

Interaction of Propagating Radicals with Copper(I) and Copper(II) Species

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ABSTRACT: The effects of copper(I) and copper(II) metal centers on the atom transfer radical polymerization (ATRP) of styrene and methyl acrylate were investigated. The free-radical polymerizations were initiated by AIBN in the presence of copper(I) and copper(II) complexes. For methyl acrylate, the rate of the polymerization was reduced in the presence of $\text{Cu}^{\text{I}}\text{Br}/\text{dNbpy}$ and $\text{Cu}^{\text{I}}\text{OTf}/\text{dTbpy}$ but was unaffected by the presence of $\text{Cu}^{\text{II}}(\text{OTf})_2/\text{dTbpy}$. For styrene, under conditions which yield relatively low molecular weight polymer (16 000), no effect was observed in the presence of $\text{Cu}^{\text{II}}(\text{OTf})_2/\text{dNbpy}$; however, under conditions which yield high molecular weight polystyrene (50 000–100 000), the polymerization was limited in the molecular weight attainable and stopped at partial conversion. No effect was observed for the free-radical polymerization of styrene in the presence of copper(I) complexes. These results indicate that control in ATRP does not originate in interactions of growing radicals with copper complexes but in the reversible halogen atom transfer.

Introduction

The advent of living polymerizations has enabled the synthesis of well-defined polymers with narrow molecular weight distribution (MWD) and predictable molecular weight by an anionic mechanism.¹ Several approaches toward controlling radical polymerizations by promoting “living” character have been proposed.² Radical processes are always accompanied by termination reactions and can therefore never be truly living; however, by maintaining a dynamic equilibrium between active radicals and a large concentration of dormant species via reversible deactivation, and enabling a fast and quantitative initiation, a controlled (or “living”) polymerization is attainable.³ To date, several processes achieve a significant level of control in radical polymerizations. These include nitroxide-⁴ and metal-mediated⁵ polymerizations. One of the most versatile methods is atom transfer radical polymerization (ATRP),⁶ which employs reversible deactivation of a propagating radical chain by repetitive transfer of (pseudo) halogen atoms from transition metals acting as a catalyst/deactivator.

Well-defined polymers with predictable molecular weights and with low polydispersities can be synthesized by ATRP. Improvements to these processes have been aimed toward application to new monomers, new initiators and new architectures, compositions, and functionalities.⁷ In ATRP, recent advances have also been in the direction of new ligands⁸ and new metals⁹ which affect the activity and selectivity of the ATRP catalysts toward the monomer. Also, improvements have been made in ATRP by the addition of small amounts of zerovalent metal.¹⁰ There are limits to this process, however. For instance, the monomers available are limited to activated alkenes such as styrenes, acrylonitrile, and (meth)acrylates. Also, the molecular weight attainable with a narrow MWD is limited for each monomer.

ATRP proceeds by a reversible redox process between an alkyl halide ($\text{R}-\text{X}$), as an initiator, and a transition metal complex ($\text{Cu}(\text{I})$). The predominant interaction is believed to be a reversible inner-sphere electron transfer

reaction transferring the halogen atom to the transition metal complex to form an organic radical and an oxidized metal complex ($\text{X}-\text{Cu}(\text{II})$).¹¹ Although this atom transfer process is the predominate reaction occurring in this system, there is the potential for other interactions between the propagating radical chain and the transition metal complexes. For instance, outer-sphere electron transfer may be an important side reaction in these systems. Electrophilic radicals could be reduced by $\text{Cu}(\text{I})$ to form an anion and $\text{Cu}(\text{II})$, whereas nucleophilic radicals could be oxidized by $\text{Cu}(\text{II})$ to form a cation and $\text{Cu}(\text{I})$. Another possibility is a direct reaction between the radical and $\text{Cu}(\text{I})$ or $\text{Cu}(\text{II})$ yielding the reactive $\text{R}-\text{Cu}(\text{II})$ or $\text{R}-\text{Cu}(\text{III})$, respectively. Such reactions have been reported in aqueous solution with unstabilized radicals and sterically unencumbered metal centers.¹²

To probe reactions in the polymerization system which may be limiting the molecular weight or otherwise affecting the control of the polymerization, experiments were designed to determine the presence of interactions of growing radical chains in the conventional radical polymerization of styrene and methyl acrylate monomers with $\text{Cu}(\text{I})$ and $\text{Cu}(\text{II})$ metal centers. Methyl acrylate and styrene were chosen since we feel they represent two limiting cases where the nucleophilic styrene-derived radical is likely to be oxidized and the electrophilic acrylate radical is most likely to be reduced; methyl methacrylate will occupy the intermediate position. Here we report AIBN-initiated free-radical polymerizations of styrene and methyl acrylate (MA) in the presence of $\text{L}_2\text{Cu}(\text{OTf})_2$ and L_2CuBr or $\text{L}_2\text{Cu}(\text{OTf})$ ($\text{L} = 4,4'$ -di-5-nonyl-2,2'-bipyridine (dNbpy) for styrene; $4,4'$ -di-*tert*-butyl-2,2'-bipyridine (dTbpy) for MA) and compare the results to the polymerizations in the absence of any copper complexes. The potential reversible interactions of radicals with Cu species should affect reaction rates and, additionally, molecular weights and polydispersities. On the other hand, outer-sphere electron transfer could produce cations or anions which could participate in other reactions.

Experimental Section

Materials. Styrene and methyl acrylate were passed through an alumina column and vacuum distilled over CaH_2 and stored at -15°C . Benzene was freshly distilled by standard procedures. $\text{Cu}(\text{OTf})_2$ was obtained from Aldrich and used without purification. The ligands 4,4'-di-5-nonyl-2,2'-bipyridine (dNbpy) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dTbpy) were prepared according to the reported procedure.¹⁶

Characterization. Monomer conversion was determined by measurement of residual monomer relative to chlorobenzene as an internal standard using a Shimadzu GC-14 gas chromatograph with a J&W Scientific 30 m DB-WAX column with a Shimadzu CR501 Chromatopac. Molecular weights and molecular weight distributions were measured using a Waters 712 WISP autosampler and the following Phenogel GPC columns: guard, linear, 1000 Å, and 100 Å. Polystyrene standards were used to calibrate the columns.

1. AIBN-Initiated Polymerization of Methyl Acrylate (MA). To a 10 mL Schlenk flask were added methyl acrylate, 3.0 mL (33 mmol); AIBN, 6 mg (0.04 mmol); toluene, 3.0 mL; and 0.6 mL of chlorobenzene as an internal standard. The reaction solution was degassed by three freeze-pump-thaw cycles and put under an atmosphere of argon. The colorless reaction solution was then heated to 60°C . During the course of the reaction, 0.2 mL aliquots were removed and diluted with THF. These samples were analyzed for % monomer conversion (GC) and for M_n and M_w/M_n (GPC).

2. AIBN-Initiated Polymerization of Methyl Acrylate (MA) in the Presence of $\text{Cu}^{\text{II}}(\text{OTf})_2/\text{dTbpy}$. A reaction solution identical to that described above was prepared. To this solution was added $\text{Cu}(\text{OTf})_2$, 6 mg (0.016 mmol); and dTbpy, 9 mg (0.033 mmol). The light blue solution was degassed by three freeze-pump-thaw cycles and heated to 60°C under argon. No color change was observed throughout the course of the reaction.

3. AIBN-Initiated Polymerization of Methyl Acrylate (MA) in the Presence of $\text{Cu}^{\text{I}}(\text{OTf})/\text{dTbpy}$. A reaction solution identical to that described in point 1 was prepared. To this solution was added $\text{Cu}(\text{OTf})_2$, 12 mg (0.033 mmol); Cu^0 , 2.1 mg (0.033 mmol); dTbpy, 18 mg (0.067 mmol); and 3.0 mL of toluene. [$(\text{dTbpy})_2\text{Cu}(\text{OTf})$ is formed in situ by the reaction of $(\text{dTbpy})_2\text{Cu}(\text{OTf})_2$ with copper powder.] The light blue solution was then degassed by three freeze-pump-thaw cycles and heated to 60°C under argon. The color of the solution changed to a dark red-brown over the course of approximately 45 min.

In a separate reaction, a $\text{Cu}^{\text{I}}\text{OTf}$ /benzene complex was synthesized by a literature preparation¹³ and complexed with dTbpy and used as the $\text{Cu}(\text{I})$ source: $[\text{Cu}(\text{OTf})_2\text{C}_6\text{H}_6]$, 8 mg (0.016 mmol); dTbpy, 17 mg (0.064 mmol).

Similarly, the reaction with $[\text{Cu}(\text{OTf})_2\text{C}_6\text{H}_6]$, 20 mg (0.039 mmol), and dTbpy, 42 mg (0.157 mmol), was performed identically to that described above.

4. AIBN-Initiated Polymerization of Styrene. **a.** To a 10 mL Schlenk flask was added styrene, 3.0 mL (26 mmol); AIBN, 48 mg (0.29 mmol); benzene, 1.5 mL; and 0.6 mL of chlorobenzene as an internal standard. The reaction solution was degassed by three freeze-pump-thaw cycles. The colorless reaction solution was then heated to 70°C under argon. During the course of the reaction, 0.2 mL aliquots were removed and diluted with THF. These samples were analyzed for % monomer conversion (GC) and for M_n and M_w/M_n (GPC). The polymerization reached a monomer conversion of 56% in 6.5 h, and M_n was around 15 000.

b. For polymer molecular weights near 50 000: styrene, 6.0 mL (52 mmol); AIBN, 6.5 mg (0.04 mmol); benzene, 3.0 mL; and 1.0 mL of chlorobenzene as an internal standard were added to a 25 mL Schlenk flask. The colorless solution was degassed and heated to 80°C . The polymerization reached a monomer conversion of 50% after 45 h, and M_n was around 50 000.

c. For polymer molecular weights near 110 000: styrene, 10.0 mL (87 mmol); AIBN, 4 mg (0.024 mmol); benzene, 3.0 mL; and 1.5 mL of chlorobenzene as an internal standard were

added to a 25 mL Schlenk flask. The colorless solution was degassed and heated to 85°C . The polymerization reached a monomer conversion of 39% after 46 h, and M_n was around 110 000.

5. AIBN-Initiated Radical Polymerization of Styrene in the Presence of $\text{Cu}^{\text{II}}(\text{OTf})_2/\text{dNbpy}$. **a.** Under identical reaction conditions to those described in **4a**, a separate reaction was run in the presence of $\text{Cu}(\text{OTf})_2$, 16 mg (0.044 mmol); and dNbpy, 68 mg (0.166 mmol). The solution was degassed and heated to 70°C . Initially the solution was light blue with a light blue precipitate. As the solution was heated, the color gradually became light yellow-brown. The polymerization reached a monomer conversion of 52% after 6 h, and M_n was around 16 000.

b. Under identical reaction conditions to that described in **4b**, a separate reaction was run in the presence of $\text{Cu}(\text{OTf})_2$, 16 mg (0.044 mmol); and dNbpy, 68 mg (0.166 mmol). The solution was degassed and heated to 80°C . The light blue solution turned a dark red-brown after 45 min of heating. After approximately 35 h of heating, the solution turned a light green color. The polymerization reached a maximum monomer conversion of 29% in 14.5 h, and M_n was around 35 000.

c. Under identical reaction conditions to that described in **4c**, a separate reaction was run in the presence of $\text{Cu}(\text{OTf})_2$, 16 mg (0.044 mmol); and dNbpy, 68 mg (0.166 mmol). The solution was degassed and heated to 85°C . The light blue solution turned a dark red-brown after 45 min of heating. After approximately 35 h of heating, the solution turned a light green color. The polymerization reached a maximum monomer conversion of 14% in 6 h, and M_n was around 40 000.

6. AIBN-Initiated Radical Polymerization of Styrene in the Presence of $\text{Cu}^{\text{I}}(\text{OTf})/\text{dNbpy}$. **a.** Under identical reaction conditions to those described for **4a**, a separate reaction was run in the presence of $\text{Cu}(\text{OTf})_2$, 16 mg (0.044 mmol); dNbpy, 68 mg (0.166 mmol); and Cu^0 , 3.0 mg (0.047 mmol). [$(\text{dNbpy})_2\text{Cu}(\text{OTf})$ is formed in situ by the reaction of $(\text{dNbpy})_2\text{Cu}(\text{OTf})_2$ with copper powder.] The solution turned from light blue to dark red-brown upon heating to 70°C over a period of 40 min. The polymerization reached a monomer conversion of 61% after 8 h, and M_n was around 15 000.

b. Under identical reaction conditions to that described for **4b**, a separate reaction was run in the presence of $\text{Cu}(\text{OTf})_2$, 16 mg (0.044 mmol); dNbpy, 68 mg (0.166 mmol); and Cu^0 , 3.0 mg (0.047 mmol).

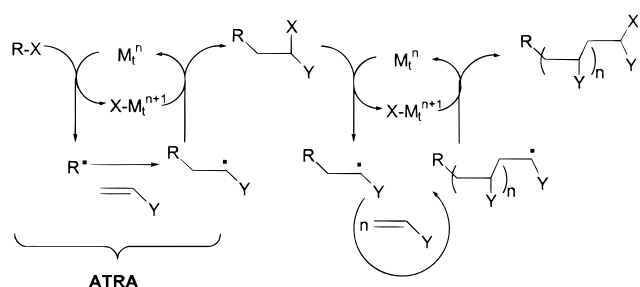
c. Under identical reaction conditions to that described for **4c**, a separate reaction was run in the presence of $\text{Cu}(\text{OTf})_2$, 16 mg (0.044 mmol); dNbpy, 68 mg (0.166 mmol); and Cu^0 , 3.0 mg (0.047 mmol).

Results and Discussion

Atom Transfer Radical Addition (ATRA) and Atom Transfer Radical Polymerization (ATRP). Atom transfer radical addition¹⁴ originates from an atom transfer from an organic halide to a transition metal complex to generate an organic radical. This radical can then add to an alkene which, followed by back-transfer of the halogen from the transition metal complex, results in the final product. The substrates are chosen such that the radical formed, after addition to an alkene, is much less stabilized than the initial radical. The back-transfer is then irreversible, and only one addition step should occur.

In ATRP, only alkenes which will form stabilized radicals can be used. In this sense, the inner-sphere electron transfer process is reversible, and the activation/addition/deactivation steps are realized until all of the unsaturated substrate is consumed. Ideally the number of these cycles should be equal to DP, defined by the ratio $[\text{M}]_0/[\text{I}]_0$. However, it is possible that either more than one monomer unit is added during one activation step or not all activations are accompanied by monomer addition. Scheme 1 shows the mechanism

Scheme 1



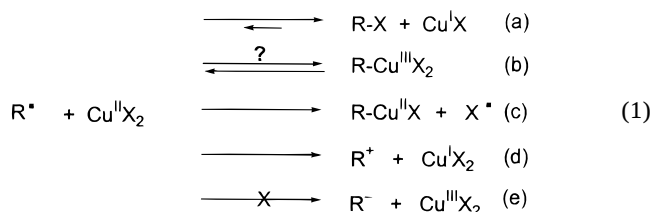
of ATRA and ATRP. A stabilized radical is formed by a reversible halide abstraction from an alkyl halide initiator by a transition metal complex. In this step, the metal catalyst undergoes a one-electron oxidation with simultaneous abstraction of a halogen atom from an alkyl halide. The radical can then add to monomer to form a propagating radical chain which can then be deactivated by back-transfer from the oxidized metal complex. The number of monomer additions which occur before deactivation, affects the control of the polymerization and, in turn, is directly related to the concentration of the deactivating transition metal complex ($X-M_t^{n+1}$).

Termination by radical coupling and disproportionation are always present in radical polymerizations, but their contribution in ATRP is limited to a few percent of the polymer chains; however, the significance of these termination reactions becomes greater at higher monomer conversion. Other side reactions have been previously identified which limit the molecular weights attainable by ATRP.¹⁵

Interaction of Radicals with $L_2Cu^{II}Br_2$. Reverse ATRP. It has been previously shown in our group that a copper(II) halide complex can be in the reaction coordinate for ATRP.¹⁶ If an AIBN-initiated free-radical polymerization of styrene, MA, or methyl methacrylate (MMA) is run in the presence of a homogeneous $CuBr_2/dNbpy$ complex, the free-radical system enters into an ATRP system.¹⁷ This "reverse ATRP" process occurs by a halogen atom transfer from $L_2Cu^{II}Br_2$ to a propagating radical to form the dormant polymer chain ($P-Br$) and $L_2Cu^{II}Br$, which is a known ATRP catalyst. These systems display properties of an ATRP polymerization: linear first-order kinetics in monomer, increasing polymer molecular weight with conversion, predictable molecular weights, and low polydispersities.

Interaction of Radicals with $L_2Cu^{II}(OTf)_2$. A variety of reactions between radicals and copper(II) are possible (eq 1). Literature reports of organic radicals interacting with a copper(II) metal center have largely dealt with nonstabilized alkyl radicals reacting with aqueous Cu^{2+} ions.^{12,18} What is typically observed under those conditions is an addition to the metal center to form a Cu(III) intermediate (metastable complex). These are reportedly very reactive species, and decomposition products are analyzed to establish involved reactions. Which reactions occur depends on the nature of the alkyl group and the metal counterion. As stated, these results were in aqueous solution mostly with free Cu^{2+} . ATRP is much different: relatively nonpolar, nonprotic solvents with a metal center complexed with two "bpy" ligands which effect both the electrochemistry and the sterics of the copper species. Equation 1 shows possible interactions of radicals with a $Cu^{II}X_2$ complex.

In ATRP, when a $CuBr_2/dNbpy$ complex is in the presence of radicals derived from styrene, MA, or MMA,



ligand transfer by an inner-sphere electron transfer is the major mode of reaction. If there are no ligands capable of an inner-sphere electron transfer then reactions with the radicals, which were previously overshadowed by this reaction, may become apparent. To probe whether other interactions between propagating radicals and Cu(II) are possible, the AIBN-initiated free-radical polymerizations of styrene and MA were run in the presence of $L_2Cu(OTf)_2$ ($L = dNbpy, dTbpy$).

For MA, there was no indication of an interaction between growing radicals and Cu(II). The polymerization proceeded with the same rate, and the polymers displayed similar molecular weights as in the absence of a Cu(II) complex. The polymerization of MA was relatively fast which may limit the appearance of side reactions with Cu(II) which may occur, but at a slow rate.

In contrast, for styrene there was a significant change in the polymerization in the presence of Cu(II) when attempting to form high molecular weight polymer. When high concentrations of AIBN was used which led to molecular weights of polystyrene around 16 000, copper(II) had no effect on the polymerization (Figure 1). When conditions were employed to reach an M_n around 50 000, some interactions with Cu(II) became visible when the polymerization was run in the presence of $L_2Cu(OTf)_2$ (Figure 2). The light blue color of $L_2Cu(OTf)_2$ turned to a red-brown color and the polystyrene molecular weights only reached about 35 000. Also, the polymerization only went to a maximum of 29% monomer conversion after 12 h; longer reaction times did not increase monomer conversion. A more dramatic effect was observed when the polymerization conditions allowed for the polymerization of polystyrene reaching an M_n of around 110 000 (Figure 3). Under identical reaction conditions but in the presence of $Cu(OTf)_2/dNbpy$, the polymerization yielded polystyrene with M_n of only 40 000, and the polymerization stopped after 8 h after only reaching 14% conversion of monomer.

Clearly an interaction between the growing polystyryl radicals and the $L_2Cu(OTf)_2$ complex limits the molecular weight of the polystyrene chain. Also, an inhibition of the polymerization is observed at later stages since monomer conversion stops at low conversion. The polystyryl radical is presumably oxidized by Cu(II) to form a polystyryl cation and Cu(I). This seems possible due to the observed color change of the reaction solution during the early stages of the polymerization. The color changed from light blue for the $Cu(OTf)_2/dNbpy$ complex to a red-brown color indicative of Cu(I) complexed with bpy ligands. When lower molecular weights are targeted, no effect is observed with Cu(II). This is likely due to the sufficiently rapid formation of the low molecular weight polymer, and negligible contribution of side reactions. Alternatively, a reaction to form $R-Cu(III)$ is possible, followed by decomposition of this reactive species.

Upon formation of the polystyrene cation, rapid termination could occur by the presence of adventitious

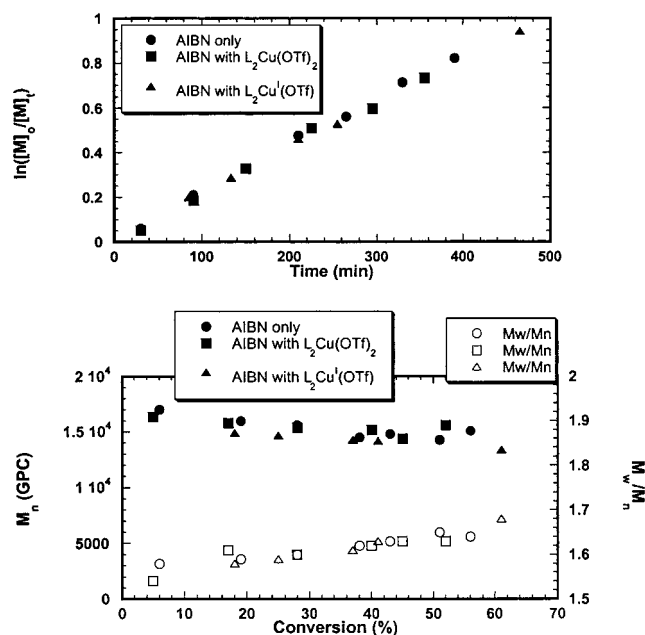


Figure 1. Kinetics and evolution of M_n and M_w/M_n with conversion in AIBN-initiated polymerization of styrene. Styrene, 3.0 mL (26 mmol); AIBN, 48 mg (0.29 mmol); benzene, 1.5 mL; 70 °C. Under the same conditions in the presence of: $[\text{Cu}(\text{OTf})_2]$, 16 mg (0.044 mmol); dNbpy, 68 mg (0.166 mmol). Under the same conditions in the presence of: $[\text{Cu}(\text{OTf})_2]$, 16 mg (0.044 mmol); dNbpy, 68 mg (0.166 mmol); copper powder, 3 mg (0.047 mmol).

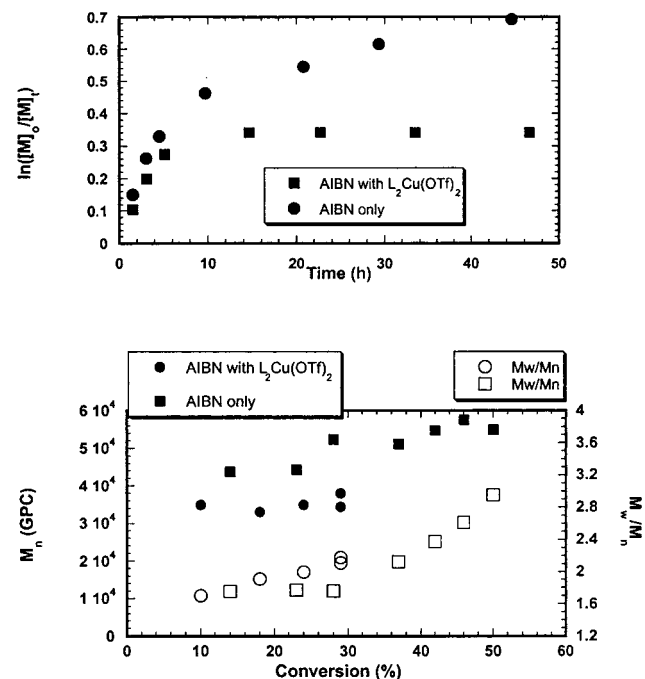


Figure 2. Kinetics and evolution of M_n and M_w/M_n with conversion in AIBN-initiated polymerization of styrene. Conditions: Styrene, 6.0 mL (52 mmol); AIBN, 6.5 mg (0.04 mmol); benzene, 3 mL; 80 °C. Under the same conditions in the presence of $\text{Cu}(\text{OTf})_2$, 16 mg (0.044 mmol); and dNbpy, 68 mg (0.166 mmol).

water and high temperature. If the radicals attack the $\text{Cu}(\text{II})$ species to yield a $\text{Cu}(\text{III})$ intermediate, then elimination, solvolysis, or displacement could occur.

Although all of the reactions in eq 1 are possible, however in our system some are more likely than others. If the copper(II) complex contains a ligand capable of

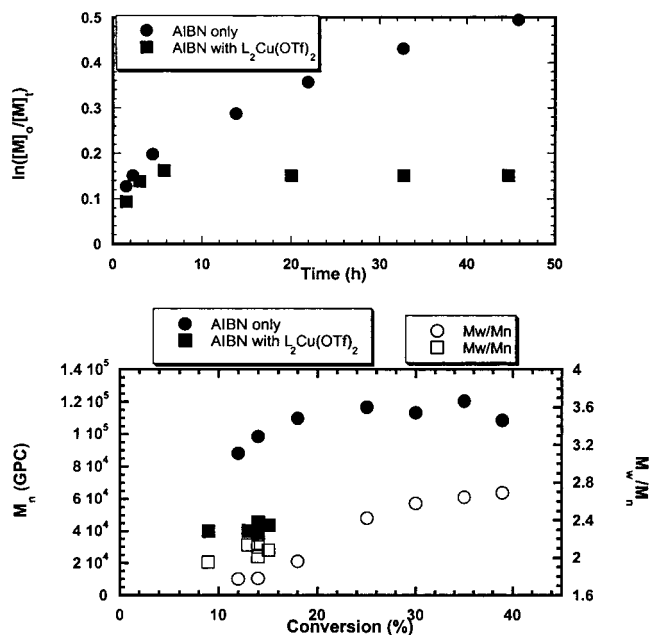
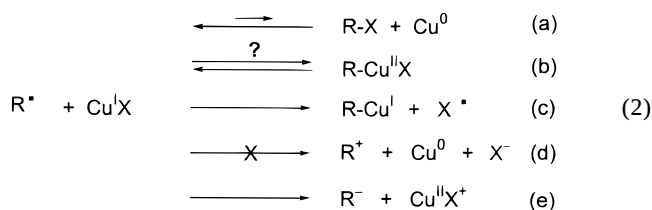


Figure 3. Kinetics and evolution of M_n and M_w/M_n with conversion in AIBN-initiated polymerization of styrene. Conditions: Styrene, 10.0 mL (87 mmol); AIBN, 4.0 mg (0.024 mmol); benzene, 3 mL; 85 °C. Under the same conditions in the presence of $\text{Cu}(\text{OTf})_2$, 16 mg (0.044 mmol); and dNbpy, 68 mg (0.166 mmol).

atom transfer (i.e. halogen), then the atom transfer reaction is most likely to occur here (eq 1a). We observe no evidence for eq 1b or 1c, but this does not rule out their existence. There is some evidence for eq 1d for styrene: polystyrene molecular weights are limited and only partial conversion is observed in the presence of $\text{Cu}(\text{OTf})_2$. Equation 1e is unlikely since the redox potentials are unfavorable for this reaction.

Interactions of Radicals with $\text{L}_2\text{Cu}^{\text{I}}\text{X}$ and $\text{L}_2\text{Cu}^{\text{II}}(\text{OTf})$. Analogous to $\text{Cu}(\text{II})$, $\text{Cu}(\text{I})$ can undergo a variety of reactions with organic radicals. Equation 2 shows possible interactions of radicals with a $\text{Cu}^{\text{I}}\text{X}$ complex.



Meyerstein has elegantly analyzed the reaction of radicals with Cu^+ in aqueous solution.^{12b,19} The predominant pathway is direct reaction to form an alkyl copper(II) complex which can decompose by a variety of pathways depending on nature of the radical: homolysis, heterolysis and carbon-carbon bond formation have all been identified. Recently, Meyerstein has reported on the halide abstraction from $\text{CCl}_3\text{CO}_2^-$ by $\text{Cu}(\text{I})$ in aqueous solution. This atom transfer to form an organic radical slowed dramatically when a Cu^{I} -(fumaric acid) complex is employed.^{19a} The radical then goes on to react with $\text{Cu}(\text{I})$ and $\text{Cu}(\text{II})$ in solution. This is the first such report on the effect of a ligand used to stabilize the $\text{Cu}(\text{I})$ species in these studies. An extension of this research to include copper(I) species in nonaqueous solutions, coordinated with bpy and other ligands, may yield valuable information germane to the mechanism of ATRP.

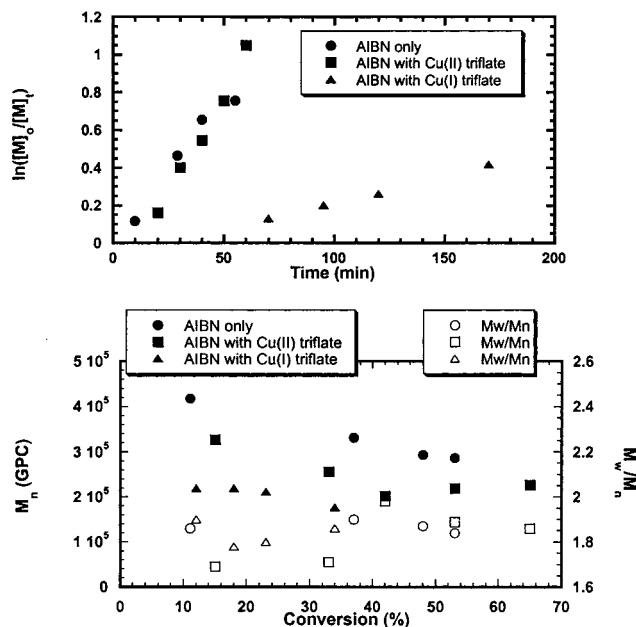


Figure 4. Kinetics and evolution of M_n and M_w/M_n with conversion in AIBN-initiated polymerization of methyl acrylate. Conditions: Methyl acrylate, 3.0 mL (33 mmol); AIBN, 6 mg (0.04 mmol); toluene, 3.0 mL; 60 °C. Under the same conditions in the presence of $\text{Cu}(\text{OTf})_2$, 6 mg (0.016 mmol); and dTbpy, 9 mg (0.033 mmol). Under the same conditions in the presence of $\text{Cu}(\text{OTf})_2$, 12 mg (0.033 mmol); dTbpy, 18 mg (0.067 mmol); and copper powder, 2.1 mg (0.033 mmol).

We have previously reported that the free-radical polymerization of styrene is unaffected by the presence of $\text{Cu}^{\text{I}}\text{Br}/\text{dNbpy}$. This indicates that propagating styrene-derived radicals do not interact in a significant manner with the active ATRP catalyst in solution. On the other hand, it was observed that the free-radical polymerization of MA is slowed by the presence of $\text{Cu}^{\text{I}}\text{Br}/\text{dNbpy}$; however, polymer molecular weights are mostly unaffected.²⁰

The AIBN-initiated free-radical polymerization of styrene and MA were also run in the presence of $\text{L}_2\text{Cu}^{\text{I}}(\text{OTf})$. Identical results were observed regardless of whether $\text{L}_2\text{Cu}^{\text{I}}(\text{OTf})$ was made from the reaction of copper powder with $\text{L}_2\text{Cu}^{\text{I}}(\text{OTf})_2$, or from the addition of ligand to $[\text{Cu}(\text{OTf})_2]\text{C}_6\text{H}_6$. For styrene, there was no change in the kinetics of the polymerization or with the polymer molecular weights or polydispersities. For MA, however, there was an effect on the polymerization (Figure 4). In the presence of $\text{L}_2\text{Cu}^{\text{I}}(\text{OTf})$, the rate of the MA polymerization decreased. These results are in accord with what was previously observed for the CuBr/dNbpy complex.²⁰

It appears that there is a reversible interaction between propagating methyl acrylate-derived radicals and the copper(I) metal center (eq 2b). This lowers the rate of the polymerization, but does not alter the percent conversion obtainable. In a sense, Cu^{I} acts as a deactivator toward the propagating radicals. We have no evidence for reactions shown in eq 2a or 2c, and the reaction in eq 2d is an unfavorable reaction due to redox potentials.

The other possible pathway could involve a reversible outer sphere electron-transfer process and reduction of propagating radicals to anions (eq 2e). We think that this reaction has a negligible contribution because homopolymerization of 2-hydroxyethyl acrylate in bulk and in 50% aqueous solution was quite successful,²¹

which eliminates enolate and carbanion species from the reaction pathway.

Conclusions

Kochi has pointed out that the typical reaction between radicals and metal complexes is that of formation of reactive alkyl-metal intermediates, and the oxidation or reduction of radicals by an outer-sphere electron-transfer process is possible if it forms stable ionic species.^{12a} The system described in this paper is much different than those previously studied in that the metal center is sterically hindered by the coordination of two substituted bpy groups and is in a nonaqueous and usually nonpolar medium. Furthermore, stabilized radicals are employed which can be oxidized or reduced to the corresponding ion.

We feel that there are two general types of reactions which are occurring between the styrene- or methyl acrylate-derived radicals and Cu^{I} or Cu^{II} metal centers: a direct reaction, which involves the formation of a $\text{R}-\text{Cu}$ species, or a redox reaction, which would reduce or oxidize the radical to an anion or a cation, respectively. Our results indicate that there is no significant direct interaction between propagating radicals and $\text{L}_2\text{Cu}^{\text{II}}(\text{OTf})_2$ in the free-radical polymerization of styrene or MA. The rates of the polymerizations are unchanged and the molecular weights and polydispersities are similar in the presence and absence of $\text{L}_2\text{Cu}^{\text{II}}(\text{OTf})_2$.

In the presence of either $\text{L}_2\text{Cu}^{\text{I}}(\text{OTf})$ or $\text{L}_2\text{Cu}^{\text{I}}\text{Br}$, it was observed that there was no effect on the AIBN-initiated polymerization of styrene: in the presence and absence of $\text{L}_2\text{Cu}^{\text{I}}(\text{OTf})$ molecular weights and reaction kinetics were unaltered. Conversely, for the AIBN-initiated free-radical polymerization of MA, a significant decrease in the rate of the polymerization was observed which might be evidence for the reversible formation of an $\text{R}-\text{Cu}$ species. However, the interactions are very weak and neither improve control of molecular weights and polydispersities nor affect tacticities which are the same as in conventional polymerization without copper complexes. We feel that since the "acrylate" radical is electrophilic, it can interact with Cu^{I} species stronger than the nucleophilic "styrene" radical.

For redox reactions, the reduction of methyl acrylate and the oxidation of styrene are both possible.^{7a} The oxidation potential for styrene-derived radicals is around 0.37 V and the reduction potential is around -1.60 V (vs SCE)²² whereas the reduction potential for acrylate radicals can be roughly estimated from pK_a and BDE data to be in the range of <-0.5 V.²³ The redox potential for (bpy)₂ CuX_2 complexes are around 0.02 V (vs SCE; i.e., (bpy)₂ CuCl_2 in CH_3CN).²⁴ No effect to an electron transfer was observed in the AIBN-initiated polymerization of MA in the presence of Cu^{II} species. There was, however, an effect in the AIBN-initiated polymerization of styrene in the presence of $\text{L}_2\text{Cu}^{\text{II}}(\text{OTf})_2$. The molecular weights were limited and only low conversions were realized. The reduction of acrylate-derived radicals by Cu^{I} species is possible by examining the redox potentials; however, no significant effect on the polymerization of 2-hydroxyethyl acrylate was observed. This does not rule out that the reduction occurs; it may occur at a slow rate relative to the

polymerization and may only be observed at high molecular weights and high conversions.

In conclusion, the presented results indicate that control in ATRP does not originate in interactions of growing radicals with copper complexes but in the reversible halogen atom transfer.

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