Supplementary Information

New insights into the mechanism of activation of atom transfer radical polymerization by Cu(I) complexes

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1. Experimental section

**Chemicals.** Acetonitrile (Carlo Erba, RS) was distilled over CaH₂ and stored under argon atmosphere. Tetraethylammonium tetrafluoroborate (Et₄NBF₄, Alfa Aesar, 99%) was recrystallized from ethanol and dried in a vacuum oven at 70 °C for 48 h. Tetraethylammonium chloride (Aldrich, 98%) and tetraethylammonium bromide (Aldrich, 99%) were recrystallized from dichloromethane-acetone-hexane (2:2:1) and ethanol-diethyl ether, respectively, and were dried in a vacuum oven at 70 °C. In the latter case, recrystallization was performed by dissolving the salt in ethanol and then adding diethyl ether until crystallization starts. Tris(2-dimethylaminoethyl)amine (Me₆TREN) was prepared according to a published procedure,¹ by methylation of tris(2-aminoethyl)amine (TREN) in a mixture of formaldehyde and formic acid and was purified by vacuum distillation. Copper(II) trifluoromethanesulfonate (Aldrich, 98%), tetrakis(acetonitrile)copper(I) tetrafluoroborate (Aldrich, 97%), benzyl chloride (Fluka, 99%), chloroacetoniitrile (Fluka, 99%), ethyl bromoacetate (Aldrich, 98%), allyl bromide (Aldrich, 97%) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, Aldrich, 98%) were used without further purification.

**Linear sweep voltammetry.** Electrochemical measurements were carried out on a computer-controlled Autolab PGSTAT30 potentiostat (Eco-Chimie, Utrecht, Netherlands). All experiments were carried out in a three-electrode airtight cell system under argon atmosphere, using a rotating disk electrode (RDE, Autolab, Eco-Chimie) with a glassy carbon tip (GC) disc (3 mm diameter, Metrohm) as a working electrode, and a Pt ring as a counter-electrode. The reference electrode was a Ag|AgI|I⁻ electrode built as described previously.² The potential of this reference electrode was always measured versus the ferrocenium/ferrocene couple (E°Fc⁺/Fc = 0.391 V vs SCE in MeCN), which was used as an internal standard. This has allowed conversion of the potentials to the aqueous saturated calomel electrode (SCE) scale to which all potentials reported in the paper are referenced. The cell had a double wall jacket through which water from a thermostated bath (Thermo Scientific, HAAKE SC100) was circulated. All experiments were carried out at 25 ± 0.1 °C, except those performed to study the temperature effect. Prior to each experiment the working electrode surface was cleaned by polishing with a 0.25-μm diamond paste, followed by ultrasonic rinsing in ethanol for 5 minutes.

**Chronoamperometry.** Kinetic experiments were carried out using the system described above. Prior to the solvent introduction, the cell with all electrodes was carefully fluxed with Ar at least for 30 min to avoid the presence of oxygen in the reaction environment. Cu₁L⁺ (L = Me₆TREN) was
prepared in-situ by mixing stoichiometric amounts of [Cu(MeCN)₄]BF₄ and Me₆TREN. When the effect of X⁻ was of interest the required amount of the halide was added as (C₂H₅)₄NCl or (C₂H₅)₄NBr. A typical concentration of the complex was 0.5 mM, whereas Cₓ⁻ varied from 0 up to 6 mM to investigate the effect of the halide ions on the activation kinetics. TEMPO was always introduced in a large excess with respect to the catalyst ([TEMPO]/[CuI⁺] ≥ 10) in order to ensure the total capture of the alkyl radicals.

The choice of the applied step potential $E_f$ was based on the voltammetric response of the system before addition of RX. The potential was stepped from an initial value before the oxidation wave of CuI⁺ to a value in the plateau region, about 200 mV after the wave. When the reaction was monitored by following the increase of the concentration of XCuII⁺, the initial potential was chosen somewhere before the reduction wave of the CuII complex, whereas the final potential was set at a value in the plateau region of the reduction wave.

2. Distribution diagrams of Cu−Me₆TREN−X⁻ systems

Speciations of CuII and CuI in the presence of Me₆TREN and halide ions were calculated with Hyperquad 2009 by using published data for the stability constants of various CuII and CuI complexes. All calculations were carried out with $C_{Cu}^0 = C_{L}^0 = 5 \times 10^{-4}$ M and variable $C_{X}^0$ (from

Figure S1. Distribution diagrams of ternary Cu−L−X⁻ systems in MeCN + 0.1 M Et₄NBF₄ at 25 °C, $C_{Cu}^0 = C_{L}^0 = 5 \times 10^{-4}$ M. a) CuI−L−Cl⁻, b) CuI−L−Br⁻, c) CuII−L−Cl⁻, d) CuII−L−Br⁻. Species representing less than 5% of the total Cu were omitted.
0 to $6 \times 10^{-3}$ M). The distribution diagrams (Fig. S1) were plotted to show the percentage of each Cu$^{II}$ or Cu$^{I}$ species as a function of the total concentration of X$^{-}$.

3. Voltammetric behavior of the ternary Cu–Me$_6$TREN–X$^{-}$ system

Linear sweep voltammetry of *in-situ* prepared Cu$_{L}^{I+}$ (L = Me$_6$TREN) in MeCN + 0.1 M Et$_4$NBF$_4$ at a glassy carbon RDE shows a well defined anodic wave with $E_{1/2} = -0.11$ V vs SCE corresponding to the monoelectronic oxidation of Cu$^{I}$ to Cu$^{II}$ (Fig. S2, curve a). This wave is attributed to the oxidation of Cu$^{I}$Me$_6$TREN$^{+}$ because this is the only Cu$^{I}$ species present in solution as long as $[\text{Cu}^{I}] = [\text{L}]$. The pattern changes in the presence of chloride ions (Fig. S2, curves b-e), showing a new wave at less positive potentials ($E_{1/2} = -0.43$ V vs SCE), which is assigned to the oxidation of ClCu$^{I}$L. A third small wave due to the oxidation of Cu$^{I}$Cl$_2^{-}$ to Cu$^{II}$Cl$_2$ could be observed at much higher potentials (not shown in the figure), especially at high Cl$^{-}$ concentrations. It is to be noted that the oxidation wave of ClCu$^{I}$L is always much higher than that of Cu$^{I}$L$^{+}$, which apparently indicates that ClCu$^{I}$L is the major species present in solution. This observation is clearly at variance with the results of the speciation calculations for the ternary Cu$^{+}$–L–Cl$^{-}$ system reported in Fig. S1, which show that the amount ClCu$^{I}$L formed at equilibrium never exceeds 15% (Fig. S1a). This apparent contradiction can be easily explained by noting that the oxidation wave at -0.43 V vs SCE involves not only the quantity of ClCu$^{I}$L present at

![Figure S2](image-url)
equilibrium but also ClCu$^+$ forming from Cu$^+$L$^+$ and Cu$^+$Cl$_2$ during the oxidation process as the speciation equilibria are perturbed near the electrode. In other words, as ClCu$^+$ is consumed at the electrode, the set of equilibrium reactions for the speciation of Cu$^+$ respond to the decrease of ClCu$^+$ concentration in the diffusion layer by continuously re-adjusting the equilibrium concentrations. The effect of all these dynamic equilibria is to produce an oxidation wave representing a [ClCu$^+$] value higher than the bulk equilibrium one.

Addition of bromides to a solution of Cu$^+$L$^+$ causes similar modifications to the voltammetric pattern of the complex (Fig. S3); a new wave appears at more negative potentials ($E_{1/2} = -0.35$ V vs SCE), while that of Cu$^+$L$^+$ decreases and eventually disappears. Also in this case, the new wave does not simply represent the quantity of BrCu$^+$L present in the bulk solution; it contains a contribution from the dynamic equilibria involving all Cu$^+$ species present in solution.

Figure S3. Linear sweep voltammetry of 0.50 mM [Cu$^+$L(MeCN)$_4$]$^+$BF$_4$ + 0.50 mM Me$_6$TREN in the absence (a) and presence of (b) 0.60 mM Br$^-$, (c) 1.09 mM Br$^-$, (d) 2.73 mM Br$^-$, (e) 5.68 mM Br$^-$, recorded at $\nu = 0.005$ V/s and $\omega = 2500$ rpm in MeCN + 0.1 M Et$_4$NBF$_4$ at 25 °C.

In the case of Cu$^{II}$ the effect of [X$^-$] on the distribution is much less complicated than that of Cu$^+$ as shown in Fig. S1 (c and d). The predominant species under a wide range of [X$^-$] values is the mixed complex XCu$^{II}$L$^+$. In particular, when [X$^-$]/[Cu$^{II}$L$^+$] = 1, XCu$^{II}$L$^+$ is the only species present in solution. Figure S4 illustrates the effect of chloride ions on the voltammetric response of Cu$^{II}$L$^{2+}$. Addition of Cl$^-$ causes disappearance of the reduction wave of Cu$^{II}$L$^{2+}$, being substituted by a new wave with $E_{1/2} = -0.43$ V vs SCE due to the reduction of ClCu$^{II}$L$^+$. It is interesting to note that a
single wave with almost a constant limiting current is observed even in the presence of excess Cl\(^-\). A similar behavior has been observed also for bromide ions.

The above described voltammetric investigations on the ternary systems involving X\(^-\), L and Cu\(^I\) or Cu\(^II\), show that a simple voltammetric response is obtained with Cu\(^II\) complexes. Conversely, the Cu\(^I\)-L-X\(^-\) system shows a more complicated voltammetric behavior. In particular, the oxidation wave observed for XCu\(^I\)L cannot be easily related to the real equilibrium concentration of the complex present in the bulk medium. This represents a big problem for the kinetic analysis if one desires to monitor the activation reaction by following the decay rate of Cu\(^I\). In contrast, there are no problems with Cu\(^II\); only one species is formed and consequently a single wave, which is proportional to its concentration, is observed. The reaction kinetics can be monitored by following the increase of XCu\(^II\)L\(^+\). Therefore, the kinetics of all experiments related to the effect of X\(^-\) on the reaction rate has been studied by using the reduction wave of XCu\(^II\)L\(^+\) as a redox probe.

![Graph](image)

Figure S4. Linear sweep voltammetry of 0.50 mM Cu\(^I\)(CF\(_3\)SO\(_3\))\(_2\) + 0.50 mM Me\(_6\)TREN in the absence (a) and presence of (b) 0.54 mM Cl\(^-\), (c) 1.13 mM Cl\(^-\), (d) 2.74 mM Cl\(^-\), (e) 5.18 mM Cl\(^-\), recorded at \(\nu = 0.005\) V/s and \(\omega = 2500\) rpm in MeCN + 0.1 M Et\(_4\)NBF\(_4\) at 25 °C.

### 4. Chronoamperometric determination of activation rate constants

The voltammetric responses shown above pointed out that when the species present in solution is Cu\(^I\)L\(^+\), the reaction with RX can be monitored by following either the disappearance of the oxidation current of Cu\(^I\)L\(^+\) or the increase of the reduction current of XCu\(^II\)L\(^+\). In general, the kinetic investigations of the activation of RX by Cu\(^I\)L\(^+\) without added X\(^-\) were performed by following the disappearance of Cu\(^I\)L\(^+\) on a rotating disc electrode (RDE) at \(\omega = 2500\) rpm. The
chronoamperometric experiment was started with a solution of CuI\(^{+}\) by stepping the RDE potential from -0.3 V to 0.1 V vs SCE. The current rises from zero to a limiting value corresponding to the diffusion-controlled oxidation of CuI\(^{+}\). Keeping the cell in this condition, the alkyl halide is added and the current is monitored until [CuI\(^{+}\)] decreases to small values. Some experiments were performed by monitoring the rate of formation of XCuI\(^{II}\). In this case the potential was stepped from \(E_{i} \geq -0.20\) V to values well beyond the reduction potential of XCuI\(^{II}\) (see Figs. S2 and S3). In all cases these two approaches gave practically the same results.

The limiting current, \(I_{L}\), for the oxidation of CuI\(^{+}\) is correlated to the bulk concentration, [CuI\(^{+}\)]*, of the metal complex thorough the Levich equation:5

\[
I_{L} = 0.62nFAD^{2/3}ω^{1/2}v^{-1/6}[\text{CuI}^{+}]^*
\]  

(S1)

where \(F\) is the Faraday constant, \(D\) is the diffusion coefficient of the electroactive species, \(ω\) is the angular velocity of rotating disc electrode, \(A\) is the area of the electrode and \(v\) is the kinetic viscosity.

For relatively slow reactions, the activation kinetics can be examined under pseudo-first-order conditions, that is, using \([RX]_{0}/[\text{CuI}^{+}]_{0} \geq 20\). The reaction rate can be expressed as the rate of disappearance of CuI\(^{+}\):

\[
-\frac{d[\text{CuI}^{+}]}{dt} = k_{\text{act}}[\text{CuI}^{+}][RX] = k'[\text{CuI}^{+}]
\]  

(S2)

\[
\ln[\text{CuI}^{+}] = \ln[\text{CuI}^{+}]_{0} - k't
\]  

(S3)

where \([\text{CuI}^{+}]_{0}\) is the initial concentration of CuI\(^{+}\) and \(k' = k_{\text{act}}[RX]_{0}\). Substituting \([\text{CuI}^{+}]\) and \([\text{CuI}^{+}]_{0}\) in eq. (S3) from eq. (S1) gives

\[
\ln I_{L} = \ln I_{L}^{0} - k't
\]  

(S4)

This approach was used in the case benzyl chloride. Reactions between CuI\(^{+}\) and RX were carried out at different RX concentrations to obtain a series of \(k'\) values as a function of [RX]. A plot of \(k'\) vs [RX] shows a straight line with a slope corresponding to \(k_{\text{act}}\) (Fig. S5).

For fast reactions, second-order conditions were chosen. If the reaction is performed using
$[\text{Cu}^{1L^+}]_0 = [\text{RX}]_0$, the kinetic rate law becomes:

$$-\frac{d[\text{Cu}^{1L^+}]}{dt} = k_{\text{act}}[\text{Cu}^{1L^+}][\text{RX}] = k_{\text{act}}[\text{Cu}^{1L^+}]^2$$  \hspace{1cm} (S5)

$$\frac{1}{[\text{Cu}^{1L^+}]} - \frac{1}{[\text{Cu}^{1L^+}]_0} = k_{\text{act}}t$$  \hspace{1cm} (S6)

Figure S5. Observed activation rate constant $k'$ as a function of initiator concentration for the reaction between Cu$^{1L^+}$ and PhCH$_2$Cl, in MeCN + 0.1 M Et$_4$NBF$_4$ at 25 °C.

The concentration of Cu$^{1L^+}$ can be calculated from the limiting current according to eq. (S1). Since during the experiment all parameters of eq. (S1) remain constant except $I_L$ and [Cu$^{1L^+}$], the relation between these two parameters can be expressed as follows

$$[\text{Cu}^{1L^+}] = \frac{I_L}{0.62nFAD^{2/3} \omega^{1/2} v^{-1/6}} = \frac{I_L}{I_L^0}[\text{Cu}^{1L^+}]_0$$  \hspace{1cm} (S7)

At least three independent experiments were carried out for each alkyl halide, which gave similar $k_{\text{act}}$ values, which were used to calculate the average values reported in the paper.

Some examples of chronoamperometry and kinetic analysis are reported in Figures S6 and S7.

5. Determination of activation rate constants in the presence of halide ions

When the system contains halide ions, different Cu$^1$ complexes are formed, with a distribution depending the concentration of X$^-$. These Cu$^1$ species give rise to a complicated voltammetric
Figure S6. Chronoamperometry of 0.50 mM [CuI(MeCN)4]BF4 + 0.50 mM Me6TREN + 0.50 mM RX + 10 mM TEMPO, recorded at RDE (ω = 2500 rpm) in MeCN + 0.1 M Et4NBF4 at 25 °C. Single step potential from -0.3 V to 0.1 V vs SCE.

Figure S7. Kinetic analysis of the reaction between CuI Li+ and RX according to eq. S6. Reaction conditions: 0.50 mM [CuI(MeCN)4]BF4 + 0.50 mM Me6TREN + 0.50 mM RX + 10 mM TEMPO in MeCN + 0.1 M Et4NBF4 at 25 °C.

pattern, which is not suitable for the monitoring of the reaction kinetics. In contrast, CuII gives essentially XCuII Li+ even in the presence of excess X– with respect CuII and L. This system shows a single cathodic wave due to the reduction of XCuII Li+ to XCuI L. We used this wave to monitor the reaction kinetics in the presence of X–. Chronoamperometric experiments were performed as described in section 4 by stepping the potential from an initial value $E_i \geq -0.20$ V vs SCE to a final value $E_f \leq -0.65$ V vs SCE for X = Cl– and $E_f \leq -0.50$ V vs SCE for X = Br–. In this case, the rate of the reaction is given by

S9
\[
\frac{d[XCu^{II}L^+]}{dt} = k_{act}[Cu^{I}L^+][RX] = k_{act}\left([Cu^{I}L^+]_0 - [XCu^{II}L^+]\right)[RX]
\]  

(S8)

where \([Cu^{I}L^+]_0\) is the initial concentration of \(Cu^I\). Resolving this differential equation under pseudo-first-order (\([RX]_0 \gg [Cu^{I}L^+]_0\)) or second-order conditions with \([Cu^{I}L^+]_0 = [RX]_0\) gives eqs (S9) and (S10), respectively.

\[
\ln\left([Cu^{I}L^+]_0 - [XCu^{II}L^+]\right) = \ln[Cu^{I}L^+]_0 - k't
\]

(S9)

\[
\frac{1}{[Cu^{I}L^+]_0 - [XCu^{II}L^+]} = \frac{1}{[Cu^{I}L^+]_0} = k_{act}t
\]

(S10)

The rate constants obtained for each RX at different \(X^-\) concentrations are listed in Table S1.

Table S1. Observed rate constants of activation of RX by \(Cu^{I}L^+\) in MeCN + 0.1 M Et\(_4\)NBF\(_4\).a

<table>
<thead>
<tr>
<th>RX</th>
<th>([X^-]^b) mM</th>
<th>(k_{obs}) M(^{-1})s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl chloride^e</td>
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<td>1.86</td>
</tr>
<tr>
<td></td>
<td>0.56</td>
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</tr>
<tr>
<td></td>
<td>1.07</td>
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<td></td>
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</tr>
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</tr>
<tr>
<td>Chloroacetonitrile</td>
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<td>230</td>
</tr>
<tr>
<td></td>
<td>0.51</td>
<td>142</td>
</tr>
<tr>
<td></td>
<td>1.05</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>58.5</td>
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<tr>
<td></td>
<td>5.69</td>
<td>15.2</td>
</tr>
<tr>
<td>Ethyl bromoacetate</td>
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<td>22.0</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>19.2</td>
</tr>
<tr>
<td></td>
<td>1.02</td>
<td>18.4</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td>5.22</td>
<td>12.4</td>
</tr>
<tr>
<td>Allyl bromide</td>
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<td>326</td>
</tr>
<tr>
<td></td>
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<td>291</td>
</tr>
<tr>
<td></td>
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<td>274</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td>5.15</td>
<td>175</td>
</tr>
</tbody>
</table>

*aUnless otherwise stated, the general reaction conditions were: \([Cu^{I}Me_6TREN]^+\)_0 = [RX]_0 = 5 \times 10^{-4} M; [TEMPO] = 5 \times 10^{-3} M; \(T = 25^\circ\)C. b\(X^- = Cl^-\) or \(Br^-\), depending on the type of RX. cInvestigated under pseudo-first-order conditions ([RX]/[Cu^{I}L^+] \geq 20).
References