# Cu$^{I}$ and Cu$^{II}$ Salts of Group VIA Elements as Catalysts for Living Radical Polymerization Initiated with Sulfonyl Chlorides

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**ABSTRACT:** The living radical polymerization of methyl methacrylate initiated from sulfonyl chlorides and catalyzed by the new catalytic systems $Cu_2Y$/Bpy and CuY/Bpy, where Y is O, S, Se, or Te and Bpy is 2,2′-bipyridine, is described. An induction time was observed in all polymerization experiments. The values of the experimental rate constants of polymerization ($k_p^{exp}$) increased whereas the corresponding induction times decreased in the order Y = O < S < Se < Te. For the entire series of catalysts, $k_p^{exp}$ for CuY was less than $k_p^{exp}$ for $Cu_2Y$. A mechanistic interpretation that involves the *in situ* generation of the CuCl/$CuCl_2$ pair, starting from $Cu_2Y$ or CuY, is provided. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 3839–3843, 2000

**Keywords:** living radical polymerization; sulfonyl chloride; methyl methacrylate; copper oxide; copper sulfide; copper selenide; copper telluride; copper chloride

## INTRODUCTION

In a recent series of publications[1] from our laboratory, we demonstrated that aryl,[1(a–f)] alkyl,[1(d–f)] and perfloroalkyl[1(h)] sulfonyl chlorides represent a universal class of initiators for the metal-catalyzed living radical polymerization of styrenes, acrylates, and methacrylates. In contrast to alkyl halide-based initiators that produce carbon-centered radicals during the initiation process, sulfonyl halide-based initiators generate sulfonyl radicals that, in contrast to carbon-centered radicals, do not dimerize via an irreversible mechanism. This property of sulfonyl halide-based initiators provides many opportunities for complex organic synthesis via living radical polymerization processes. Although a large variety of catalysts[2] have been employed in this polymerization process, copper halide-based catalysts are the least expensive. However, there are several disadvantages associated with CuCl and CuBr catalysts. First, they oxidize easily to Cu$^{II}$ species in the presence of air.[3] Second, the solubilities of Cu$^{I}$ and Cu$^{II}$ species in the presence of bidentate or tridentate ligands are different, so mechanistic investigations and the dynamic equilibrium between radical and covalent propagating species are affected by an unknown Cu$^{I}$/Cu$^{II}$ ratio. Third, the polymerization mixture catalyzed by CuCl or CuBr is acidic and, therefore, generates numerous preparative limitations.

Recently, we demonstrated that Cu(0)[1(f,g)] and $Cu_2O$[1(f,g)] in the presence of ligands such as 2,2′-bipyridine (Bpy),[1(a,b)] 4,4′-dinonyl-2,2′bipyridine, and 2-(2-pyridyl)-4,5-dihydrooxazole[1(f)] provide a valuable alternative to CuCl-based and CuBr-based catalysts. In addition, the catalytic activity of $Cu_2O$ is enhanced and the induction time of this reaction is eliminated by phase-transfer catalysis.[1(f)] We believe that $Cu_2O$ generates, *in situ*, extremely reactive and soluble CuCl species.

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**Table I.** Polymerization of MMA Initiated with PDSC and Catalyzed by $Cu_2O$, $Cu_2S$, $Cu_2Se$, $Cu_2Te$, CuCl, CuO, CuS, and CuSe in the Presence of Bpy at 90 °C in $Ph_2O$ ([MMA] = 6.3*M*)

| Run | Catalyst | [M]/[I]/ [Catalyst]/ [Bpy] | $k_p^{\exp} \times 10^3$ ($\min^{-1}$) | $t_{\text{ind}}$ (min) | $M_w/M_n$ | Time (h) | Conversion (%) | Initiator Efficiency[a] (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | $Cu_2O$ | 200/1/2/6 | 3.2 | 74 | 1.11 | 21.5 | 98 | 98 |
| 2 | $Cu_2S$ | 200/1/2/6 | 16.8 | 20 | 1.11 | 4.0 | 98 | 98 |
| 3 | $Cu_2Se$ | 200/1/2/6 | 27.7 | 12 | 1.11 | 2.0 | 95 | 98 |
| 4 | $Cu_2Te$ | 200/1/2/6 | 57.6 | 9 | 1.11 | 1.2 | 97 | 99 |
| 5 | CuCl | 200/1/2/6 | 37.3 | 0 | 1.12 | 1.2 | 93 | 98 |
| 6 | CuO | 200/1/4/12 | <0.1 | — | 2.5 | 38 | 19 | — |
| 7 | CuS | 200/1/4/12 | 2.0 | 58 | 1.11 | 23.2 | 93 | 99 |
| 8 | CuSe | 200/1/4/12 | 14.3 | 11 | 1.13 | 2.8 | 90 | 96 |

[a] Determined as the slope of the plot of $M_{n,\text{GPC}}$ versus $M_{th}$ ($M_{th}$ = [M]/[I] × 100.12 × conversion (%)/100 + 367).

At the same time, this catalyst maintains neutral reaction conditions throughout the polymerization process.

The results obtained with $Cu_2O$ prompted us to investigate an entire series of $Cu^I$ and $Cu^{II}$ salts of group VI elements to identify more soluble and active catalysts for living radical polymerization.

$Cu_2O$[4(a,f–i)] and CuO[4(a–g)] were previously reported as catalysts for the Kharasch addition of alkyl halides to olefins and related radical addition reactions. CuS was used as a catalyst in other radical reactions[5(a)] and for the oxidative polymerization of 2,6-dimethylphenol.[5(b)] CuSe was employed as a catalyst for olefin epoxidation[6(a)] and other radical oxidations,[6(b,c)] whereas $Cu_2Te$ was used as a catalyst for the synthesis of alkylhalosilanes[7(a)] and acrolein.[7(b)] To the best of our knowledge, there are no reports on the $Cu_2Y$-catalyzed or CuY-catalyzed (where Y is S, Se, or Te) radical polymerization of vinyl monomers initiated with alkyl halides or sulfonyl halides. Also, there are no previous reports on the radical addition of alkyl or arylsulfonyl chlorides to multiple bonds catalyzed by $Cu_2Y$ or CuY (where Y is S, Se, or Te). Here, we report the first examples of the catalytic use of these compounds together with Bpy as a ligand in the sulfonyl chloride-initiated living radical polymerization of methyl methacrylate (MMA).

## RESULTS AND DISCUSSION

Table I presents the polymerization of MMA initiated from 4,4′-bis(chlorosulfonyl)diphenylether[1(c)] at 90 °C in diphenyl ether ($Ph_2O$) and catalyzed by $Cu_2Y$/Bpy and CuY/Bpy (where Y is O, S, Se, or Te). A CuCl/Bpy-catalyzed polymerization under the same conditions is included for comparison. The corresponding first-order kinetic plots for the $Cu_2Y$-catalyzed and CuY-catalyzed polymerizations are shown in Figure 1(a,b). As evidenced by Figure 1, the number of growing chains for each system was constant in time. A continuous increase in the experimental rate constant of polymerization ($k_p^{\exp}$) in the order O < S < Se < Te and a simultaneous decrease in the induction times of the polymerization were observed. These trends qualitatively paralleled the decrease in the ionic character and strength of the Cu—Y bond, the increase in the softness of $Y^{-2}$ anion, and the increase in the solubility and metallic character of the $Cu_2Y$ or CuY salt in going from O to S to Se to Te. The corresponding linear dependencies of the experimental molecular weights, as determined by gel permeation chromatography (GPC), versus the theoretical molecular weights are plotted in Figure 2. With the exception of the CuO-based polymerization, which did not progress further than a 20% conversion, as calculated from Figure 2 and listed in Table I, the initiator efficiency was in all cases greater than or equal to 98%. As shown in Figure 3, although the polydispersities started from higher values for the $Cu_2Y$ catalysts, in all cases they converged to values lower than 1.15. These features are typical of a living polymerization mechanism. In addition, in all cases $Cu_2Y$-based catalysts provided higher $k_p^{\exp}$ values and shorter induction times than the corresponding CuY catalysts.

A potential explanation for these results is provided by mechanistic considerations. Although

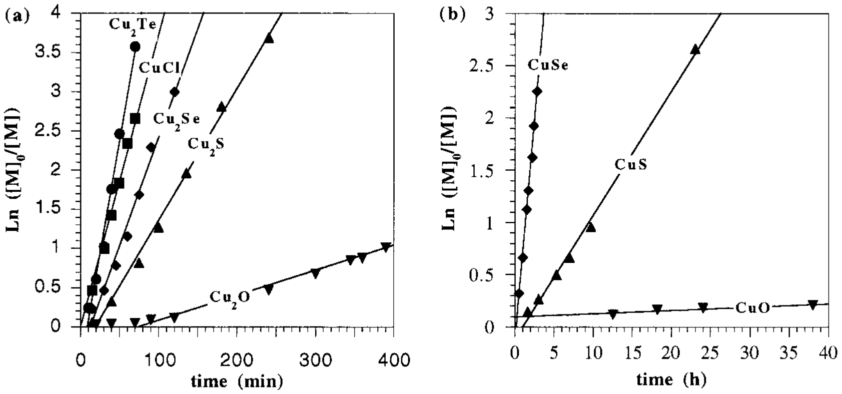

**Figure 1.** First-order kinetic plots for the polymerization of MMA at 90 °C in $Ph_2O$ catalyzed by (a) $Cu_2Te$, CuCl, $Cu_2Se$, $Cu_2S$, and $Cu_2O$, [MMA]/[PDSC]/[catalyst]/[Bpy] = 200/1/2/6, and (b) CuSe, CuS, and CuO, [MMA]/[PDSC]/[catalyst]/[Bpy] = 200/1/4/12 ([MMA] = 6.3 M).

the mechanism for the $Cu_2O$-catalyzed and CuO-catalyzed Kharasch addition was never unequivocally elucidated,[4(e)] it is reasonable to assume that the polymerization was mediated via the *in situ* generation of the $CuCl/CuCl_2$ pair, which catalyzed the process as previously described.[1] The formation mechanism of CuCl and $CuCl_2$ from $Cu_2Y$ and CuY might have occurred as described next, where R is either the initiator fragment or the growing chain:

$$\text{R-Cl} + Cu_2Y \rightarrow R^\bullet + \text{CuCl} + \text{CuY} \quad (1)$$

$$2\text{R-Cl} + Cu_2Y \rightarrow 2\,R^\bullet + 2\text{CuCl} + [Y] \quad (2)$$

$$Cu_2Y \rightarrow \text{Cu}(0) + \text{CuY} \quad (3)$$

$$\text{Cu}(0) + \text{R-Cl} \rightarrow R^\bullet + \text{CuCl} \quad (4)$$

$$\text{R-Cl} + \text{CuCl} \rightarrow R^\bullet + CuCl_2 \quad (5)$$

$$\text{R-Cl} + \text{CuY} \rightarrow [\text{R-Cu}^{III}\text{YCl}] \rightarrow R^\bullet + \text{CuCl} + [Y] \quad (6)$$

$$\text{R-Cl} + \text{CuY} \rightarrow [\text{R-Y-Cu-Cl}] \rightarrow \text{R-Y}^\bullet + \text{CuCl} \quad (7)$$

$$Cu_2Y + CuCl_2 \rightarrow \text{CuY} + 2\text{CuCl} \quad (8)$$

$Cu_2Y$ and CuY may also act as reversible terminators of the growing chain:

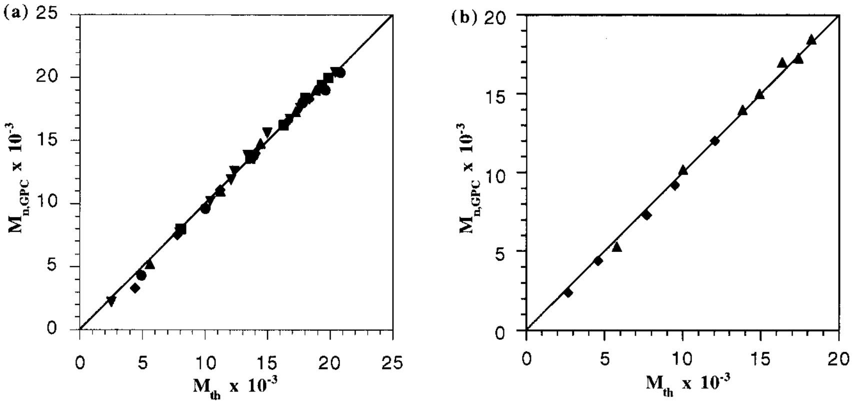

**Figure 2.** Dependence of the experimental (GPC) molecular weight on the theoretical molecular weight for the metal-catalyzed living radical polymerization of MMA at 90 °C in $Ph_2O$ catalyzed by (a) $Cu_2Te$ (●), CuCl (■), $Cu_2Se$ (◆), $Cu_2S$ (▲), and $Cu_2O$ (▼), [MMA]/[PDSC]/[catalyst]/[Bpy] = 200/1/2/6, and (b) CuSe (◆), and CuS (▲), [MMA]/[PDSC]/[catalyst]/[Bpy] = 200/1/4/12 ([MMA] = 6.3 M).

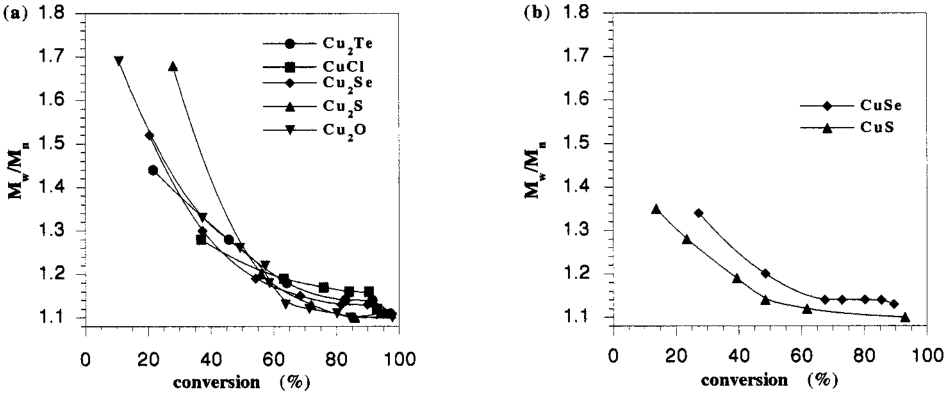

**Figure 3.** Dependence of the polydispersity on the conversion for the metal-catalyzed living radical polymerization of MMA at 90 °C in $Ph_2O$ catalyzed by (a) $Cu_2Te$, CuCl, $Cu_2Se$, $Cu_2S$, and $Cu_2O$, [MMA]/[PDSC]/[catalyst]/[Bpy] = 200/1/2/6, and (b) CuSe and CuS, [MMA]/[PDSC]/[catalyst]/[Bpy] = 200/1/4/12 ([MMA] = 6.3 M).

$$R^\bullet + Cu_2Y \rightarrow \text{R-Cu-Y-Cu} \rightarrow \text{R-Cu}^\bullet + CuY \quad (9)$$

$$R^\bullet + CuY \rightarrow \text{R-Y-Cu} \rightarrow \text{R-Y}^\bullet + Cu(0) \quad (10)$$

The formation of the elemental [Y] in similar reactions was previously proposed.[4(e),8] Therefore, the continuous increase in $k_p^{exp}$ and the decrease in the corresponding induction times on going from Y = O to Y = Te may be explained by a combination of factors. First, because of the weakening of the Cu—Y bond in the Y = O to Y = Te series, the rate of CuCl generation in the system increased accordingly. Second, the inhibiting/retarding ability of the elemental [Y] species, which might have been generated as outlined, decreased in the same way, which was reflected in the parallel decrease of the induction times. For the polymerization catalyzed by CuO, the effect of the *in situ* generation of [O] was appreciable because the polymerization stopped at a 20% conversion. These arguments hold both for $Cu_2Y$ and CuY catalysts. For the same Y, the difference in the catalytic activity between $Cu_2Y$ and CuY could be explained by a combination of their different solubilities and reactivities (i.e., rates of CuCl generation). Of course, the real mechanism might have been more complex, as it is known that $Cu_2S$, CuS, $Cu_2Se$, CuSe, and $Cu_2Te$ display semiconductor/photosensitizer[9(a–c)] or even metallic[9(d)] properties. In addition, the values of $k_p^{exp}$ include the $[Cu^I]/[Cu^{II}]$ ratios,[1(d)] which in reality may be determined not only by [CuCl] and $[CuCl_2]$ but also by a combination of $[Cu_2Y]$ and [CuY].

Although CuTe was not available for comparison, it was interesting to note that $k_p^{exp}{}_{CuSe}$ was greater than $k_p^{exp}{}_{Cu2O}$ and $k_p^{exp}{}_{CuSe}$ was similar to $k_p^{exp}{}_{Cu2S}$. It is possible that the higher solubility and increased reactivity of CuSe were responsible for this result. As seen in Table I, CuCl had the second highest $k_p^{exp}$ value and had no induction time. Interestingly, the $k_p^{exp}$ value for the $Cu_2Te$-catalyzed polymerization was 1.57 times larger than the one for the CuCl-catalyzed polymerization. In this case, according to the speculative mechanism previously described, it is possible that both Cu atoms in $Cu_2Te$ led to the formation of CuCl in a concentration that was higher than in the CuCl-catalyzed polymerization experiment. In addition, the *in situ* generated CuCl was more reactive and more soluble than the commercial CuCl.

In conclusion, $Cu_2Y$/Bpy and CuCl/Bpy (where Y is O, S, Se, or Te) represent a new, extremely efficient, and valuable class of catalysts for the living radical polymerization initiated with sulfonyl chlorides.

## EXPERIMENTAL

### Materials

All materials, unless otherwise noted, were purchased from Aldrich. Copper (I) oxide (Alfa; >95%), copper (II) oxide (99.995%), copper (I) sulfide (99.99%), copper (II) sulfide (>99%), copper (I) selenide (99.95%), copper (II) selenide (99.99%), copper (I) telluride (Alfa; 99.5%), and copper (I) chloride (>99.995%) were used as received. MMA (Fisher; >98%) was first distilled from $CaH_2$ and then was passed through a basic $Al_2O_3$ chromatographic column (flash). Bpy was recrystallized from hexane. Phenoxybenzene-4,4′-disulfonyl chloride (PDSC) was synthesized as previously reported.[1c] $Ph_2O$ was distilled prior to use.

### Techniques

$^1H$ NMR (500-MHz) spectra were recorded on a Bruker DRX500 at 20 °C in $CDCl_3$ with tetramethylsilane as an internal standard. GPC analyses were performed on a PerkinElmer series 10 high-pressure liquid chromatograph equipped with an LC-100 column oven (40 °C), a Nelson Analytical 900 series integrator data station, a PerkinElmer 785A ultraviolet–visible detector (254 nm), a PerkinElmer LC-25 refractive index detector, and two AM gel columns (10 $\mu$m, 500 Å; 10 $\mu$m, $10^4$ Å). Tetrahydrofuran (Fisher; high-performance liquid chromatography grade) was used as an eluent at a flow rate of 1 mL/min. Number-average and weight-average molecular weights ($M_n$ and $M_w$, respectively) were determined from calibration plots constructed with poly(methyl methacrylate) (PMMA) standards.

### Typical Procedure for Polymerization Kinetics

Monomer (MMA, 2 mL, 18.8 mmol), solvent ($Ph_2O$, 1 mL), initiator (PDSC, 34.4 mg, 0.094 mmol), catalyst ($Cu_2Te$, 47.7 mg, 0.187 mmol), and ligand (Bpy, 87.8 mg, 0.562 mmol) were weighted directly in a 25-mL Schlenk tube. After four freeze–pump–thaw cycles, the tube was filled with argon, and the reaction mixture was heated at 90 °C in an oil bath. The side arm of the tube was purged with argon for at least 5 min before it was opened for samples to be removed at predetermined times with an airtight syringe. Samples were dissolved in $CDCl_3$, and the conversion was measured by $^1H$ NMR spectroscopy. A part of the solution was also injected in the GPC, and the number-average and weight-average molecular weights were measured versus PMMA standards with the refractive index detector. A UV signal was also observed for all samples because of the phenyl groups derived from the initiator.

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