <sup>a</sup>	3	89.4	1.63	9,138	15,129	0.6
5 <sup>a</sup>	4	96.1	2.11	9,804	12,203	0.8
6 <sup>b</sup>	1	44.0	1.58	4,589	11,527	0.4
7 <sup>b</sup>	2	61.3	1.49	6,326	13,559	0.5
8 <sup>b</sup>	3	72.2	1.53	7,417	16,278	0.5
9 <sup>b</sup>	4	77.4	1.59	7,937	17,302	0.5
10 <sup>b</sup>	5	83.0	1.67	8,496	16,456	0.5
11 <sup>c</sup>	1	18.7	1.32	2,056	7,312	0.3
12 <sup>c</sup>	2	60.7	1.45	6,264	13,862	0.5
13 <sup>c</sup>	3	73.2	1.41	7,515	14,382	0.5
14 <sup>c</sup>	4	78.1	1.52	8,005	18,609	0.4
15 <sup>c</sup>	8	99.0	1.50	10,095	17,209	0.6

The conditions were as follows: temperature = 90°C; toluene concentration = 60% (v/v); [Monomer]/[Initiator]/[CuBr]/[Ligand] = 100 : 1 : 1 : 1; and [MMA]<sub>0</sub> = 3.8M.

<sup>a</sup> No addition of CuBr<sub>2</sub>.

<sup>b</sup> Addition of 20 mol% CuBr<sub>2</sub> with respect to CuBr.

<sup>c</sup> Addition of 40 mol% CuBr<sub>2</sub> with respect to CuBr.

<sup>d</sup>  $M_n$  (theo) =  $[(\text{Monomer})_0/(\text{Initiator})_0] \times \text{Conversion} \times \text{MW}_{\text{monomer}}] + \text{MW}_{\text{initiator}}$ , where  $\text{MW}_{\text{monomer}}$  is the monomer molecular weight and  $\text{MW}_{\text{initiator}}$  is the initiator molecular weight.

<sup>e</sup> Initiation efficiency =  $M_n$  (theo)/ $M_n$  (exp).

This was probably due to the faster and slower rates in the activation and deactivation steps, respectively, with the high concentration of active radicals in the system. Therefore, CuBr<sub>2</sub> was added as an additive to increase the rate of the deactivation step. In the results shown in Table I (entries 6–10), it is apparent that the addition of CuBr<sub>2</sub> led to an improvement in PDI (lower  $M_w/M_n$ ) with decreasing rate of polymerization. The addition of CuBr<sub>2</sub> increased the concentration of Cu(II) species, and then, the concentration of dormant species (R–X) was increased. Therefore, the radical coupling termination was suppressed, and this resulted in lower  $M_w/M_n$  values in the range 1.49–1.67 [eqs. (1) and (2)]<sup>4</sup> with  $K_{eq} = k_{act}/k_{deact}$ ; cf. Scheme 1 for an explanation of all symbols] and a slower rate of polymerization [ $k_{obs} = 1.1 \times 10^{-4} \text{ s}^{-1}$ ; Fig. 2(B)].<sup>18,28</sup> Moreover, this system also performed effectively at the higher concentration of 40 mol % CuBr<sub>2</sub> with respect to CuBr (Table I, entries 11–15), which led to the lower  $M_w/M_n$  (in the range 1.32–1.52). The comparable rate of polymerization [ $k_{obs} = 1.1 \times 10^{-4} \text{ s}^{-1}$ ; Fig. 2(C)] to the 20 mol % system indicated that the rate of propagation in this system was relatively faster than the rate of initiation. However, the addition of CuBr<sub>2</sub> did not improve the initiation efficiency because the production of the Cu(II) complex decreased the concentration of the Cu(I) complex for the production of the active radicals in the initial step. The narrow PDI, due to the CuBr<sub>2</sub> addition, showed that the TRENFcImine system was an efficient catalytic system

for copper-based ATRP, although the initiation efficiency was relatively low:

$$R_p = k_p K_{eq} [M] [R-X] ([Cu^I]/[X-Cu^{II}]) \quad (1)$$

$$M_w/M_n = 1 + (k_p [R-X]/k_{deact} [X-Cu^{II}]) (2/p - 1) \quad (2)$$

where  $R_p$  is the rate of polymerization,  $[M]$  is the monomer concentration, and  $p$  is the monomer conversion.

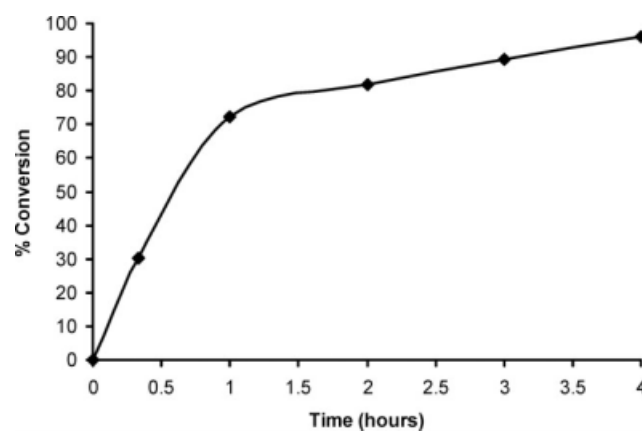
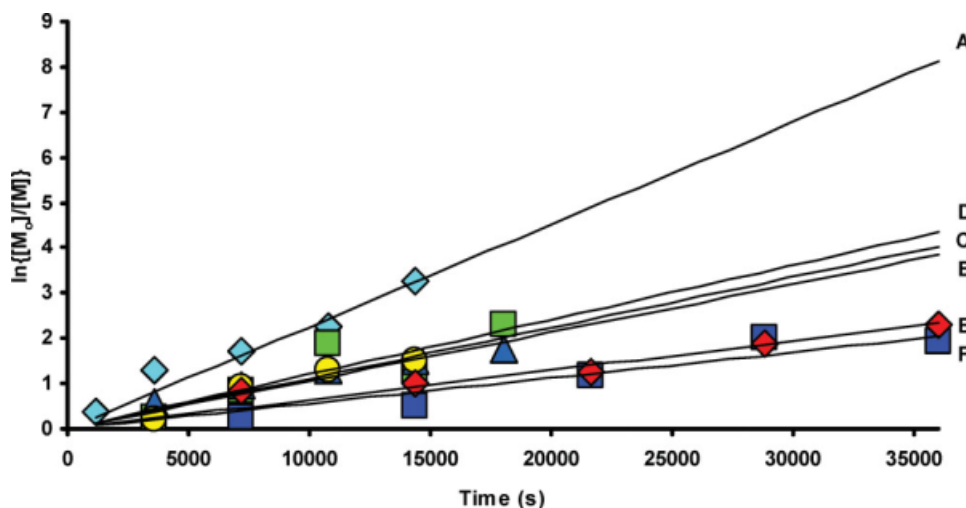


Figure 1 Solution polymerization of MMA catalyzed by CuBr/TRENFcImine with PEBr as the initiator in toluene (60% v/v) at 90°C ([Monomer]/[Initiator]/[CuBr]/[Ligand] = 100 : 1 : 1 : 1).





**Figure 2** Kinetic plots of  $\ln([M]_0/[M]_t)$  versus time for the solution polymerization of MMA catalyzed by CuX/TRENFCImine with PEX as the initiator in toluene (60% v/v) at 90°C with the following monomer/initiator/CuX/ligand molar ratios: (A) 100 : 1 : 1 : 1 ( $k_{\text{obs}} = 2.3 \times 10^{-4} \text{ s}^{-1}$ ; blue diamonds), (B) 100 : 1 : 1 : 1 with 20% CuBr<sub>2</sub> ( $k_{\text{obs}} = 1.1 \times 10^{-4} \text{ s}^{-1}$ ; blue triangles), (C) 100 : 1 : 1 : 1 with 40% CuBr<sub>2</sub> ( $k_{\text{obs}} = 1.1 \times 10^{-4} \text{ s}^{-1}$ ; yellow circles), and (D) 250 : 1 : 1 : 1 ( $k_{\text{obs}} = 1.2 \times 10^{-4} \text{ s}^{-1}$ ; green squares) for the CuBr systems and (E) 100 : 1 : 1 : 1 ( $k_{\text{obs}} = 6.5 \times 10^{-5} \text{ s}^{-1}$ ; blue squares) and (F) 250 : 1 : 1 : 1 ( $k_{\text{obs}} = 5.7 \times 10^{-5} \text{ s}^{-1}$ ; red diamonds) for the CuCl systems. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### Polymerizations of MMA with the tripodal ligand/CuCl catalyst

The effect of halides on the ATRP of MMA was investigated in this study (Table II, entries 1–5). The catalytic activity of CuCl/TRENFCImine was tested for the ATRP of MMA with 1-chloroethyl benzene

(PECl) as an initiator at 90°C in toluene. PDI of the CuCl system (Table II, entries 1–5) was slightly similar to that of the CuBr system (Table I, entries 1–5), whereas  $M_n(\text{exp})$  of the CuCl system was slightly higher than that of the CuBr system. The lower initiation efficiency was due to the stronger bond of

**TABLE II**  
ATRP of MMA Catalyzed by CuCl/TRENFCImine

Entry	Time (h)	Yield (%)	$M_w/M_n$	$M_n$ (theo) <sup>d</sup>	$M_n$ (exp)	Initiation efficiency <sup>e</sup>
1 <sup>a</sup>	2	23.5	1.88	2,497	13,215	0.2
2 <sup>a</sup>	4	39.3	1.68	4,079	14,732	0.3
3 <sup>a</sup>	6	69.5	1.74	7,102	15,877	0.4
4 <sup>a</sup>	8	86.4	2.26	8,793	21,730	0.4
5 <sup>a</sup>	10	85.2	1.85	8,667	39,752	0.2
6 <sup>b</sup>	2	27.6	1.65	2,899	20,380	0.1
7 <sup>b</sup>	4	35.0	1.56	3,641	22,705	0.2
8 <sup>b</sup>	6	85.8	2.20	8,727	20,241	0.4
9 <sup>b</sup>	8	75.9	2.26	7,739	39,397	0.2
10 <sup>b</sup>	10	80.5	1.95	8,199	24,203	0.3
11 <sup>c</sup>	1	35.3	1.92	3,676	46,321	0.1
12 <sup>c</sup>	2	44.3	1.95	4,577	47,814	0.1
13 <sup>c</sup>	3	59.7	2.00	6,113	32,302	0.2
14 <sup>c</sup>	4	84.8	2.03	8,633	62,112	0.1

The conditions were as follows: temperature = 90°C; toluene concentration = 50% (v/v); [Monomer]/[Initiator]/[Metal catalyst]/[Ligand] = 100 : 1 : 1 : 1; and [MMA]<sub>0</sub> = 4.7M.

<sup>a</sup> No addition of CuCl<sub>2</sub>·2H<sub>2</sub>O.

<sup>b</sup> Addition of 2 mol % CuCl<sub>2</sub>·2H<sub>2</sub>O with respect to CuCl.

<sup>c</sup> Addition of 2 mol % CaCl<sub>2</sub>·2H<sub>2</sub>O with respect to CuCl.

<sup>d</sup>  $M_n$  (theo) =  $[(\text{[Monomer]}_0/\text{[Initiator]}_0) \times \text{Conversion} \times \text{MW}_{\text{monomer}}] + \text{MW}_{\text{initiator}}$ , where  $\text{MW}_{\text{monomer}}$  is the monomer molecular weight and  $\text{MW}_{\text{initiator}}$  is the initiator molecular weight.

<sup>e</sup> Initiation efficiency =  $M_n$  (theo)/ $M_n$  (exp).

TABLE III  
ATRP of MMA Catalyzed by CuBr/TRENFCimine and CuCl/TRENFCimine

Entry	[Monomer] : [Initiator] : [CuX]	Time (h)	Yield (%)	$M_w/M_n$	$M_n$ (theo) <sup>c</sup>	$M_n$ (exp)	Initiation efficiency <sup>d</sup>
1 <sup>a</sup>	100 : 1 : 0.5	0.5	52.8	1.80	5,475	9,317	0.6
2 <sup>a</sup>	100 : 1 : 0.5	1	57.2	1.60	5,911	13,045	0.5
3 <sup>a</sup>	100 : 1 : 0.5	1.5	60.9	1.94	6,281	8,140	0.8
4 <sup>a</sup>	100 : 1 : 0.5	2	78.8	1.74	8,071	15,389	0.5
5 <sup>a</sup>	250 : 1 : 0.5	1	46.2	1.55	11,761	33,966	0.3
6 <sup>a</sup>	250 : 1 : 0.5	2	53.7	1.58	13,639	20,841	0.7
7 <sup>a</sup>	250 : 1 : 0.5	4	65.8	1.56	16,645	30,937	0.5
8 <sup>a</sup>	250 : 1 : 0.5	6	67.9	1.39	17,170	29,934	0.6
9 <sup>a</sup>	250 : 1 : 0.5	8	50.2	1.56	12,755	24,380	0.5
10 <sup>a</sup>	250 : 1 : 0.5	12	47.5	1.62	12,064	23,468	0.5
11 <sup>a</sup>	250 : 1 : 1	1	20.7	1.52	5,374	16,745	0.3
12 <sup>a</sup>	250 : 1 : 1	2	56.2	1.56	14,242	25,049	0.6
13 <sup>a</sup>	250 : 1 : 1	3	84.5	1.60	21,347	28,625	0.7
14 <sup>a</sup>	250 : 1 : 1	4	71.1	1.72	17,976	27,434	0.7
15 <sup>a</sup>	250 : 1 : 1	5	89.9	1.65	22,690	41,908	0.5
16 <sup>b</sup>	250 : 1 : 1	2	57.1	2.11	14,440	36,257	0.4
17 <sup>b</sup>	250 : 1 : 1	4	63.9	2.22	16,145	21,809	0.7
18 <sup>b</sup>	250 : 1 : 1	6	70.9	2.03	17,894	23,284	0.8
19 <sup>b</sup>	250 : 1 : 1	8	84.5	2.15	21,298	26,480	0.8
20 <sup>b</sup>	250 : 1 : 1	10	90.1	2.28	22,690	25,533	0.9

<sup>a</sup> The conditions were as follows: temperature = 90°C; toluene concentration = 60% (v/v); initiator = PEBr; [CuBr]/[Ligand] = 1 : 1; and [MMA]<sub>0</sub> = 3.8M.

<sup>b</sup> The conditions were as follows: temperature = 90°C; toluene concentration = 50% (v/v); initiator = PECl; [CuCl]/[Ligand] = 1 : 1; and [MMA]<sub>0</sub> = 4.7M.

<sup>c</sup>  $M_n$  (theo) =  $[(\text{Monomer})_0/(\text{Initiator})_0] \times \text{Conversion} \times \text{MW}_{\text{monomer}} + \text{MW}_{\text{initiator}}$ , where  $\text{MW}_{\text{monomer}}$  is the monomer molecular weight and  $\text{MW}_{\text{initiator}}$  is the initiator molecular weight.

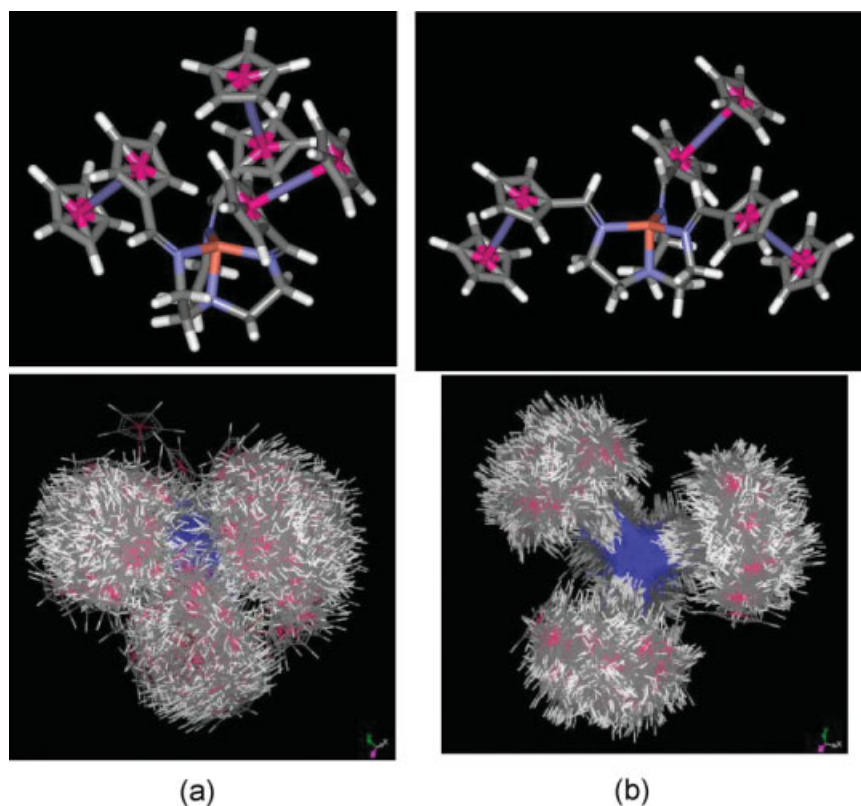
<sup>d</sup> Initiation efficiency =  $M_n$  (theo)/ $M_n$  (exp).

the C—Cl of the chloride system compared to the C—Br of the bromide system. The addition of 2 mol % CuCl<sub>2</sub>·2H<sub>2</sub>O with respect to CuCl (Table II, entries 6–10) showed that PDI was not significantly different from that of the CuCl system (Table II, entries 1–5), but the rate of propagation was faster (Table II). This was possibly due to the trace of water from CuCl<sub>2</sub>·2H<sub>2</sub>O to accelerate the rate of propagation, in which the halogen transfer equilibrium was shifted from the dormant to the active species.<sup>27,29</sup> The addition of a salt with hydrated water, such as in CaCl<sub>2</sub>·2H<sub>2</sub>O (Table II, entries 11–14), also accelerated the rate of propagation with a  $k_{\text{obs}}$  of  $1.0 \times 10^{-4} \text{ s}^{-1}$ , which led to higher molecular weight polymers to support the acceleration rate by a trace of water.

#### Effects of the monomer-to-catalyst ratio on ATRP

The comparison of the ATRPs of MMA at molar ratios of monomer to catalyst of 100 : 1, 100 : 0.5, 250 : 1, and 250 : 0.5 was studied, and the results are shown in Table III. These led us to determine the catalyst position in the atom transfer equilibrium and the dynamics of exchange between the dormant and active species in the ATRP process.<sup>27</sup> Also, the catalytic activity at the higher ratio of monomer to

catalyst indicated the efficiency of the catalytic system. One of the disadvantages of ATRP is the large amount of catalyst that is commonly required to achieve polymerization control. This causes additional cost for the amount of metal catalysts that are used in the polymerization. Moreover, the metal residues in the final products can be a limitation for industrial applications. Table III shows the solution polymerization under the conditions of the CuBr and CuCl systems with different molar ratios of monomer to catalyst. The CuBr systems (Table III, entries 1–15) showed that the optimum conditions with a 250 : 1 : 0.5 molar ratio of monomer to initiator to catalyst were good controlled polymerization conditions. The 250 : 1 molar ratio of monomer to catalyst indicated that the rate of polymerization [ $k_{\text{obs}} = 1.2 \times 10^{-4} \text{ s}^{-1}$ , Fig. 2(D)] slowed and the PDI was narrower. This was probably because the rate of ATRP,  $M_n$ , and PDI were dependent on the concentration of the Cu(I) complex catalyst, as shown in eqs. (1) and (3).<sup>30</sup> Increasing the molar ratio of monomer to catalyst led to a lower concentration of catalysts and a slower rate of polymerization. The CuCl systems (Table III, entries 16–20) with a 250 : 1 molar ratio of monomer to catalyst showed slightly broader PDIs with higher efficiencies in the



**Figure 3** Model structures and overlay minimized conformers generated with the conformer search module in Cerius<sup>2</sup>: (a) Cu(I)-TREN(*cis*-FcImine) and (b) Cu(I)-TREN(*trans*-FcImine). The *cis* and *trans* configurations were assigned with respect to the copper center. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

initiation step than the CuBr systems (Table III, entries 11–15):

$$M_w/M_n = 1 + (2/k_{\text{act}}[\text{Cu}^{\text{I}}]t) \quad (3)$$

#### Conformer search studies of the copper-tripodal complexes

The conformational search was carried out by CERIU<sup>2</sup> with a universal force field to study the steric effect of the Cu(I)-tripodal complexes: Cu(I)-TREN(*cis*-FcImine) and Cu(I)-TREN(*trans*-FcImine). The *cis* and *trans* configurations were assigned relatively to the copper center. The structures and the overlay minimized structures of the two models are shown in Figure 3. According to the universal force field on CERIU<sup>2</sup>, the *trans* model had a lower energy than the *cis* model. Therefore, the TRENFcImine ligand must have adopted a *trans* configuration with distortion from tetrahedral geometry. Moreover, it was obvious from the overlay structures that the *trans*-FcImine model had a pore structure for the incoming ligand to enter the copper center with less steric interactions on the ferrocene moieties than in the *cis*-

FcImine model. The restricted rotation of the C=N imine functional groups relieved the steric interactions from the bulky ferrocene moieties for the incoming ligand. Here, we propose that the less controlled polymerization catalyzed by Cu(I)-TRENFcImine may not have been governed by the steric effect on the ferrocene moieties. In contrast, the electronic effect resulting from the redox active on the ferrocene moieties in the induction of the copper center to bind halides tightly might have been more pronounced in the explanation of the slower rate of the deactivation step. An investigation of the electronic effect of the ferrocene moieties on the ATRP is in progress.

#### CONCLUSIONS

Copper-tripodal complexes with ferrocene moieties (CuX/TRENFcImine, where X is Br or Cl) were used in the ATRP of MMA. The high activity of the catalysts was probably due to the facilitation of the electron transfer process of the ferrocene moieties. However, this led to a broader PDI, which was improved effectively with the addition of CuBr<sub>2</sub> to the bromide system. The CuBr/TRENFcImine

system was more active than the CuCl/TRENFCI-mine system. Slight changes in the rate of polymerization and PDI of the CuCl/TRENFCI-mine were observed with increasing molar ratio of monomer to catalyst and with the addition of CuCl<sub>2</sub>·2H<sub>2</sub>O. The trace of water in CuCl<sub>2</sub>·2H<sub>2</sub>O accelerated the rate of propagation, which led to a higher molecular weight.

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