Several Effects on Atom Transfer Radical Polymerization of Methyl Methacrylate Using CuX/Cyclopentyl Pyridine-2-Carboximidate Catalyst

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Abstract: Cyclopentyl pyridine-2-carboximidate (CpPCI) has been prepared from the reaction of 2-cyanopyridine with cyclopentanol. The catalytic system CuBr/CpPCI was found to be highly effective for atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA). The effects of solvents, temperature, catalyst/initiator ratio, solvent/monomer ratio, deactivator, and halide on the ATRP of MMA have been studied systematically for the CuX/CpPCI (X = Cl, Br) catalytic system. The optimum conditions for the ATRP of MMA were found to be a [CuBr]/[CpPCI],/[EBB],/[MMA], ratio of 1 : 2 : 1 : 400 at 60°C in a verrato solution, which yielded well-defined PMMA with a narrow molecular weight distribution of 1.14. Polydispersity (Mw/Mn) was as low as 1.06 for the CuBr/CpPCI catalytic system when employing 10% of the deactivator CuBr2.

Keywords: atom transfer radical polymerization (ATRP), carboximidate, controlled“living” radical polymerization

Introduction

Since the 1930s, more than 50% of synthetic polymers have been produced by radical polymerizations. Although the radical polymerizations have been applied to many commercial processes, the molecular weight and molecular weight distributions have been difficult to control because of the high reactivity of the propagating radical species. Much effort in the last several decades has been focused on living radical polymerizations [1]. Among the controlled/ “living” radical polymerizations (CRPs), nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT) are the most efficient [2-4]. One of the most efficient CRPs is ATRP, which was reported independently by Sawamoto [5] and Matyjaszewski [6] in 1995. The generally accepted mechanism in ATRP is the equilibrium between active and dormant species shown in Scheme 1.

Since the discovery of ATRP, various catalytic systems using transition metals, such as Cu [7-19], Ru [19-25], Fe [26-31], and Ni [32-35], have been developed, and the CuX/L catalytic systems have shown to be effective [X = Cl, Br, L = diimines (e.g., derivatives of 2,2'-bipyridine) [2,3,6-19,36] and multitender amines (e.g., N,N,N',N', N''-pentamethyldiethylene diamine (PMDETA)] [37-40]. In this paper, I report a systematic study of the ATRP of methyl methacrylate (MMA) using the catalytic system comprising CuX/cyclopentyl pyridine-2-carboximidate (CpPCI) [41].

Scheme 1. Equilibrium between Active and Dormant Species in ATRP.

Experimental

General Information

All syntheses and polymerizations were performed
under purified argon using standard Schlenk techniques. Methyl methacrylate (MMA, Aldrich, 99%) was distilled from CaH₂ before use. CuBr (Aldrich, 98%) and CuCl (Aldrich, 98+%) were purified by washing sequentially with glacial acetic acid, absolute EtOH, and Et₂O, drying under vacuum, and then storing under a purified argon atmosphere [42]. Ethyl 2-bromoisoamylate (EBiB, Aldrich, 98%) was distilled from CaH₂. Cyclopentyl pyridine-2-carboximidate (CpPCI) was prepared by a previous method [41]. Chlorobenzene (Aldrich, 99.8%), phenyl ether (Aldrich, 99+%), and veratrole (Aldrich, 99%) were deoxygenated by bubbling purified argon through them for at least 1 h. Unless specified, all other reagents were received from commercial sources and used without further purification. All solvents were dried by standard methods [43].

Characterizations

All prepared compounds were characterized by ¹H NMR (Varian 400 MHz FT-NMR Spectrometer) spectroscopy. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS) and were referenced to the residual solvents used. The monomer conversion was estimated from the ¹H NMR spectral integration ratio of the OCH₃ signals from the polymer (δ 3.60 ppm) and monomer (δ 3.75 ppm) and from the gas chromatogram (Hewlett Packard 5890 Gas Chromatograph) integration ratio of the residual monomer and used solvents or dodecane as the internal standard. Number-averaged molecular weights ($M_n$), weight-averaged molecular weights ($M_w$), and molecular weight distributions ($M_w/M_n$) were determined by gel permeation chromatography (Waters 150-C Gel Permeation Chromatograph) using tetrahydrofuran (THF) as the eluent at 40°C. Calibration was performed using poly (methyl methacrylate) (PMMA) standard samples.

General Procedures for the Solution ATRP of MMA

A 50-mL Schlenk flask containing a stirring bar was charged with the appropriate amounts of CuBr, CpPCI, MMA (20.02 g, 0.20 mol), and solvent (w/w = 1 : 1) in a glove box. The flask was immersed in an oil bath thermostatted at the desired temperature. The magnetic stirring rate was kept at 500 rpm. After stirring for 10 min, the appropriate amount of initiator (EBiB) was charged using a degassed micro-syringe. Samples were withdrawn periodically using a degassed syringe (2 mL), and then added to 5 mL of CH₂Cl₂. The CH₂Cl₂ solutions were injected into the GC and the monomer conversion was calculated relative to the reference solvent. More often, NMR spectra of samples in CDCl₃ were taken from the CH₂Cl₂ solutions and the monomer conversion was calculated from the ¹H NMR spectral integration ratio of the OCH₃ signals. The GPC samples were obtained by pouring a large amount of MeOH into the CH₂Cl₂ solutions and drying at 60°C under vacuum.

Results and Discussion

Solvent Effects

To choose the best solvent for the solution ATRP of MMA, several solvents were applied. The polar solvents, anisole and phenyl ether, have been used previously for the solution ATRP of MMA and they create homogeneous solutions throughout the entire polymerization period [17,44]. More often, bulk systems have been used because of the better solubility of catalysts in MMA. As shown in Table 1 and Figure 1, veratrole was the best among the solvents used. Phenyl ether (Ph₂O) was also a good solvent, but the first-order plot of ln[Mₙ]/[M] vs. time is curved and the $M_w/M_n$ ratio was a little higher (1.21 vs. 1.14). In addition, chlorobenzene (PhCl) was

\[
\begin{array}{cccccc}
\text{Entry} & \text{Solvent} & \text{Conversion}^a (%) & M_n^b & M_w/M_n & k_{obs} \times 10^3 \text{s}^{-1} \\
1 & \text{Veratrole} & 79 & 31720 & 39110 & 1.14 & 1.19 \\
2 & \text{PhCl} & 62 & 24990 & 33370 & 1.16 & 0.82 \\
3 & \text{Ph₂O} & 71 & 28670 & 46560 & 1.21 & 0.98 \\
4 & \text{Toluene} & 46 & 18570 & 36090 & 1.21 & 0.46 \\
5^d & \text{Bulk} & 89 & 35590 & 56610 & 1.48 & 4.44 \\
\end{array}
\]

$^a$ [CuBr]: [CpPCI]: [EBiB]: [MMA] = 1 : 2 : 1 : 400; reaction time: 3.5 h; temp.: 60°C; in a solution (w/w = 1 : 1). $^b$ Determined by GC and ¹H NMR spectroscopy. $^c$ $M_w = M_{EBiB} + M_{MMA} \times [MMA]/[EBiB] \times \text{(conversion)}$. $^d$ Reaction time: 1.25 h.
Table 2. Temperature Effects in the Solution ATRP of MMA

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp. (°C)</th>
<th>Conversion (%)</th>
<th>M_0,obs</th>
<th>M_0,GPC</th>
<th>M_0/M_0</th>
<th>k_0bs (10^4 s^-1)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>26</td>
<td>48</td>
<td>19360</td>
<td>35110</td>
<td>1.20</td>
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<td>2</td>
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<td>62</td>
<td>24880</td>
<td>35840</td>
<td>1.21</td>
<td>0.74</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>79</td>
<td>31720</td>
<td>39110</td>
<td>1.14</td>
<td>1.19</td>
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<td>4</td>
<td>80</td>
<td>71</td>
<td>28400</td>
<td>34310</td>
<td>1.15</td>
<td>0.89</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>59</td>
<td>23870</td>
<td>33790</td>
<td>1.18</td>
<td>0.59</td>
</tr>
</tbody>
</table>

*[^CuBr]_2 [CpPCl]_2 [EBB]_2 (MMA)]_0 = 1:2:1:400; reaction time: 3.5 h; in a veratrole solution (w/w = 1:1). Determined by GC and 1H NMR spectroscopy. *M_0,obs = M_0,GPC + {[(M_0,MMA) × [MMA]]/[EBB]_2} × (conversion).

Figure 2. Plots of M_0 (closed symbols) and M_0/M_0 (open symbols) vs. conversion for the ATRP of MMA at 60°C in the bulk and in various solvents. See Table 1 for conditions.

one of the better solvents in view of its first-order plot and M_0/M_0. However, the activity was lower (k_0bs = 1.19 \times 10^4 s^-1 for veratrole vs. 8.2 \times 10^3 s^-1 for PhCl) under the same polymerization conditions. In bulk, the polymerization rate was very fast (k_0bs = 4.44 \times 10^4 s^-1), but the experimental M_0 had a large deviation from the theoretical M_0 and the M_0/M_0 was relatively high (1.48 vs. 1.14), as shown in Figure 2. Other solvents, such as THF, CHCl_3, and cyclohexane, were also applied to the solution ATRP of MMA. In THF, the molecular weight was lower (maximum: several thousands) relative to those obtained from other solvents. In cyclohexane, the activity was comparable to that in toluene, but there was a stirring problem because of the slight solubility of PMMA in cyclohexane, which resulted in a broad polydispersity. In chloroform, no activity was observed because the catalyst was inactive on account of the abstraction of chloride from the solvent. In view of these results, the suitability of the solvents decreases in the order veratrole > PhCl > toluene > cyclohexane > THF >> CHCl_3.

**Temperature Effects**

Polymerization temperature is one of the most important factors to control in commercial plants. High temperatures require high-energy sources and low temperatures are too difficult to operate in plants. Therefore, the appropriate temperature must be suitable for operating plants and also be cost effective. Generally as the temperature increases, the polymerization rate also increases as a result of the increase of both the radical propagation rate constants and the equilibrium constant. Concurrently, the extent of side reactions, such as chain transfer and self-termination of radical species, increases at higher temperatures. To choose the most appropriate temperature for the solution ATRP of MMA, several temperatures were applied.

As shown in Table 2 and Figure 3, the initial conversion was higher at elevated temperatures, but at high temperatures (80°C), the propagation rates slowed down after 2 h when compared to that at the relatively lower temperature, 60°C. Polymerization of MMA proceeded even at room temperature, although the rate was slow (k_0bs = 4.9 \times 10^3 s^-1). Above 100°C, the propagation rate was higher (k_0bs = 1.84 \times 10^4 s^-1 at 100°C vs. 1.19 \times 10^4 s^-1 at 60°C) in the first hour, but was much lower (4.23 \times 10^3 vs. 1.19 \times 10^4 s^-1) in the second hour, and then the propagation remained almost steady after 2 h. At 80°C or below, the first-order plot of ln[M]/[M] vs. time was linear, which indicates that living polymerization of MMA occurs. In view of these results, the best polymerization temperature of MMA was 60°C. It is much lower than previously applied temperatures (usually 80°C or higher) for ATRP catalyst systems using MMA. Molecular weight distributions were narrower as the temperature increased.
Table 3. Solution ATRP of MMA using Different Catalyst/Initiator Ratios

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Cat] : [EB/B]</th>
<th>Conversion (%)</th>
<th>$M_w$</th>
<th>$M_{w,GPC}$</th>
<th>$k_{obs}$ ($10^5$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 : 2</td>
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<td>18290</td>
<td>21560</td>
<td>1.17</td>
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<tr>
<td>2</td>
<td>1 : 1</td>
<td>79</td>
<td>31720</td>
<td>39110</td>
<td>1.14</td>
</tr>
<tr>
<td>3</td>
<td>1 : 0.5</td>
<td>48</td>
<td>41550</td>
<td>51130</td>
<td>1.20</td>
</tr>
</tbody>
</table>

$^{a}$ [Cat] : [MMA] = 1:400; reaction time: 3.5 h; temp.: 60°C; in a veratrole solution (w/w = 1 : 1). $^b$ Determined by GC and $^b$H NMR spectroscopy. $M_w$ = $M_w$EB/B + $M_w$MMA[MMMA]/[EB/B].

Figure 4. Plots of $M_n$ (closed symbols) and $M_w/M_n$ (open symbols) vs. conversion for the solution ATRP of MMA at several temperatures. See Table 2 for conditions.

Figure 5. Catalyst/initiator effects on the first-order plots of the ATRP of MMA in a veratrole solution (w/w = 1 : 1). See Table 3 for conditions.

Figure 6. Plots of $M_w$ (closed symbols) and $M_w/M_n$ (open symbols) vs. conversion for the veratrole-solution-ATRP of MMA at several catalyst/initiator ratios. See Table 3 for conditions.

As shown in Figure 4.

Initiator Concentration Effects

In general, the higher the concentration of initiator, the faster the polymerization rate should be because the number of active propagating species is larger. To choose the optimum amount of initiator for the solution ATRP of MMA, different ratios of catalyst/initiator were applied. In veratrole-solution-ATRP of MMA, the propagation rates were faster, as expected, as the concentration of EB/B increased, as shown in Table 3 and Figure 5. In a chlorobenzene solution, however, the increase in the propagation rate was small ($k_{obs} = 9.7 \times 10^5$ vs. $8.2 \times 10^5$ s$^{-1}$). Furthermore, in a propylene carbonate solution, the higher the concentration of initiator, the slower the propagation rate ($k_{obs} = 6.94 \times 10^5$ vs. $8.17 \times 10^5$ s$^{-1}$). In this catalytic system, the generality is not really true. In other words, it can be said that the higher the concentration of initiator, a faster or slower propagation rate depends upon the solvents used. The lower the concentration of initiator, the higher the molecular weight and the broader the molecular weight distributions, as shown in Figure 6. From these results, we believe that a 1 : 1 ratio of catalyst/initiator is optimal.

Solvent/Monomer Effects

Most ATRPs of monomers were carried out in the bulk. Since the polymerization rate is first-order in the concentration of initiator and catalyst, 50% dilution yields a rate 4 times slower relative to the bulk polymerization. To determine the appropriate solvent/monomer (S/M) ratio for the solution ATRP of MMA, different S/M ratios were applied to this catalytic system. As expected, 50% dilution (S/M = 1 : 1) led to a ca. four-fold (exactly 3.7 times) slower rate compared to that of the bulk polymerization. Another 50% dilution (S/M = 2 : 1) led to a ca. three-fold slower rate compared to the S/M = 1 : 1 polymerization. Further 50% dilution (S/M = 4 : 1) led to only a 1.3-times slower rate when compared to the S/M
Table 4. Solution ATRP of MMA at Different Solvent/Monomer (S/M) Ratios$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>S/M $^b$</th>
<th>Conversion (%)</th>
<th>$M_n, \text{cal}$$^d$</th>
<th>$M_n, \text{GPC}$</th>
<th>$M_n/M_w$</th>
<th>$k_{obs} (10^{-3} \text{ s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^c$</td>
<td>0 : 1</td>
<td>89</td>
<td>35590</td>
<td>56610</td>
<td>1.48</td>
<td>4.44</td>
</tr>
<tr>
<td>2</td>
<td>1 : 1</td>
<td>79</td>
<td>31720</td>
<td>39110</td>
<td>1.14</td>
<td>1.19</td>
</tr>
<tr>
<td>3</td>
<td>2 : 1</td>
<td>41</td>
<td>16530</td>
<td>29300</td>
<td>1.22</td>
<td>0.39</td>
</tr>
<tr>
<td>4$^d$</td>
<td>4 : 1</td>
<td>33</td>
<td>13350</td>
<td>27820</td>
<td>1.31</td>
<td>0.30</td>
</tr>
</tbody>
</table>

$^a$ [CuBr]$_2$: [CpPCl]$_2$: [EBB/B]$_2$: [MMA]$_2$ = 1 : 2 : 1 : 400; reaction time: 3.5 h; temp: 60°C; in a veratrole solution. $^b$ By weight. $^c$ Determined by GC and $^d$ NMR spectroscopy. $^d$ $M_n, \text{cal} = M_w,\text{EBB} + M_w,\text{MMA}/[\text{MMA}]/[\text{EBB/B}])$(conversion). $^e$ A reaction time of 1.25 h gave a higher $M_n$ (416000) in the GPC diagram. $^f$ A higher $M_n$ (309000) was observed in the GPC diagram.

Figure 7. Solvent/monomer effects on the first-order plots of the ATRP of MMA in a veratrole solution (w/w = 1 : 1). See Table 4 for conditions.

= 2 : 1 reaction (Table 4 and Figure 7). As shown in Figure 8, the molecular weight increased as the conversion increased in all cases. In the bulk, $M_n/M_w$ was larger with increasing conversion. It might be that there was poor stirring due to the high viscosity at the higher conversions of MMA. This problem also led to some portions of high-molecular-weight products. Even though there was no stirring problem in the case where S/M = 4 : 1, some portions of high molecular weight (M$_n$ = ca. 300000) were also observed in the GPC diagram. It might be that too much dilution resulted in inefficient initiator efficiency. In view of these results, the ratio S/M = 1 : 1 led to the best controlled/“living” polymerization in the CuBr/CpPCI catalytic system.

Monomer Concentration Effects

Since the polymerization rate is directly proportional to the concentration of catalyst, the rate is 2-times slower if the concentration of the catalyst is halved. Previously, most ATRP have been performed using [catalyst]/[monomer] ratios of 1 : 200 or less to increase the polymerization rate. The higher the concentration of catalyst, the lower the molecular weight should be. Use of large amounts of catalysts can lead to some problems, such as high costs and the need to remove the catalyst after polymerization.

In view of these concepts, using a minimal amount of catalyst is preferred, when possible. When the [Cat]/[MMA] ratio of 1 : 100 was applied to the veratrole-solution (w/w = 1 : 1) ATRP of MMA using CuBr/CpPCI catalyst, the polymerization was complete within 1 h. Half the amount of the catalyst ([Cat]/[MMA] = 1 : 200) led to a 2-times slower rate when compared to the [Cat]/[MMA] = 1 : 100 system (Table 5, entries 1, 2). In a similar way, the lower the concentration of catalyst, the slower the polymerization rate, as shown in Table 5 and Figure 9. No polymerization was observed when the [Cat]/[MMA] ratio of 1 : 1600 was used. As shown in Figure 10, the molecular weight increased as the monomer conversion increased, as expected. On the other hand, when using [Cat]/[MMA] = 1 : 800, the molecular weight could not be controlled. Some portions of high molecular weight (M$_n$ = 480000-580000) were detected in the GPC diagram, as we had also observed when S/M = 4 : 1. Molecular weight distributions were as narrow as 1.14, except for [Cat]/[MMA] = 1 : 800 (M$_w$/M$_n$ = 1.3-1.4). From these results, the ratio of catalyst to monomer of 1 : 400 was optimum for the solution ATRP of MMA in view of cost and polymerization behavior. Removal of used catalysts from polymers is one of the key problems of ATRP. Recently, the removal or recycling of used catalysts has received a lot of attention [45-47]. Our catalysts could be removed easily from by adding MeOH to CH$_2$Cl$_2$ or THF.
Table 5. Solution ATRP of MMA at Different Catalyst/Monomer Ratios

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Cat]: [MMA]</th>
<th>Conversion (%)</th>
<th>M₀,h</th>
<th>M₀,GPC</th>
<th>Mₐ/M₀</th>
<th>kobs (10⁻⁴ s⁻¹)</th>
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<tr>
<td>1′</td>
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<td>8860</td>
<td>21050</td>
<td>1.14</td>
<td>6.58</td>
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<tr>
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<td>1:200</td>
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<td>16230</td>
<td>27340</td>
<td>1.14</td>
<td>3.19</td>
</tr>
<tr>
<td>3′</td>
<td>1:400</td>
<td>79</td>
<td>31720</td>
<td>39110</td>
<td>1.14</td>
<td>1.19</td>
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<td>1:800</td>
<td>33</td>
<td>26890</td>
<td>43840</td>
<td>1.41</td>
<td>0.33</td>
</tr>
<tr>
<td>5′</td>
<td>1:1600</td>
<td>0</td>
<td>-</td>
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<td>-</td>
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</tbody>
</table>

*Catalyst: CuBr/CpPCI; initiator: EBBB; reaction time: 3.5 h; temp: 60°C; in a veratrole solution (w/w = 1 : 1). Determined by GC and 'H NMR spectroscopy. M₀,h = M₀,EHBB + M₀,MMA × [(MMA)/[EBBB];(conversion). Reaction time: 0.83 h. Reaction time: 1.33 h. A higher Mₐ (581000) was observed in the GPC diagram. No polymerization occurred during the observed time.

Table 6. Deactivator Effects in the Solution ATRP of MMA

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Act]: [Deact]</th>
<th>Conversion (%)</th>
<th>M₀,h</th>
<th>M₀,GPC</th>
<th>Mₐ/M₀</th>
<th>kobs (10⁻⁴ s⁻¹)</th>
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<tr>
<td>1′</td>
<td>1:0</td>
<td>79</td>
<td>31720</td>
<td>39110</td>
<td>1.14</td>
<td>1.19</td>
</tr>
<tr>
<td>2′</td>
<td>1:0.1</td>
<td>79</td>
<td>31610</td>
<td>37500</td>
<td>1.17</td>
<td>1.17</td>
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<tr>
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<td>12800</td>
<td>149030</td>
<td>1.19</td>
<td>0.27</td>
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</tbody>
</table>


Figure 9. Catalyst/monomer effects on the first-order plots of the ATRP of MMA in a veratrole solution (w/w = 1 : 1). See Table 5 for conditions.

Figure 10. Plots of Mₐ (closed symbols) and Mₐ/M₀ (open symbols) vs. conversion for the veratrole-solution-ATRP of MMA at several catalyst/monomer ratios. See Table 5 for conditions.

In Table 6 (entries 1-3) and Figure 11, while the average rate constants during the observed polymerization periods were almost the same (kobs = 1.19 × 10⁻⁴ vs. 1.17 × 10⁻⁴ s⁻¹), the initial rate constants were a little lower (kobs = ca. 9 × 10⁻⁵ s⁻¹) upon adding 10~20% of a deactivator (CuBr₂). In the ATRP of methyl acrylate (MA) using CuBr/4,4’-di-tert-butyl-2,2’-bipyridine (dBBpy), the polymerization rate was not affected by the concentration of CuBr₂ because of its low solubility [48]. The final molecular weights and polydispersities were almost the same irrespective of the deactivator concentration, as shown in Figure 12.

To investigate the effect of deactivator more thoroughly, the preformed catalyst and deactivator were synthesized [41]. To compare the polymerization activity
of the \textit{in situ} catalyst (CuBr/CpPCI) and the preformed catalyst (assumed to be [Cu(CpPCI)Br])\textsubscript{2} Br), these species were applied to the veratrole-solution-ATRP of MMA at 60°C. As shown in Figure 13, the observed polymerization rate using the preformed catalyst was slightly higher ($k_{\text{obs}} = 1.24 \times 10^{-4}$ s\textsuperscript{-1}) compared to that when using the \textit{in situ} catalyst ($k_{\text{obs}} = 1.19 \times 10^{-5}$ s\textsuperscript{-1}) (Table 6, entries 1, 4). When adding 10% of the preformed deactivator (assumed to be [Cu(CpPCI)Br]\textsubscript{2} Br) to this solution, the deactivator was very effective. The polymerization rate was much lower ($8.7 \times 10^{-5}$ vs. $1.24 \times 10^{-4}$ s\textsuperscript{-1}, entries 4, 5 in Table 6) and the $M_w/M_n$ ratio was narrower, as low as 1.06 (Figure 14).

\textbf{Halide Effects}

Most copper-mediated ATRPs use CuBr instead of CuCl because of its faster polymerization rate. When a higher-molecular weight is needed, CuCl is preferred to CuBr because of its slow initiation. Matyjaszewski and coworkers reported that mixed-halide systems, such as RBr/CuCl, can be beneficial [49]. They can provide fast initiation and reduce side reactions. In our catalyst system, the mixed-halide system, EB/B/CuCl, was no better than the non-mixed halide system, EB/B/CuBr. While the first-order plot of $ln[M]/[M]$ vs. time gave linearity in the EB/B/CuBr system, the EB/B/CuCl system gave the curvature shown in Figure 15. As expected, the polymerization rate was much lower ($k_{\text{obs}} = 2.7 \times 10^{-5}$ vs. $1.19 \times 10^{-4}$ s\textsuperscript{-1}, entries 1, 6 in Table 6). The molecular weight increased with increasing conversion of monomer in both catalytic systems, but $M_n$ in that obtained from the EB/B/CuCl was lower compared to that obtained from the EB/B/CuBr system at the same conversion percentage ($M_n = 19000$ for Cl vs. 24000 for Br), as shown in Figure 16.
Conclusions

Using the catalytic system CuX/CpPCI, several effects on the ATRP of MMA have been studied in a systematic way. From the several effects we studied, such as solvent, temperature, initiator concentration, solvent/monomer ratio, catalyst/monomer ratio, deactivator, and halide, the following conclusions are drawn: (1) The polymerization activity of MMA using the catalytic system CuBr/CpPCI decreased among the solvents used in the order veratrole > PhO > PhCl > toluene > cyclohexane > THF >> CHCl₃. (2) Polymerization activity occurred in the range from room temperature to 100°C. The best polymerization temperature was 60°C. (3) The higher the concentration of initiator, the faster or slower the propagation rate, depending on the solvents used. A 1 : 1 ratio of catalyst/initiator was optimum. (4) A ratio of solvent/monomer of 1 : 1 gave the best controlled “living” polymerization for this catalyst system. (5) Use of a minimal amount of catalyst is necessary, if possible, in view of costs and catalyst removal. The optimum ratio of catalyst/monomer was 1 : 400. (6) Use of a deactivator, CuBr₂, had little effect on the solution ATRP of MMA because of its slight solubility. On the other hand, use of a preformed deactivator had a dramatic effect on the polymerization rate. (7) CuBr as the metal halide was superior to CuCl in view of its activity. A mixed-halide system (RB/Br/CuCl) was not good in this catalytic system. The catalytic system, [CuBr]/[CpPCI]/[EBBr]/[MMA] = 1 : 2 : 1 : 400, showed high activity in veratrole solution (w/w = 1 : 1) at 60°C, and yielded well-defined polymers having narrow molecular weight distributions (as low as 1.14). Mechanistic studies and structural determinations of these catalysts are currently underway.

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References

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