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Copper Triflate as a Catalyst in Atom Transfer Radical Polymerization of Styrene and Methyl Acrylate

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ABSTRACT: The use of copper triflate complexes as catalysts for atom transfer radical polymerization (ATRP) of styrene and methyl acrylate (MA) is presented. The ability to start with $Cu(OTf)_2$ catalyst precursors allows for a simple experimental setup without catalyst oxidation. Reduction with copper(0) powder occurs quickly in most cases to form the copper(I) catalysts. The traditional bipyridine-based ATRP ligands were less efficient for styrene polymerization, but for methyl acrylate polymerization resulted in faster polymerizations relative to the CuBr analogues. The methylated triamine ligand was used for the $Cu(OTf)_2/Cu^0$ system and also yielded good results for the polymerization of styrene ($M_w/M_n = 1.10$). This catalyst gave a rapid polymerization of MA with low polydispersities ($M_w/M_n = 1.15$) even at high conversions. The Cu(OTf) complexes are more active than their CuBr counterpart; however, this may be detrimental to having a controlled polymerization. In the case of styrene, it is possible that radical generation is too great, leading to termination through bimolecular coupling. For MA, molecular weights somewhat lower than predicted were observed and an exothermic reaction occurred in the presence of a molar excess of Cu^0. Lowering the amount of Cu^0 effectively lowers the amount of catalyst and allows for a well-controlled polymerization with a low contribution of termination reactions. Thus, Cu(OTf) complexes prepared from $Cu(OTf)_2$ in the presence of Cu^0 appear to be an excellent catalytic species for styrene and MA polymerization especially with the methylated triamine ligand.

Introduction

Controlled/"living" radial polymerizations yielding well-defined polymers has been the subject of intense interest. Currently, nitroxide-catalyzed,[1] metal-mediated,[2] and atom transfer radical polymerization (ATRP)[3] are at the forefront of controlled radical polymerizations. Expansion of these processes has been aimed toward application to new monomers, new initiators, and new architectures, compositions and functionalities.[4] In ATRP, recent advances have also been in the direction of new ligands[5] and new metals[6] which affect the activity and selectivity of the ATRP catalysts for various monomers. Also, improvements have been made in ATRP by the addition of small amounts of zerovalent metal.[7]

ATRP proceeds by a reversible redox process between an alkyl halide (R−X), as an initiator, and a transition metal complex capable of expanding its coordination sphere by one and with the appropriate redox activity. 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 ($X-Cu^{II}$).[8]

ATRP has its roots in atom transfer radical addition (ATRA),[9] which originates in a halogen atom transfer from an organic halide to a transition metal complex to generate an organic radical. This radical can then add to an alkene followed by back-transfer of the halogen from the transition metal complex, resulting 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 that form stabilized radicals can be used. In this sense, the inner-sphere electron transfer process is reversible and the activation/addition/deactivation steps are repeated until all of the unsaturated substrate is consumed. Ideally the number of these cycles should be equal to the degree of polymerization, defined by the ratio $[monomer]_0/[initiator]_0$.

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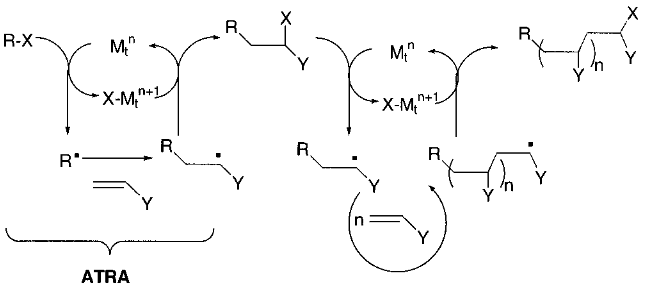
Scheme 1



However, it is possible that more than one monomer unit is added during one activation step. Scheme 1 shows the mechanism of ATRA and ATRP. A stabilized radical is formed by a reversible halogen 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 halogen 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 ($X-Cu^{II}$).[5b]

The effect of the catalyst's counterion on ATRP has been studied in some cases. Results comparing the use of chloride vs bromide as the copper(I) source have recently been published.[10] Since the halogen is also the deactivating species and is likely coordinated to the metal, the major differences are attributed to the relative bond strengths of Cu−X and R−X (X= Cl, Br). Some results of ATRP with copper carboxylates[11] and $CuPF_6$[12] as the catalysts have also been reported. In each of these cases, rates of polymerization were higher than in the ATRP with CuBr.

In our ongoing search for more efficient ATRP catalysts, copper triflate was targeted since it contains a weakly coordinating (labile) anion which may allow for an available coordination site. The different counterion could also effect the electrochemistry and solubility of the catalyst and $Cu(OTf)_2$ may be a catalyst precursor for use with a variety of ligands. Copper(I) triflate can be isolated as a benzene complex;[13] however, this complex is reactive toward oxidation and must be handled under inert conditions. Starting with $Cu(OTf)_2$ as a catalyst precursor is an attractive option. It has been previously reported,[14] and recently exploited by our group,[7,15] that, in the presence of stabilizing ligands, copper(II) complexes can be reduced by copper(0) powder to generate copper(I) complexes. This forms, in situ, an active catalyst for ATRP. This paper presents results of the ATRP of styrene and methyl acrylate from LCu(OTf) catalysts formed from the reaction of $Cu(OTf)_2$ with copper(0) powder, in the presence of nitrogen-based ligands, L.

Results and Discussion

As discussed previously, $LCuBr_2$ is a deactivating species in ATRP and increasing concentrations of $LCuBr_2$ will slow or prohibit ATRP.[5b] Copper(II) can be reduced by copper(0) to form copper(I) (eq 1) and, in the presence of stabilizing ligands, the equilibrium is shifted toward copper(I). Polymerizations can therefore be catalyzed by $LCuBr_2$ (as a catalyst precursor) by reduction with copper(0) powder to form the copper(I) species. Of course, enough copper(0) powder must be used to fully reduce the $CuBr_2$; otherwise, ATRP would be retarded or not occur due to an excess of the deactivating species.

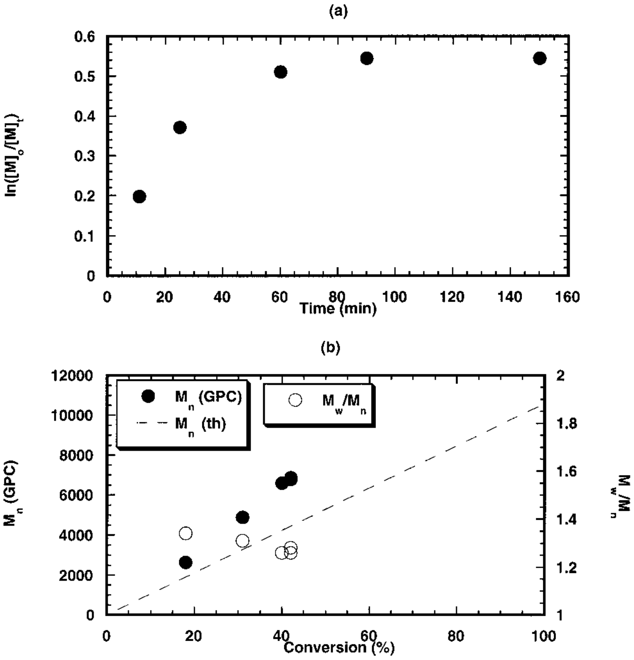


Figure 1. (a) Kinetic plot of the bulk polymerization of styrene by ATRP at 110 °C: styrene = 52.4 mmol; 1-phenylethyl bromide = 0.53 mmol; $Cu(OTf)_2$ = 0.053 mmol; Cu^0 = 0.27 mmol; dNbpy = 0.26 mmol. (b) Dependence of number average molecular weight, M_n (closed symbols), and polydispersity, M_w/M_n (open symbols), vs percent conversion for the bulk polymerization of styrene by ATRP at 110 °C.

$$\mathrm{Cu^{II}} + \mathrm{Cu^{0}} \rightleftharpoons 2\mathrm{Cu^{I}} \tag{1}$$

Starting with a $LCu(OTf)_2$/copper(0) powder system, ATRP should commence with the initial formation of copper(I), and the amount of copper(I) formed will be determined by the amount of Cu^0 present, relative to the amount of $LCu(OTf)_2$. The copper(II) triflate complex will not be a deactivating species in ATRP since it does not contain a ligand capable of an inner sphere electron transfer; therefore, excess $LCu(OTf)_2$ is just a spectator in the reaction. To achieve control in this system, a copper(II) complex containing a halogen ligand, capable of deactivating the propagating radical, must be present (see Scheme 1). Formation of a deactivating species occurs only during the initiation of the polymerization. Halogen atom transfer from the alkyl bromide initiator to the LCu(OTf) species, generated in situ, forms a Cu^{II}−halogen complex which should quickly build to a steady-state concentration by the persistent radical effect[16] to control the polymerization.

2,2′-Bipyridine and its 4,4′-Disubstituted Derivatives. A series of 4,4′-disubstituted-2,2′-bipyridine ligands were studied for the $LCu(OTf)_2$/copper(0) powder catalyst system (L = 2,2′-bipyridine (bpy), 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy), and 4,4′-di(*tert*-butyl)-2,2′-bipyridine (dTbpy)). Each ligand showed similar behavior (Table 1). The initial $LCu(OTf)_2$ species was light blue and partially soluble. Upon heating, the solutions became dark red-brown, indicative of Cu^I−bpy complexes. As shown in Figure 1, the polymerization

Table 1. Styrene/1-PEBr/Cu(OTf)$_2$/ligand/Cu^0 = 100/1/0.1/0.5/1.0 (T = 110) °C) and Methyl Acrylate/MBP/Cu(OTf)$_2$/ligand/Cu^0 = 200/1/0.1/0.4/0.1 (T = 80 °C) Data

monomer	ligand	time (min)	con-version	M_n	M_n(th)	M_w/M_n
styrene	bpy	150	55	7100	5800	1.42
	dTbpy	60	42	7500	4450	1.28
	dNbpy	66	61	11500	6500	1.61
	TMEDA	180	21	8230	2200	2.57
	PMDETA	180	65	7466	6760	1.09
	HMTETA	180	73	10840	7600	1.20
methyl acrylate	bpy	60	53	11000	9200	1.25
	dTbpy	40	75	12300	13050	1.25
	dNbpy	55	93	16520	16180	1.33
	PMDETA	75	75	12900	13400	1.16
	HMTETA	70	67	26200	12000	1.86

of styrene with Cu(OTf)$_2$/dNbpy/Cu^0 shows linear behavior at early reaction times in the semilogarithmic plot; however, as conversion increased, linear kinetics were no longer observed. Molecular weights increased with increasing conversion, but the molecular weights were higher than theoretical predictions based on quantitative initiation. As illustrated in the Experimental Section, a 5-fold molar excess of Cu^0 relative to Cu(OTf)$_2$ was used. Under these conditions, the polymerization went to only 42% conversion at which point all the Cu^0 had reacted and the polymerization stopped. Irreversible termination reactions must be occurring and the excess Cu^0 is used up by reaction with Cu^{II} formed by these termination reactions. In fact, to achieve conversion >70%, a 10-fold excess of Cu^0 (relative to Cu(OTf)$_2$) must be used. The polydispersity decreases and then increases at higher conversion.

Due to the prevalence of these irreversible termination reactions in styrene, the use of (dNbpy)$_2$Cu^{I}OTf as a catalyst does not produce polymer or at least stops at very low conversion. It was observed that the color of the solution quickly changes from dark red-brown to green upon heating in the presence of monomer and initiator.

Figure 2 shows the ATRP of methyl acrylate with Cu(OTf)$_2$/dNbpy/Cu^0 at 80 °C. The initial color of the solution was light blue-green and upon heating (forming LCu^I(OTf)), turned to a dark red-brown color. It was observed that a 25 min induction period is present before the polymerization commences. This was the length of time it took for the reaction solution to become a dark red-brown color, characteristic of Cu^I(bpy) complexes. This indicates that the induction period is mainly due to slow reduction of the (dNbpy)Cu(OTf)$_2$ complex by Cu^0. Linear kinetics on a semilogarithmic scale are observed, and the polymerization achieves greater than 90% conversion. Polymer molecular weights began higher than predicted but became close to theoretical as monomer conversion increased, indicative of slow initiation. Polydispersities decreased continuously, ending around M_w/M_n = 1.3. For dTbpy, molecular weights increased linearly with increasing conversion and agreed well with the theoretical values, and low polydispersities were observed (M_w/M_n = 1.20). For bpy, the molecular weights increased linearly with increasing conversion; however the molecular weights were higher than predicted but still yielded low polydispersities (M_w/M_n = 1.20).

When (dNbpy)$_2$Cu^{I}OTf was used as the catalyst for the ATRP of MA, a controlled polymerization resulted, but at a slower rate than that observed for the Cu(OTf)$_2$/dNbpy/Cu^0 case. After 3 h, 97% monomer conversion resulted with M_n = 16 100 (M_n(th) = 16 880); M_w/M_n = 1.21.

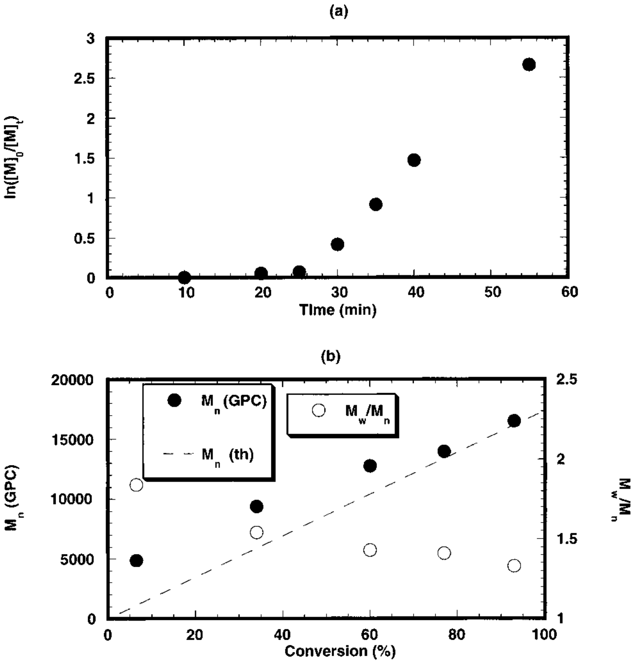


Figure 2. (a) Kinetic plot of the bulk polymerization of methyl acrylate by ATRP at 80 °C: methyl acrylate = 66.6 mmol; methyl 2-bromopropionate = 0.33 mmol; Cu(OTf)$_2$ = 0.033 mmol; Cu^0 = 0.032 mmol; dNbpy = 0.13 mmol. (b) Dependence of number average molecular weight, M_n (closed symbols), and polydispersity, M_w/M_n (open symbols), vs percent conversion for the bulk polymerization of methyl acrylate by ATRP at 80 °C.

Linear Amine Ligands. The use of methylated linear amine ligands in the LCuBr-catalyzed ATRP of styrene, methyl acrylate, and methyl methacrylate was recently reported.[5e] Here we report the bulk ATRP of styrene with copper triflate complexes of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), or 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (Table 1). The preliminary results shown in Table 1 indicate good control for styrene and MA with PMDETA and HMTETA; subsequently, a kinetic study of the ATRP of styrene in the presence of Cu(OTf)$_2$/PMDETA/Cu^0 catalyst system was performed. The results for this kinetic study are shown in Figure 3 and are compared with data from CuBr$_2$/PMDETA/Cu^0 under identical conditions. In each case, a 3:1 ratio of Cu^0:Cu(OTf)$_2$ was employed. The solution was a light blue color and did not change much during the polymerization. It was observed that the Cu(OTf)$_2$ system was actually slower than the CuBr$_2$ system. At increasing time, the polymerization slows, and some curvature is observed in the semilogarithmic plot. This correlates with what was observed for the Cu(OTf)$_2$/dNbpy case; however, not as much termination is apparent. Similar molecular weight growth was observed for both cases. Molecular weights evolved linearly with conversion and are higher than theoretical indicating indicating incomplete initiation or some contribution of termination by coupling. Polydispersities were around M_w/M_n = 1.15, but for the Cu(OTf)$_2$ system, the polydispersity increased at higher conversion.

The series of linear amine ligands was also used in conjunction with copper triflate for the ATRP of methyl

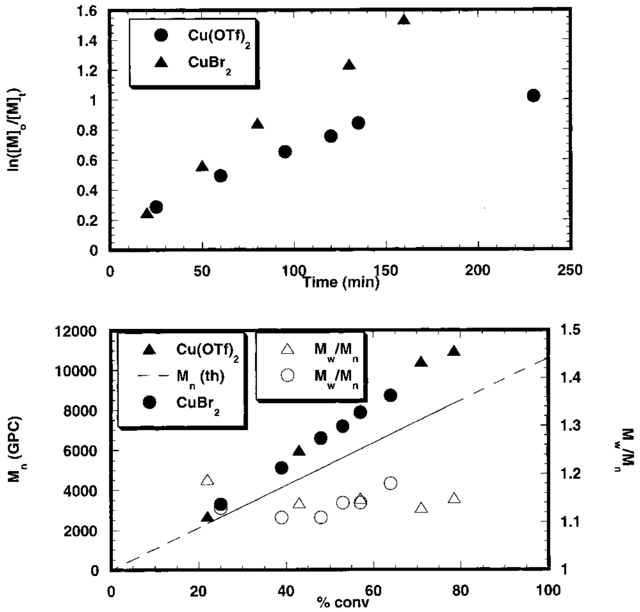


Figure 3. (a) Kinetic plot of the bulk polymerization of styrene by ATRP at 110 °C with PMDETA ligand: styrene = 43.7 mmol; 1-phenylethyl bromide = 0.44 mmol; $Cu(OTf)_2 = CuBr_2 = 0.044$ mmol; $Cu^0 = 0.13$ mmol; PMDETA = 0.087 mmol. (b) Dependence of number average molecular weight, M_n (closed symbols), and polydispersity, M_w/M_n (open symbols), vs percent conversion for the bulk polymerization of styrene by ATRP at 110 °C.

acrylate in bulk. The solution was a light blue color and did not change much during the polymerization. The results given in Table 1 show that, again, PMDETA is the most effective of the linear amine ligands studied. A kinetic study is shown in Figure 4. The reactions were fast and it was observed that with the ratio of $Cu(OTf)_2/PMDETA/Cu^0$ equal to 1/2/1, an exothermic process caused the solution to reflux (methyl acrylate bp = 80 °C). The kinetic plot was nonlinear and high conversions were not achieved. When the amount of Cu^0 was reduced (1/2/0.5), linear kinetics were observed and high conversions realized. In this case, a molar ratio of Cu^0 to $Cu(OTf)_2$ of less than one still leads to an efficient ATRP system since $Cu(OTf)_2$ cannot act as a deactivating species. If the same conditions were used for $CuBr_2$, the polymerization would be exceedingly slow or inhibited due to the high concentration of the $CuBr_2$, which is capable of deactivating the radical species, shifting the equilibrium toward dormant species.

Conclusions

This paper presents the use of copper triflate complexes as ATRP catalysts for styrene and methyl acrylate. The ability to start with $Cu(OTf)_2$ catalyst precursors allows for a simple experimental setup without fear of catalyst oxidation. Reduction with copper(0) powder occurs quickly in most cases to form the copper(I) catalysts. The traditional bipyridine-based ATRP ligands were less efficient for styrene polymerization, but for methyl acrylate polymerization, they resulted in faster polymerizations relative to the CuBr analogues.

The methylated triamine ligand recently reported for CuBr systems[5e] was used for the $Cu(OTf)_2/Cu^0$ system and also yielded good results for the polymerization of styrene. This catalyst gave a rapid polymerization of methyl acrylate with low polydispersities even at high conversions.

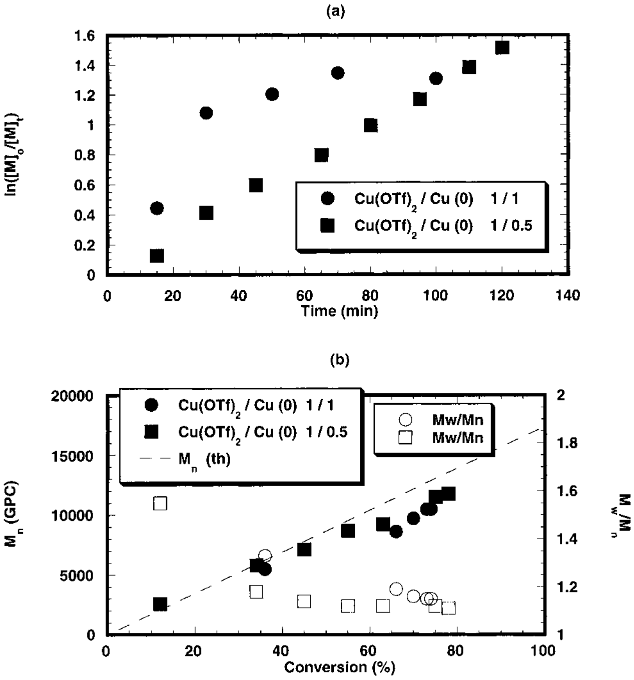


Figure 4. (a) Kinetic plot of the bulk polymerization of methyl acrylate by ATRP at 80 °C with PMDETA ligand: methyl acrylate = 66.6 mmol; methyl 2-bromopropionate = 0.33 mmol; $Cu(OTf)_2 = 0.033$ mmol; $Cu^0 = 0.032$ mmol (0.016 mmol); PMDETA = 0.067 mmol. (b) Dependence of number average molecular weight, M_n (closed symbols), and polydispersity, M_w/M_n (open symbols), vs percent conversion for the bulk polymerization of methyl acrylate by ATRP at 80 °C.

The Cu(OTf) complexes may be more active than their CuBr counterpart; however, this may be detrimental to having a controlled polymerization. In the case of styrene, it is possible that radical generation is too great, leading to termination through bimolecular coupling. The activation may be too great relative to deactivation, especially since no deactivating species is present initially. For MA, molecular weights somewhat lower than predicted were observed, and an exothermic reaction causes the polymerization to boil when in the presence of a molar excess of Cu^0. Lowering the amount of Cu^0 effectively lowers the amount of catalyst and allows for a well-controlled polymerization with a low contribution of termination reactions.

Since Cu^{II} salts were the starting point, the addition of Cu^0 was necessary. This prevents an accurate comparison of the rates of polymerization with other catalyst systems. We have previously reported the effect and use of Cu^0 in ATRP, which we feel is mainly to reduce the concentration of Cu^{II} species in solution.[8,15] Nevertheless, $Cu(OTf)_2$ appears to be an excellent catalytic species for acrylate polymerization with the PMDETA ligand in the presence of Cu^0.

Experimental Section

General Procedures. Styrene and methyl acrylate were passed through a column of alumina and then distilled under vacuum and stored under argon. 4,4′-Di(5-nonyl)-2,2′-bipyridine (dNbpy) and 4,4′-di(*tert*-butyl)-2,2′-bipyridine (dTbpy) were synthesized as previously reported.[5b] 2,2′-Bipyridine (bpy) was purchased from Aldrich and recrystallized from methanol prior to use. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) were purchased from Aldrich and used as received. Copper powder (so-called copper bronze−copper for organic synthesis), $CuBr_2$, $Cu(OTf)_2$, and $[Cu(OTf)]_2{\cdot}C_6H_6$ were used as received from Aldrich. The initiators, 1-phenylethyl bromide and methyl 2-bromopropionate, were used as received from Aldrich.

Characterization. Conversion was determined by GC by measuring residual monomer relative to an internal reaction standard. The M_n and M_w/M_n of the polymer samples were measured with a Waters 712 WISP auto sampler and Phenogel gel permeation chromatography (GPC) columns (guard, linear, 1000 Å, and 100 Å), using PSS software. Molecular weights of polystyrene and poly(methyl acrylate) were calibrated against polystyrene standards.

Bulk Polymerization of Styrene/1-Phenylethyl Bromide. bpy. As a representative example, a 10 mL Schlenk flask was charged with Cu^0 (28 mg; 0.44 mmol), $Cu(OTf)_2$ (16 mg; 0.044 mmol), 2,2′-bipyridine (34 mg; 0.22 mmol), 1-phenylethyl bromide (60 μL; 0.44 mmol), and styrene (5 mL; 43.7 mmol) followed by 0.5 mL of chlorobenzene as an internal reference. The reaction flask was charged with a stir bar and then fitted with a rubber septum. The reaction solution was put through freeze−vacuum−thaw cycles three times to remove dissolved gases and then put under an argon atmosphere. The flask was immersed in an oil bath and held by a thermostat at 110 °C with rigorous stirring. This resulted in a colorless polymerization solution with a heterogeneous catalyst. At various times, samples were taken via syringe and diluted with THF. The volume lost by sample removal was replaced with argon. The samples were used to monitor percent monomer conversion relative to the internal reference (GC) and molecular weight (SEC).

dTbpy. Cu^0 (20 mg; 0.31 mmol), $Cu(OTf)_2$ (16 mg; 0.044 mmol), 4,4′-di(*tert*-butyl)-2,2′-bipyridine (59 mg; 0.22 mmol), 1-phenylethyl bromide (60 μL; 0.44 mmol), and styrene (5 mL; 43.7 mmol) were used. Upon heating, a homogeneous, dark red-brown solution results. Within 45 min, all of the copper metal was reacted, and the polymerization reached a maximum of about 40% conversion.

dNbpy. (a) Cu^0 (28 mg; 0.44 mmol), $Cu(OTf)_2$ (16 mg; 0.044 mmol), 4,4′-di(5-nonyl)-2,2′-bipyridine (88 mg; 0.22 mmol), 1-phenylethyl bromide (60 μL; 0.44 mmol), and styrene (5 mL; 43.7 mmol) were used. A dark red-brown solution forms within minutes of heating, and the catalyst is homogeneous. The copper metal is present throughout the reaction, and 61% monomer conversion was observed after 66 min of heating.

(b) Cu^0 (17 mg; 0.27 mmol), $Cu(OTf)_2$ (19 mg; 0.053 mmol), 4,4′-di(5-nonyl)-2,2′-bipyridine (107 mg; 0.26 mmol), 1-phenylethyl bromide (72 μL; 0.53 mmol), and styrene (6 mL; 52.4 mmol) were used; 42% monomer conversion was observed after 150 min of heating.

(c) Cu^0 (17 mg; 0.27 mmol), $CuBr_2$ (12 mg; 0.053 mmol), 4,4′-di(5-nonyl)-2,2′-bipyridine (107 mg; 0.26 mmol), 1-phenylethyl bromide (72 μL; 0.53 mmol), and styrene (6 mL; 52.4 mmol) were used; 69% monomer conversion was observed after 200 min of heating.

(d) $[Cu(OTf)]_2{\cdot}C_6H_6$ (27 mg; 0.053 mmol), 4,4′-di(5-nonyl)-2,2′-bipyridine (107 mg; 0.26 mmol), 1-phenylethyl bromide (72 μL; 0.53 mmol), and styrene (6 mL; 52.4 mmol) were used. A Schlenk flask was charged with dNbpy and put into a glovebox under an argon atmosphere. In the glovebox, $[Cu(OTf)]_2{\cdot}C_6H_6$ was added, and then distilled, degassed monomer was added, resulting in a dark red-brown solution. The flask was fitted with a septum and removed from the glovebox and placed under Ar on a Schlenk line. 1-phenylethyl bromide was added and the solution was heated to 110 °C. Shortly after heating, the solution became a light brown color and eventually greenish. No monomer conversion was observed after 2 h.

PMDETA. Cu^0 (8.3 mg; 0.13 mmol), $Cu(OTf)_2$ (16 mg; 0.044 mmol), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (18 μL; 0.087 mmol), 1-phenylethyl bromide (60 μL; 0.44 mmol), and styrene (5 mL; 43.7 mmol) were used. A blue reaction solution forms and polymerization ensued without an induction period. After 240 min, 65% monomer conversion was observed.

Bulk Polymerization of Methyl Acrylate/Methyl 2-Bromopropionate. PMDETA. As a representative example, a 10 mL Schlenk flask was charged with Cu^0 (2 mg; 0.032 mmol), $Cu(OTf)_2$ (12 mg; 0.033 mmol), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (14 μL; 0.067 mmol), methyl 2-bromopropionate (37 μL; 0.33 mmol), and methyl acrylate (6 mL; 66.6 mmol) followed by 0.6 mL of chlorobenzene as an internal reference. The reaction flask was charged with a stir bar and then fitted with a rubber septum. The reaction solution was then put through freeze−vacuum−thaw cycles three times to remove dissolved gases and then put under an argon atmosphere. The flask was then immersed in an oil bath and held by a thermostat at 80 °C with rigorous stirring. A homogeneous blue solution was observed. At various times, samples were taken via syringe and diluted with THF. The volume lost by sample removal was replaced with argon. The samples were used to monitor percent monomer conversion relative to the internal reference (GC) and molecular weight (SEC). After 60 min, 75% monomer conversion was observed. (After 120 min, 80% monomer conversion was observed.)

bpy. Cu^0 (2 mg; 0.032 mmol), $Cu(OTf)_2$ (12 mg; 0.033 mmol), 2,2′-bipyridine (21 mg; 0.13 mmol), methyl 2-bromopropionate (37 μL; 0.33 mmol), and methyl acrylate (6 mL; 66.6 mmol) were used. The solution rapidly turned a dark red-brown. After 15 min, all the copper metal was reacted, and after 60 min, 52% monomer conversion was observed. At the end of the polymerization, a red precipitate was observed, which was soluble in THF.

dTbpy. Cu^0 (2 mg; 0.032 mmol), $Cu(OTf)_2$ (12 mg; 0.033 mmol), 4,4′-di(*tert*-butyl)-2,2′-bipyridine (36 mg; 0.13 mmol), methyl 2-bromopropionate (37 μL; 0.33 mmol), and methyl acrylate (6 mL; 66.6 mmol) were used. A dark red-brown solution was quickly formed upon heating and copper metal was observed throughout the polymerization. After 40 min, 73% monomer conversion was observed.

dNbpy. (a) Cu^0 (2 mg; 0.032 mmol), $Cu(OTf)_2$ (12 mg; 0.033 mmol), 4,4′-di(5-nonyl)-2,2′-bipyridine (54 mg; 0.13 mmol), methyl 2-bromopropionate (37 μL; 0.33 mmol), and methyl acrylate (6 mL; 66.6 mmol) were used. The solution became dark red-brown only after 40 min of heating. After a total of 115 min, 71% monomer conversion was observed.

(b) $[Cu(OTf)]_2{\cdot}C_6H_6$ (17 mg; 0.033 mmol), 4,4′-di(5-nonyl)-2,2′-bipyridine (54 mg; 0.13 mmol), methyl 2-bromopropionate (37 μL; 0.33 mmol), and methyl acrylate (6 mL; 66.6 mmol) were used. A Schlenk flask was charged with dNbpy and put into a glovebox under an argon atmosphere. In the glovebox, $[Cu(OTf)]_2{\cdot}C_6H_6$ was added, and then distilled, degassed monomer was added, resulting in a dark red-brown solution. The flask was fitted with a septum and removed from the glovebox and placed under Ar on a Schlenk line. Methyl 2-bromopropionate was added, and the solution was heated to 80 °C. After 200 min of heating, 97% conversion was observed.

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References and Notes

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