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Ultrafast Synthesis of Ultrahigh Molar Mass Polymers by Metal-Catalyzed Living Radical Polymerization of Acrylates, Methacrylates, and Vinyl Chloride Mediated by SET at 25 °C

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Abstract: Conventional metal-catalyzed organic radical reactions and living radical polymerizations (LRP) performed in nonpolar solvents, including atom-transfer radical polymerization (ATRP), proceed by an inner-sphere electron-transfer mechanism. One catalytic system frequently used in these polymerizations is based on Cu(I)X species and *N*-containing ligands. Here, it is reported that polar solvents such as H_2O, alcohols, dipolar aprotic solvents, ethylene and propylene carbonate, and ionic liquids instantaneously disproportionate Cu(I)X into Cu(0) and Cu(II)X_2 species in the presence of a diversity of *N*-containing ligands. This disproportionation facilitates an ultrafast LRP in which the free radicals are generated by the nascent and extremely reactive Cu(0) atomic species, while their deactivation is mediated by the nascent Cu(II)X_2 species. Both steps proceed by a low activation energy outer-sphere single-electron-transfer (SET) mechanism. The resulting SET-LRP process is activated by a catalytic amount of the electron-donor Cu(0), Cu_2Se, Cu_2Te, Cu_2S, or Cu_2O species, not by Cu(I)X. This process provides, at room temperature and below, an ultrafast synthesis of ultrahigh molecular weight polymers from functional monomers containing electron-withdrawing groups such as acrylates, methacrylates, and vinyl chloride, initiated with alkyl halides, sulfonyl halides, and *N*-halides.

Introduction

Metal-catalyzed living radical polymerization (LRP) initiated with alkyl halides,[1] sulfonyl halides,[2] and *N*-halides[3] has been accomplished in organic and aqueous media[1a−f] as well as in ionic liquids,[3] mostly for activated monomers such as styrene,[1,2a,b] acrylates,[1a−f,5] methacrylates,[1a−f,2,3,7] and acrylonitrile.[6] Complex macromolecular architectures, such as dendrimers, have also been synthesized by metal-catalyzed LRP.[7]

Metal-catalyzed LRP is considered to proceed by an inner-sphere electron-transfer mechanism in which a low oxidation state metal complex acts as the catalyst, mediating a fast exchange between radicals and their dormant alkyl halide species.[1c,f,g,h,2b] The equilibrium between active and dormant species is shifted toward the dormant species by an excess of a high oxidation state catalyst generated by a small extent of bimolecular radical dimerization during the initial stages of the polymerization. This concept is known as internal suppression of fast reactions or the persistent radical effect (PRE).[8] The inner-sphere radical process is also known as atom-transfer radical addition (ATRA). The corresponding radical polymerization was, therefore, named atom-transfer radical polymerization (ATRP).[1b,c,f] Nonactivated monomers that generate stable alkyl halide dormant species, such as vinyl acetate, vinyl chloride, and ethylene, do not and are not expected to polymerize by the current generation of ATRP catalysts.[9] Of specific interest is vinyl chloride (VC) because it has proven impossible to polymerize by any living mechanism.[10] Recently,[11a,b] our laboratory reported the metal-catalyzed LRP of VC initiated by CHI_3 and mediated by a competition between outer-sphere

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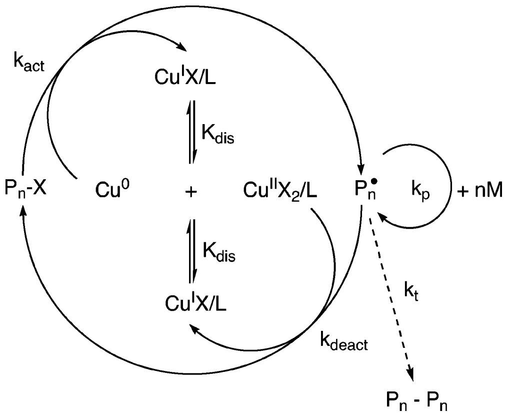
Scheme 1. Mechanism of SET-LRP



single-electron transfer (SET)[11d] and degenerative chain transfer (DT) mechanisms (SET-DTLRP). This polymerization proceeds at 25 °C in H_2O and uses Cu(0) and/or "nascent" Cu(0) generated in situ by the disproportionation of various Cu(I) precursors as a catalyst. In this polymerization, Cu(0) species act as electron donors, and the initiator and dormant propagating species act as electron acceptors. The Cu(I) species generated during the formation of radicals spontaneously disproportionate into extremely reactive nascent Cu(II) and Cu(0) atomic species that mediate the initiation and the reversible termination. This disproportionation generates, by a self-regulated mechanism, in situ, the Cu(II) species that, in the case of VC, would not be accessible by a conventional PRE mechanism since the radical polymerization of VC is dominated by chain transfer to monomer[1c,11a,b] rather than bimolecular termination. By this mechanism, the inactive Cu(I) species are spontaneously consumed and the catalytically active Cu(0) species are continuously produced. Here, we report that, under suitable conditions, the DT part of the SET-DTLRP[11a,b] can be eliminated and the newly elaborated LRP becomes SET-LRP. This polymerization process takes place in H_2O, protic, dipolar aprotic, and other polar solvents that, in the presence of *N*-ligands (Supporting Scheme SS1), were discovered to disproportionate Cu(I) into Cu(0) and Cu(II). These solvent and ligand combinations also favor an SET process.[11c] SET-LRP occurs under very mild reaction conditions, at room temperature and below, uses a catalytic rather than a stoichiometric amount of catalyst, and, although proceeds ultrafast, generates polymers with unprecedently high molecular weight. SET-LRP is general and applies to both nonactivated and activated monomers containing electron-withdrawing functional groups, such as vinyl chloride and other halogenated monomers, acrylates, and methacrylates. It also applies to organic reactions and tolerates a diversity of functional groups.

Results and Discussion

Selecting Catalysts. The mechanism proposed for SET-LRP is outlined in Scheme 1.

The initiation (activation) step (k_{act}) is mediated by an SET from the Cu(0) electron donor (or other donor species) to the electron-acceptor alkyl halide, sulfonyl halide, or *N*-halide initiator.[11a,b] Subsequently, the Cu(I) generated in this step instantaneously disproportionates into Cu(II) and Cu(0) species. The disproportionation of Cu(I) in H_2O has been known for over 100 years (eq 1) and proceeds in the presence of chelating compounds with an equilibrium constant (K_{dis}, eq 2) of about 10^7.[12]

Table 1. E_{HOMO} of Various Cu Catalysts Calculated Using HF/DFT Methods

E_{HOMO} (eV)	catalyst	method
−7.00	Cu_2Te	HF/LACVP+*//B3LYP/LACVP*
−7.34	Cu_2Se	HF/6-31+G*//B3LYP/6-31G*
−7.62	Cu(0)	UHF/6-31+G*//UB3LYP/6-31G*
−7.67	Cu_2S	HF/6-31+G*//B3LYP/6-31G*
−8.26	Cu_2O	HF/6-31+G*//B3LYP/6-31G*
−8.84	CuI	HF/6-31+G*//B3LYP/6-31G*
−9.71	CuBr	HF/6-31+G*//B3LYP/6-31G*
−10.24	CuCl	HF/LACVP+*//B3LYP/LACVP*

$$2\mathrm{Cu(I)X} \xrightleftharpoons{K_{\mathrm{dis}}} \mathrm{Cu(0)} + \mathrm{Cu(II)X_2} \tag{1}$$

$$K_{\mathrm{dis}} = [\mathrm{Cu(II)X_2}]\,[\mathrm{Cu(I)X}]^{-2} = 10^6 \text{ to } 10^7 \tag{2}$$

Previously, we have shown that Cu(I) spontaneously disproportionates in H_2O in the presence of tris(2-aminoethyl)amine (TREN) and poly(ethylene imine) (PEI).[11a] The very reactive, nascent Cu(II) species generated from the disproportionation reaction provide the reversible deactivation (k_{deact}) of the radicals into dormant alkyl halide species. Cu(0) promotes the reactivation of the dormant species. Both processes occur by an SET mechanism. To assess the electron-donating character of Cu(0) and various Cu(I) species, their E_{HOMO} values were calculated. E_{HOMO} correlates with the ionization potential (I_P) and therefore, estimates the electron-donor ability of various Cu derivatives. Table 1 reports the E_{HOMO} in electronvolts (eV) for Cu(0), CuCl, CuBr, CuI, Cu_2O, Cu_2S, Cu_2Se, and Cu_2Te. Cu(0) is known to be an efficient single-electron donor agent.[14] In addition, Cu_2O, Cu_2S, Cu_2Se, and Cu_2Te were investigated because our laboratory has developed them as the most efficient self-regulated catalysts for LRP initiated with sulfonyl halides and *N*-halides in nonpolar[2c,d,3,7,15e] and polar solvents,[6] in ionic liquids,[4a] and for SET-DTLRP of VC in H_2O.[11a] Their mechanism of catalysis for any of the previously reported LRP reactions, however, is not known. CuCl, CuBr, and CuI were studied because, depending on the structure of the initiator, they are expected to be transient, inactive species, as outlined in the reaction mechanism in Scheme 1. The results from Table 1 are

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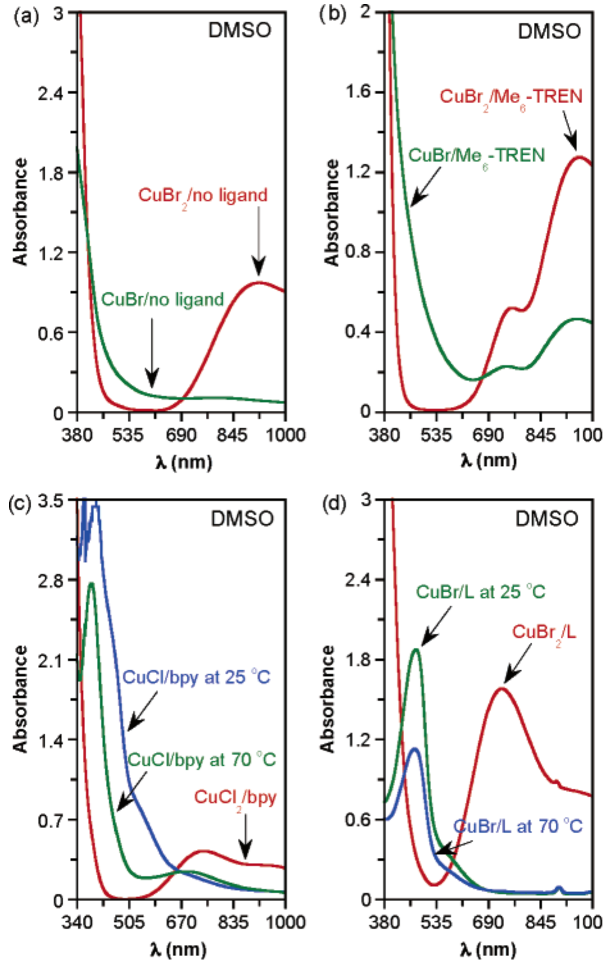

Figure 1. UV−vis spectra of (a) $CuBr_2$ (0.01 mmol/mL, red) and CuBr (0.01 mmol/mL, green) in DMSO (both $CuBr_2$ and CuBr are soluble in DMSO without ligand); (b) $CuBr_2$/Me_6-TREN (0.01 mmol/mL, red) and CuBr/Me_6-TREN (0.01 mmol/mL, green) in DMSO; (c) $CuCl_2$/bpy, 1/3 (0.005 mmol/mL, red) and CuCl/bpy, 1/3 (0.005 mmol/mL, green/blue) in DMSO at 25 °C after 12 h (blue) and at 70 °C (green); (d) $CuBr_2$/*N*-*n*-propyl-2-pyridylmethanimine, 1/2 (0.01 mmol/mL solution) and CuBr/*N*-*n*-propyl-2-pyridylmethanimine (0.005 mmol/mL, green/blue) in DMSO at 25 °C after 12 h (green) and at 70 °C after 12 h (blue).

rewarding. According to the data from Table 1, the most efficient electron-donor SET catalysts are Cu_2Te followed by Cu_2Se, Cu(0), Cu_2S, and Cu_2O. Under the polymerization conditions these Cu derivatives disproportionate,[11a] and therefore, their role in catalysis is determined by the ratio between their rate of disproportionation and direct activation by SET.

CuI, CuBr, and, specifically, CuCl are very poor electron donors although they are catalysts of choice for inner-sphere ATRA and ATRP.[1a−f] Since the lifetime of Cu(I)X is very short in comparison with that of Cu(0) and Cu(II)X_2 species, during reaction conditions that favor disproportionation of Cu(I) into Cu(II) and Cu(0), the SET catalytic activity of Cu(I)X halides can be neglected. Therefore, Cu_2Te, Cu_2Se, Cu(0), Cu_2S, and Cu_2O (but not Cu(I)X) are expected to provide the most efficient catalysts for the SET-LRP.

Selecting Ligands and Solvents. A UV−vis spectroscopy study was performed to assess the activity of various solvents (in addition to H_2O) and ligands for the disproportionation of Cu(I) into Cu(II) and Cu(0). Representative examples of UV−vis experiments are shown in Figure 1.

Deoxygenated mixtures containing solvent, ligand, and Cu(I)X or Cu(II)X_2 were prepared, and their UV−vis spectra were recorded after 10 min in order to allow the sedimentation of Cu(0) at the bottom of the UV−vis cell, unless otherwise noted.[11a] The Cu(II)X_2 solution was used as a standard to assess the disproportionation of Cu(I)X. Figure 1a shows that, in the absence of a ligand, CuBr does not disproportionate in DMSO. However, complete and instantaneous disproportionation of CuBr into $CuBr_2$ and Cu(0) occurs in the presence of tris(2-dimethylaminoethyl)amine (Me_6-TREN) in DMSO (Figure 1b). When Me_6-TREN was replaced with 2,2′-bipyridine (bpy), disproportionation of CuCl was also observed in DMSO, but it was not as fast as that in the presence of Me_6-TREN in DMSO (Figure 1c). A survey of different combinations of ligands and solvents is available in Supporting Figures SF1 to SF28. Me_6-TREN, TREN, PEI, bpy, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), and many other *N*-ligands disproportionate Cu(I)X into Cu(II)X_2 and Cu(0), not only in H_2O[11a,12] but also in protic solvents (MeOH, EtOH, ethylene glycol, diethylene glycol, triethylene glycol, 2-(2-ethoxyethoxy)ethanol, tetraethylene glycol, glycerine, HEMA, phenols), dipolar aprotic solvents (DMSO, DMF, DMAc, NMP, etc.), ionic liquids,[4] and ethylene and propylene carbonate, but not in CH_3CN which is a good stabilizing ligand for Cu(I)X and, therefore, does not favor disproportionation. However, *N*-*n*-propyl-2-pyridyl-methanimine[16] in DMSO does not disproportionate CuBr (Figure 1d). This suggests that, from the ligands investigated (SS1), only Haddleton's ligand[16] may mediate an inner-sphere "ATRP" metal-catalyzed LRP in both nonpolar and polar solvents. Therefore, any combination of catalyst, ligand, and solvent that favored disproportionation of Cu(I) into Cu(0) and Cu(II) in this study is expected to be efficient in mediating SET-LRP.

Selecting Initiators. The inner-sphere atom transfer mechanism[1f,g,h,11d] is known to show a strong dependence of the metal-catalyzed k_{act} on the nature of the halogen from the structure of R−X. In two independent series of experiments the ratio $k_{act}(R{-}Br)/k_{act}(R{-}Cl)$ was in the range of 10^3 to 9×10^4.[17] However, in the case of the outer-sphere mechanism, k_{act} has a much smaller dependence on the nature of the halogen from R−X. For example the ratio, $k_{act}(R{-}I)/k_{act}(R{-}Br) \approx k_{act}(R{-}Br)/k_{act}(R{-}Cl) \approx 1$ to 10.[18] Based on these data, it is expected that the range of initiators available for the case of metal-mediated SET-LRP must be much broader than that for the case of the metal-mediated inner-sphere process. Alkyl halides, sulfonyl halides, and *N*-halides containing Cl, Br, and I as the halide must be efficient in the case of SET-LRP (Supporting Scheme SS2). In the case of metal-catalyzed inner-sphere ATRP, iodine-containing initiators undergo a competition

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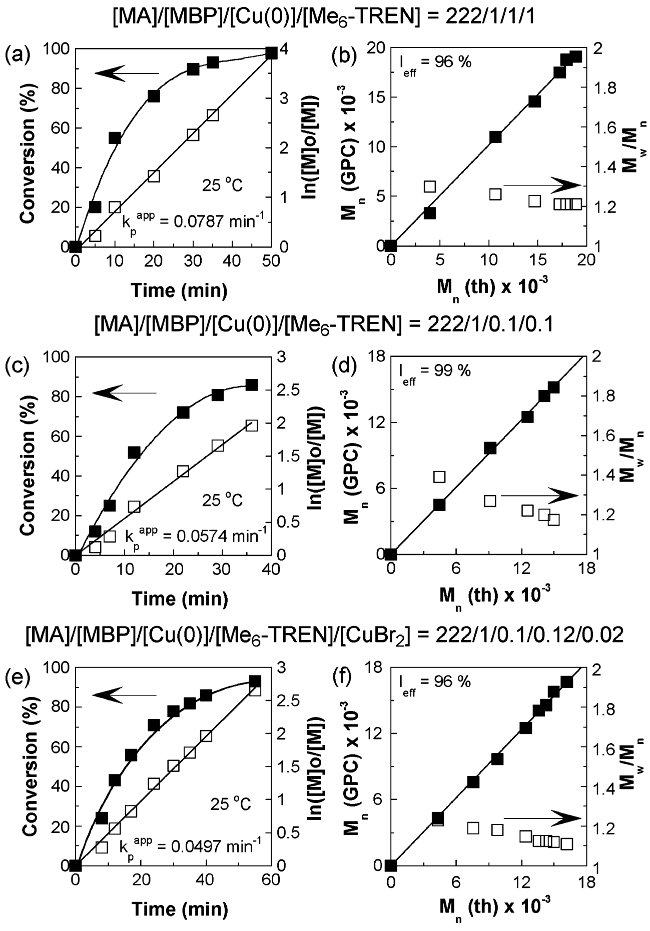

Figure 2. Kinetic plots for the Cu(0)-mediated living radical polymerization of methyl acrylate (MA) at 25 °C in DMSO, initiated with methyl 2-bromopropionate (MBP) using Me_6-TREN as a ligand (conditions: MA = 2 mL, DMSO = 1 mL, $[MA]_0 = 7.4$ mol/L, and $[MA]_0/[MBP]_0 = 222$).

between inner-sphere and degenerative transfer[1c] that is expected to be eliminated in the case of the outer-sphere SET-LRP process.

SET-LRP of Acrylates Initiated with Methyl-2-bromopropionate (MBP) and 2-Bromopropionitrile (BPN) and Catalyzed with Cu(0)/Me_6-TREN in DMSO. Cu(0)/bpy-catalyzed LRP of acrylates initiated with sulfonyl halides in nonpolar solvents at high temperatures was reported by our laboratory[15a,d] and was shown to be accelerated by many additives, including ethylene glycol.[15a] Mixtures of Cu(0)/Cu(II)X_2 or even Cu(0) alone were used to catalyze the LRP initiated with alkyl halides at high temperature in bulk and in nonpolar solvents.[19] It was concluded that Cu(0) increases the rate of the reaction since it reduces Cu(II)X_2 to Cu(I)X, the latter being considered the catalyst.[19a,b,d] Cu(0) alone was shown to provide poor control of molecular weight and molecular weight distribution since the Cu(I)X species generated cannot react with radicals to produce the dormant alkyl halides.[19a,b]

Figure 2 shows examples of LRP of methyl acrylate (MA) catalyzed by MBP/Cu(0)/Me_6-TREN carried out at 25 °C in DMSO. Complete conversions are obtained in less than 50 min for $[MBP]_0/[Cu(0)]_0 = 1/1$ (mole/mole) (Figure 2a, b). The reaction time is similar when $[MBP]_0/[Cu(0)]_0 = 1/0.1$ (mole/mole) (Figure 1c, d) and even with some excess of externally added $CuBr_2$ (in addition to the one generated by disproportionation) (Figure 2e, f). In all cases, kinetic plots show an internal first order of reaction in monomer and growing species, and the resulting poly(methyl acrylate) (PMA) has a low molecular weight distribution. Additional examples with MBP and BPN initiators are depicted in SF29, SF30, and SF31. These figures also describe the LRP of several different acrylates. The amount of catalyst can be decreased from 100% versus the initiator to 10% and even to 1%. When it contains less than 10% catalyst, the reaction mixture is colorless.

External Orders of the Polymerization in $[Cu(0)]_0$, $[CuBr_2]_0$, and $[DMSO]_0$. Kinetic experiments, processed according to the method used previously,[2b] provided the external orders of reaction of the polymerization in $[Cu(0)]_0$, $[DMSO]_0$, and $[CuBr_2]_0$ (Figure 3). As expected for the mechanism illustrated in Scheme 1, a complex, less than one, order of reaction in $[Cu(0)]_0$ is observed. The orders of reaction in $[DMSO]_0$ and $[CuBr_2]_0$ are about one. This demonstrates the expected catalytic effect of DMSO in this reaction and establishes that the LRP may be performed at a reasonably high rate in the presence of a high concentration of $CuBr_2$. These data provide instructions on how to control the rate of polymerization. For example, the amount of DMSO used in these experiments can be less than the amount of monomer. Therefore, the reaction mixture can be diluted with only a catalytic amount of solvent and be performed almost in bulk.

Synthesis of Ultrahigh Molecular Weight PMA by Cu(0)/Me_6-TREN Catalyzed LRP Initiated with MBP. The simplest test of the efficiency of a living polymerization is to assess its ability in the synthesis of polymers with ultrahigh molecular weight, i.e., with number average molecular weight (M_n) larger than 10^6. Previously the highest molecular weight linear polymers synthesized by the inner-sphere LRP metal-catalyzed technique were $M_n = 300\,000$ for poly(*n*-butyl methacrylate),[15e] $M_n = 367\,000$ for poly(methyl methacrylate),[20a] $M_n = 554\,000$ for poly(methyl acrylate),[5,20b] and $M_n = 823\,000$ for poly(*tert*-butyl acrylate).[20c]

Figure 4 shows representative examples of kinetic experiments in which $[MA]_0/[MBP]_0 = 11\,000$ (Figure 4a−d) and 22 200 (Figure 4e, f). PMAs with $M_n = 690\,000$ ($M_w/M_n = 1.10$), 950 000 ($M_w/M_n = 1.12$), and 1 420 000 ($M_w/M_n = 1.15$), respectively, with a narrow molecular weight distribution were obtained in 3, 6, and 10 h, respectively. The higher molecular weight polymers obtained by SET-LRP suggests significantly less termination and a much higher rate of polymerization at room temperature than those in previous metal-catalyzed LRP performed in nonpolar solvents at higher temperature.[1a−f,2,3] These are remarkable results considering that the reaction conditions used were not optimized. Radical polymerizations and LRPs of acrylates are known to be accompanied by intramolecular chain transfer to polymer and, therefore, to produce branched polyacrylates when the reaction is performed at high temperatures.[21] The analysis of the HSQC and HMBC

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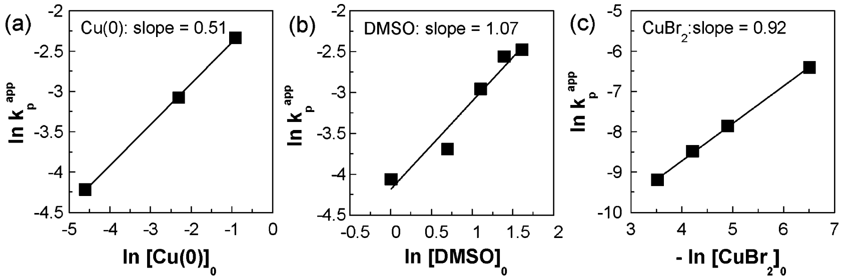

Figure 3. Determination of the external order of reaction in $[Cu(0)]_0$, $[CuBr_2]_0$, and $[DMSO]_0$ for the Cu(0)/Me_6-TREN-catalyzed polymerization of methyl acrylate (MA) in DMSO at 25 °C initiated with methyl 2-bromopropionate (MBP). $[MA]_0/[MBP]_0 = 200/1$; (a) ln k_p^{app} vs ln$[Cu(0)]_0$, ratio $[Cu(0)]_0/[MA]_0$ was varied from 0.01 to 1 at an equal ratio of $[Cu(0)]_0/[$ Me_6-TREN$]_0$ (MA = 2 mL, DMSO = 1 mL, $[MA]_0 = 7.4$ mol/L); (b) ln k_p^{app} vs $[DMSO]_0$, DMSO was varied from 0.2 to 0.8 mL with 1.8 mL of MA. ($[MA]_0/[MBP]_0/[Me_6$-TREN$]_0/[Cu(0)]_0 = 200/1/0.4/0.4$); (c) ln k_p^{app} vs $-\ln[CuBr_2]_0$, ratio of $[CuBr_2]_0/[Cu(0)]_0$ was varied from 0.1 to 2, $[Me_6$-TREN$]_0$ was equal to sum of $[Cu(0)]_0$ and $[CuBr_2]_0$. ($[MA]_0/[MBP]_0/[Cu(0)]_0 = 200/1/0.4$).

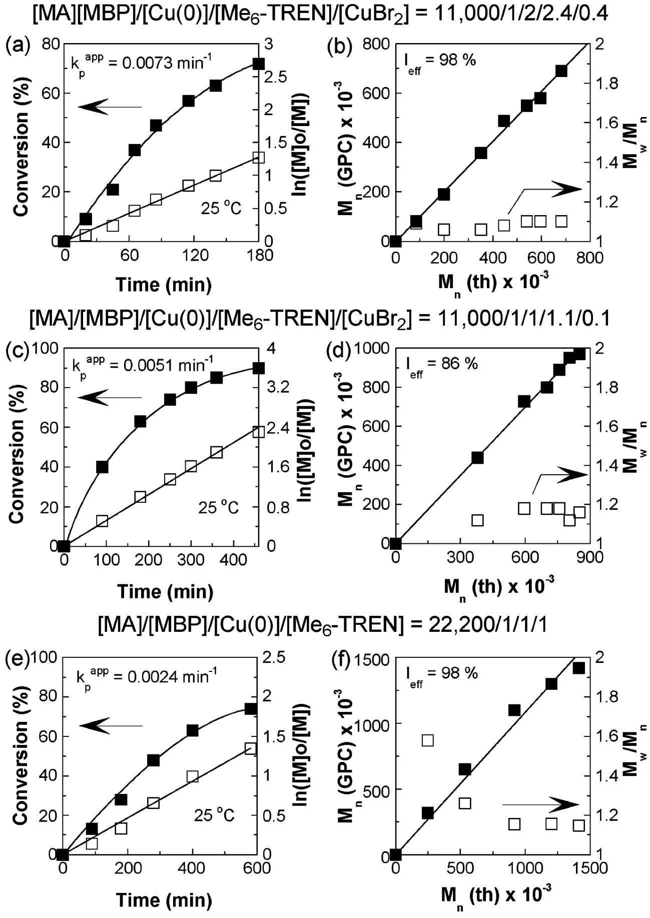

Figure 4. Kinetic plots for the Cu(0)-mediated living radical polymerization of MA initiated with methyl 2-bromopropionate (MBP) at 25 °C in DMSO using Me_6-TREN as a ligand. Conditions: (a and b) MA = 2.5 mL, DMSO = 2.5 mL, $[MA]_0 = 5.55$ mol/L, and $[MA]_0/[MBP]_0 = 11\,000$; (c and d) MA = 5 mL, DMSO = 2.5 mL, $[MA]_0 = 7.4$ mol/L, and $[MA]_0/[MBP]_0 = 11\,000$; (e and f) MA = 2 mL, DMSO = 4 mL, $[MA]_0 = 3.7$ mol/L, and $[MA]_0/[MBP]_0 = 22\,200$.

NMR spectra of linear poly(*n*-butyl acrylate) obtained at 25 °C revealed no detectable branching in the polymer sample (Supporting Figures SF57 and SF58). A linear PMA, free of branching, was obtained in the polymerization executed at 25 °C.

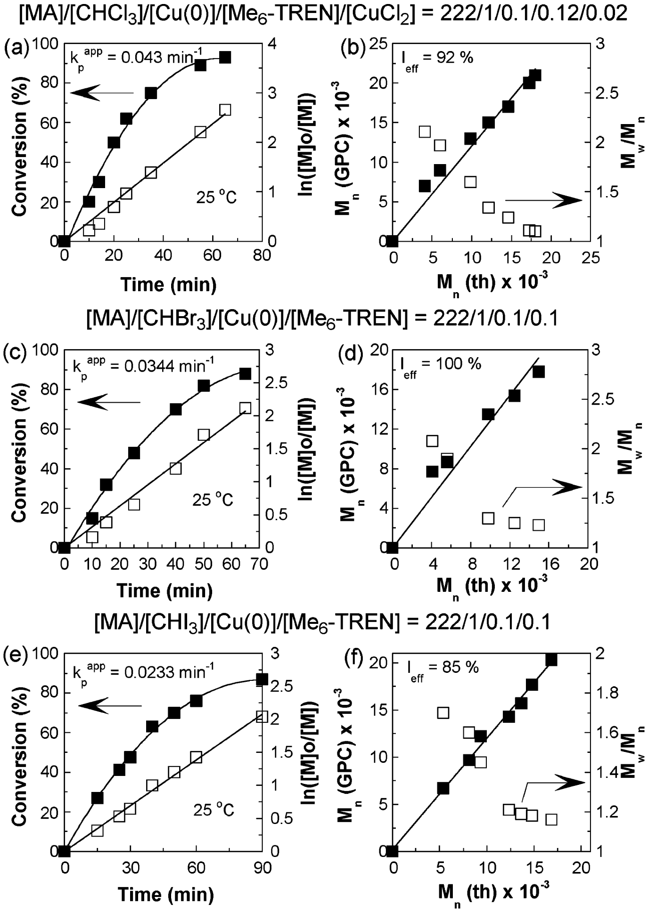

Figure 5. Kinetic plots for the Cu(0)-mediated living radical polymerization of MA initiated from: $CHCl_3$, $CHBr_3$, CHI_3 using Me_6-TREN as a ligand. Conditions: (a and b) MA = 1 mL, DMSO = 1 mL, $[MA]_0 = 5.55$ mol/L, and $[MA]_0/[CHCl_3]_0 = 222$; (c and d) MA = 1 mL, DMSO = 1 mL, $[MA]_0 = 5.55$ mol/L, and $[MA]_0/[CHBr_3]_0 = 222$; and (e and f) MA = 2 mL, DMSO = 1 mL, $[MA]_0 = 7.4$ mol/L, and $[MA]_0/[CHI_3]_0 = 222$.

$CHCl_3$, $CHBr_3$, and CHI_3 as Monofunctional and Bifunctional Initiators for the LRP of MA Catalyzed by Cu(0), Cu_2Te, Cu_2Se, Cu_2S, Cu_2O/Me_6-TREN in DMSO. The simplest monofunctional and difunctional initiators[11a,b] for the synthesis of α,*ω*-difunctional telechetic polyacrylates with different or identical chain ends are $CHCl_3$, $CHBr_3$, and CHI_3.

Figure 5 shows kinetic experiments for all initiators with Cu(0)/Me_6-TREN as the catalyst. Only $CHCl_3$ requires a small amount of additional $CuCl_2$ to control the LRP. The most important message provided by this figure is that the apparent

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(21) (a) Farcet, C.; Belleney, J.; Charleux, B.; Pirri, R. *Macromolecules* **2002**, *335*, 4912−4918. (b) Plessis, C.; Arzamendi, G.; Alberdi, J. M.; van Herk, A. M.; Leiza, J. R.; Asua, J. M. *Makromol. Chem., Rapid Commun*. **2003**, *24*, 173−177.

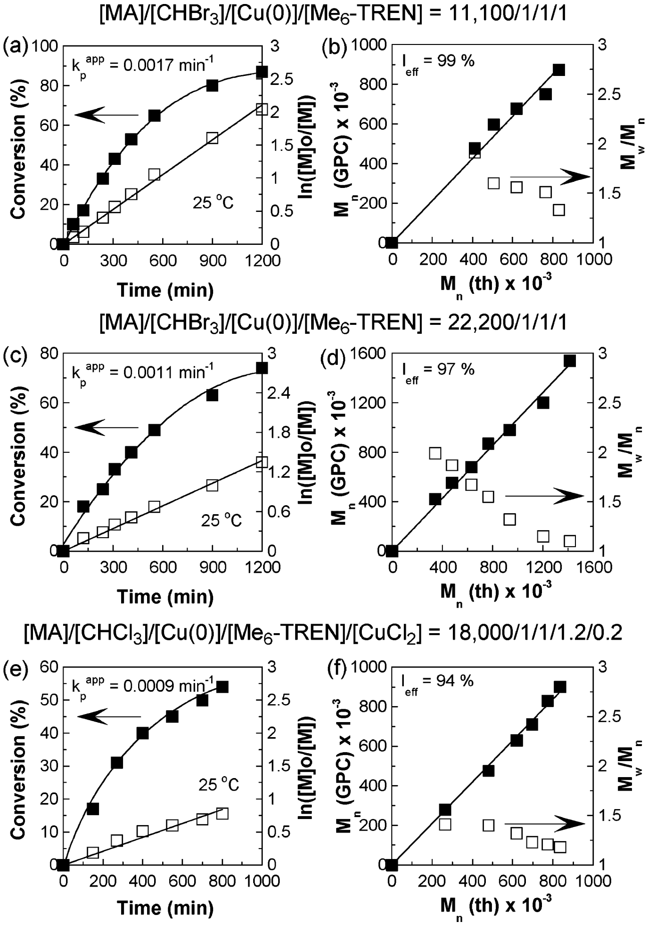

Figure 6. Kinetic plots for the Cu(0)-mediated living radical polymerization of MA initiated from $CHBr_3$ using Me_6-TREN as a ligand. Conditions: MA = 2 mL, DMSO = 4 mL, $[MA]_0 = 3.7$ mol/L. (a and b) $[MA]_0/[CHBr_3]_0 = 11\,100$; (c and d) $[MA]_0/[CHBr_3]_0 = 22\,200$; (e and f) $[MA]_0/[CHCl_3]_0 = 18\,000$).

rate constant of propagation (k_p^{app}) does not depend strongly on the structure of the haloform. Although this is a complex rate constant, its trend resembles that observed in other SET-mediated processes[18] and differs from that seen in ATRA and ATRP.[1,19] Additional kinetic experiments mediated by Cu(0) are shown in Figures SF32 and SF33, while kinetic experiments mediated by Cu_2O, Cu_2S, Cu_2Se, and Cu_2Te are depicted in Figures SF34, SF35, SF36, SF37, SF38, and SF39. Under these reaction conditions, CHX_3 with X = Cl, Br provide monofunctional initiators, while X = I behaves as a bifunctional initiator (SF51 to SF58). The resulting PMAs are telechelic in the case of $CHCl_3$ (SF51) and $CHBr_3$ (SF52, SF53), with their two chain ends having different chemical functionalities (one derived from initiator and one from growing species) and reactivities. When iodoform is used as an initiator, the resultant polymer contains two chain ends which at low conversion are different. However, at high conversion and high $[M]_0/[I]_0$ ratio the two chain ends exhibit identical structure and reactivity (SF55). A detailed kinetic analysis of this process and demonstrations of its synthetic capabilities will be reported.

Synthesis of Ultrahigh Molecular Weight PMA by Cu(0)/Me_6-TREN Catalyzed LRP Initiated with Haloforms. The initiators $CHBr_3$ and $CHCl_3$ were used to demonstrate the synthesis of ultrahigh molecular weight PMA (Figure 6).

The bifunctional CHI_3 and the monofunctional $CHCl_3$ and $CHBr_3$ initiators were also tested for the synthesis of ultrahigh molecular weight linear PMA. The results of selected kinetic experiments using these initiators are presented in Figure 6.

PMA with an M_n up to 1 400 000 and a narrow molecular weight distribution is easily accessible in a reasonable reaction time. The best results using $CHCl_3$ as an initiator were obtained when a small amount of $CuCl_2$ additive was used to regulate the polymerization. The nature of the haloform does not significantly change the kinetic parameters (including k_p^{app}) of these polymerizations under similar reaction conditions. This observation was also valid (see above) when various haloforms were employed for the synthesis of low molecular weight PMA (Figure 5). The use of these easily available and inexpensive solvents as dual mono- and bifunctional initiators for the synthesis of ultrahigh molecular weight PMA could be attractive from an industrial point of view and for the synthesis of AB, ABA, and more complex block copolymers that are not accessible with the more expensive monofunctional and bifunctional initiators based on MBP.

Synthesis of Ultrahigh Molecular Weight 8- and 4-Arm Star PMA. The Cu(0) based catalytic system was also utilized for the synthesis of 4- and 8-arm star PMA. The bromopropionate based 4-armed (4BrPr derived from pentaerythritol)[1d] and 8-armed (8BrPr derived from 4-*tert*-butyl calyx[8]arene)[1d] (Supporting Scheme SS2) initiators were used in these experiments. Representative kinetic plots of LRP of MA initiated with 4BrPr and 8BrPr star-shaped initiators are shown in Figures 7 and SF40 to SF42. In all experiments, the monomer conversion reaches up to 90%. The plots of $\ln[MA]_0/[MA]_0$ as a function of time and those of experimental versus theoretical M_n increase linearly. The M_w/M_n values remain very low throughout the polymerization. These results indicate the living nature of these polymerizations and the absence of star−star coupling as well as of other side reactions. It is remarkable that both 4- and 8-arm star PMA with an M_n up to 1 000 000 can be obtained in a living manner at room temperature in a very short time (SF40 to SF42). The decreased catalyst concentration (Figure 7a and b) as well as the use of a small amount of $CuBr_2$ as an additive (Figure 7c and d) provide an excellent control of the polymerization, yielding high molecular weight 4- and 8-arm PMA with a low molecular weight distribution. Reports on the synthesis of multiarm star polyacrylates and polymethacrylates using the same 4BrPr and 8BrPr and other multifunctional initiators under inner-sphere metal-catalyzed LRP conditions are available.[1d,7,15c,f] All previous synthetic procedures required high polymerization temperatures and long reaction times and were performed in nonpolar solvents.

LRP of MA Initiated with Haloforms and Catalyzed by Cu(0), Cu_2O, Cu_2S, Cu_2Se, Cu_2Te/TREN in DMSO. The simplest and the least expensive ligands that can be used in this LRP are TREN and PEI. They were previously used in the LRP of VC in H_2O together with the same catalysts.[11a,b] Figure 8 provides several examples of kinetics that demonstrate the very fast synthesis of different medium molecular weight (Figure 8 a, b) and very high molecular weight PMAs (Figure 8c, d). This polymerization can be carried out in the presence or absence of CuX_2 (Figures 8, SF43, SF44). Catalysis by Cu_2O, Cu_2S, Cu_2Se, and Cu_2Te/TREN in DMSO was demonstrated by the kinetic experiments summarized in Figure SF45. The

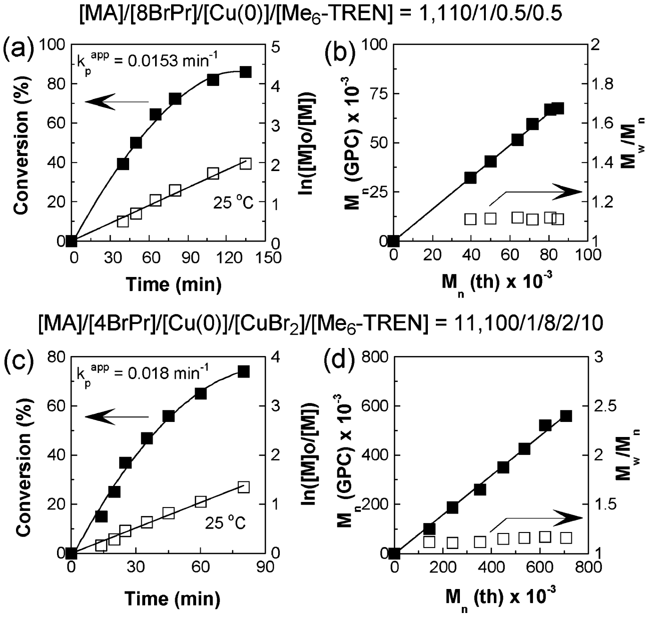

Figure 7. Kinetic plots for the living radical polymerization of MA initiated with (a and b) (8BrPr)5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octakis-(2-bromopropionyloxy) calyx[8]arene (conditions: MA = 1 mL, DMSO = 0.5 mL, $[MA]_0 = 7.4$ mol/L, and $[MA]_0/[8BrPr]_0 =$ 11 100); (c and d) (4BrPr) pentaerythritol tetrakis(2-bromopropionate) (conditions: MA = 2.5 mL, DMSO = 2.5 mL, $[MA]_0 = 5.55$ mol/L, and $[MA]_0/[4BrPr]_0 = 11\ 100$) using Me_6-TREN as a ligand.

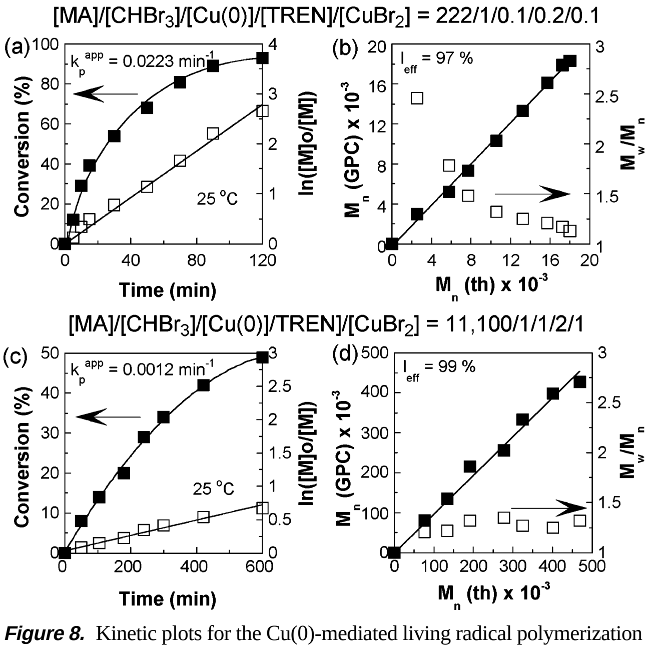

Figure 8. Kinetic plots for the Cu(0)-mediated living radical polymerization of MA initiated from $CHBr_3$ using TREN as a ligand. Conditions: (a and b) MA = 2 mL, DMSO = 1 mL, $[MA]_0 = 7.4$ mol/L, and $[MA]_0/[CHBr_3]_0 = 222$; (c and d) MA = 2 mL, DMSO = 2 mL, $[MA]_0 = 5.55$ mol/L, and $[MA]_0/[CHBr_3]_0 = 11\ 100$.

resulting PMA contains two different chain ends one derived from initiator and one from growing species that have different reactivities (SF52, SF54). This suggests new strategies for the synthesis of multifunctional block copolymers and other complex architectures.

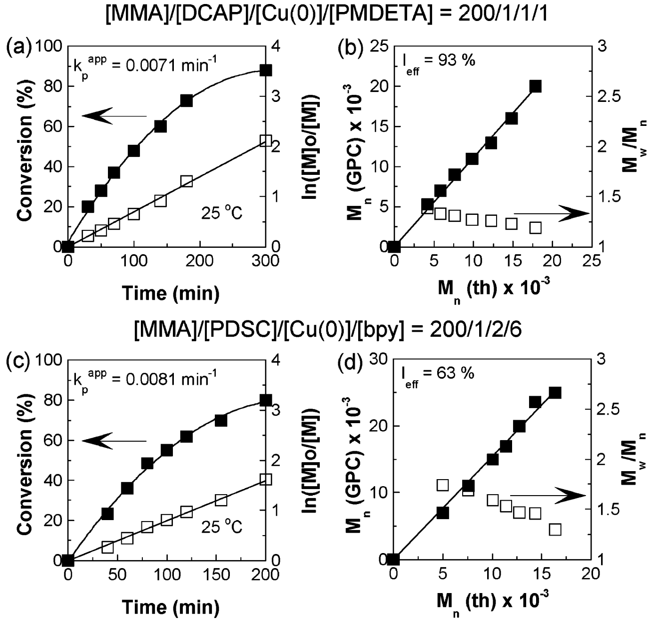

Figure 9. Kinetic plots for the Cu(0)-mediated living radical polymerization of MMA initiated with the following: (a and b) 2,2-dichloroacetophenone (DCAP) (conditions: MMA = 1 mL, DMSO = 0.5 mL), $[MMA]_0 = 6.2$ mol/L, and $[MMA]_0/[DCAP]_0 = 200$) using PMDETA as a ligand; (c and d) phenoxybenzene-4,4′-disulfonyl chloride (PDSC) (conditions: MMA = 1 mL, NMP = 0.5 mL, $[MMA]_0 = 6.2$ mol/L, and $[MMA]_0/[PDSC]_0 = 200$) using bpy as a ligand.

LRP of MMA Initiated with 2,2-Dichloroacetophenone (DCAP) and Phenoxybenzene-4,4′-Disulfonyl Chloride (PDSC) Catalyzed by Cu(0)/PMDETA and bpy in Dipolar Aprotic Solvents. Two examples of preliminary, nonoptimized kinetic experiments are presented in Figure 9. The first one is initiated with DCAP and catalyzed by Cu(0)/PMDETA in DMSO (Figure 9a, b). The second one is initiated with the bifunctional PDSC (Supporting Scheme SS2) and catalyzed with Cu(0)/bpy in NMP. Both experiments were performed at 25 °C. Since sulfonyl halides are known to undergo side reactions in the presence of DMSO[22a] and of aliphatic *N*-containing ligands,[21b] the classic bpy ligand employed previously with sulfonyl halide initiators[2−5,7,15] was used. These two examples demonstrate a dramatic acceleration when compared with related experiments carried out in nonpolar solvents.[1c,d,2−4,6,7,15] Additional kinetic experiments are presented in Figures SF46 and SF47.

LRP of VC Initiated with $CHBr_3$ and Catalyzed with Cu(0), Cu_2O, Cu_2S, Cu_2Se, Cu_2Te/TREN in DMSO. Previously, the SET-DTLRP of VC initiated with CHI_3 and catalyzed by the same catalytic systems in H_2O at 25 °C was reported.[11a,b] The resulting PVC contains two functional chain ends that were used in further functionalization and block copolymerization experiments. However, since CHI_3 is a good chain transfer agent and the polymerization mixture was heterogeneous, a two-stage kinetic process leading to a limited VC conversion was observed. $CHBr_3$ would be a less reactive, more UV and thermally stable, and less expensive initiator for the LRP of VC. Since reactivity studies on MA have demonstrated little difference between the nature of X from the structure of R−X and its k_{act}, reaction conditions for the LRP of VC initiated with $CHBr_3$ were investigated. Me_6-TREN as ligand in conjunction with Cu(0) mediates the polymerization of VC only to low conversion. However, the replacement of Me_6-TREN with TREN in DMSO provided a rewarding result that is determined by the difference between the ratio of the rates of activation/deactivation mediated

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[22] (a) Boyle, R. E. *J. Org. Chem.* **1966**, *31*, 3880−3882. (b) Gurr, P. A.; Mills, M. F.; Qiao, G. G.; Solomon, D. H. *Polymer* **2005**, *46*, 2097−2104.

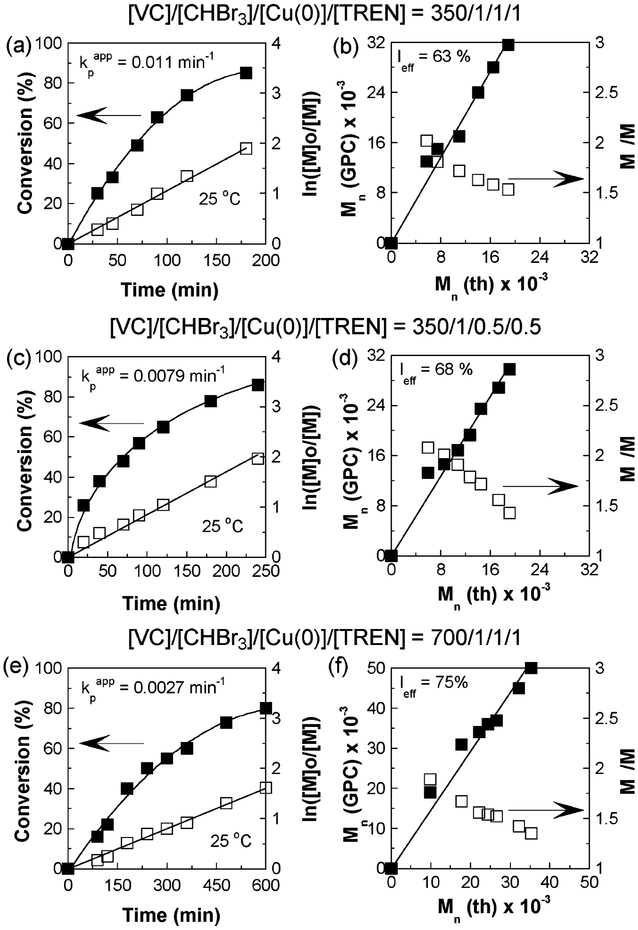

Figure 10. Kinetic plots for the Cu(0)-mediated living radical polymerization of VC initiated with $CHBr_3$ using TREN as a ligand (conditions: VC = 2.2 g, DMSO = 2 mL, $[VC]_0 = 8.8$ mol/L).

by these two ligands. Figure 10 shows selected experiments of preliminary experiments catalyzed with different concentrations of Cu(0)/TREN and DMSO.

Without optimization, about 90% VC conversion can be reached in a very short period of time. The molar ratio $[CHBr_3]_0$/$[Cu(0)]_0$ can be reduced from 1/1 (Figure 10 a, b) to 1/0.5 (Figure 10 c, d) and to 1/0.1 (SF48) with higher rates than previously reported with CHI_3 as the initiator.[11a,b] Since the amount of DMSO used in these polymerizations is very small, at the end of the polymerization the reaction mixture contains a white solid PVC plasticized with some DMSO. Therefore, purification of the PVC requires only washing with H_2O or MeOH. The limited amount of Cu(0) powder required to mediate this polymerization suggested that Cu(0) wire or any other solid form of a Cu alloy would be sufficient to promote it. Indeed, Figure 11 demonstrates this concept (compare Figure 10 a, b with Figure 11 a, b). Higher molecular weight PVC was obtained with higher $[VC]_0/[CHBr_3]_0$ ratios in the presence of Cu(0) (Figure 10 e, f and SF48), Cu_2Te, Cu_2Se, Cu_2S, and Cu_2O (SF49). All kinetic data demonstrate an SET-LRP single stage process. Depending on the reaction conditions and conversion, the resulting PVC can be designed as a bifunctional initiator with two different or identical chain ends. Therefore, it can be used for the synthesis of AB and ABA block copolymers (SF59 to SF65). This telechelic PVC can also be used for the synthesis of new complex architectures based on PVC. Details of these synthetic capabilities will be reported.

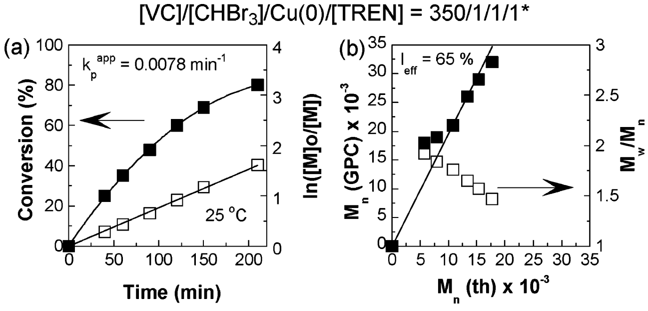

Figure 11. Kinetic plots for the living radical polymerization of VC initiated with $CHBr_3$ using TREN as a ligand (conditions: VC = 2.2 g, DMSO = 2 mL, $[VC]_0 = 8.8$ mol/L, and $[VC]_0/[CHBr_3]_0 = 350$). * denotes Cu(0) catalyst was used as a wire wrapped on the magnetic stirring bar.

Mechanistic Considerations. The experimental observations that Cu(I)X formed in situ undergoes spontaneous disproportionation under the polymerization conditions and that most of these polymerizations do not require externally added Cu(II)-X_2 deactivator demonstrate that the active catalyst is the nascent Cu(0) atomic species (Scheme 1). When Cu_2Te, Cu_2Se, Cu_2S, and Cu_2O are used, depending on the ratio between SET initiation and disproportionation they also can act as initial electron-donor catalysts. The rather interesting question is the following: By what mechanism are the radicals formed under these conditions? Several experimental observations as well as literature data help to elaborate the most probable mechanistic hypothesis for the activation of the dormant species. On one hand, the k_p^{app} during LRP of MA strongly depends on the concentration of DMSO used in the polymerization mixture (Figure 3b). Increasing DMSO concentration leads to faster polymerization while maintaining good control over molecular weight and molecular weight distribution. If the radicals were formed through an inner-sphere homolytic atom-transfer process, like in the case of ATRA and ATRP,[1c,f] then the polymerization rate and, hence, the k_p^{app} would have to exhibit very little dependence on the polarity of the reaction medium. The rate of a reaction in which radical intermediates are involved is not strongly dependent on the polarity of the medium. In principle, the opposite effect should be observed, i.e., the polymerization rate must decrease when the monomer, catalyst, and/or initiator concentrations decrease. This observation is an indication that the formation of radicals occurs by a different mechanism. One option is that ionic intermediates[23] are involved in the rate-limiting step of the radical formation. In this case, the rate of radical generation must dependent strongly on the polarity of the reaction medium and this was indeed observed experimentally (Figure 3b). The radicals are most likely generated through the decomposition of radical-anion intermediates[23] that are initially formed by the SET reaction between Cu(0) species and the halogen-containing substrates, such as the initiator, and halogen-terminated polymeric chain ends. These considerations are supported by literature data that show that dipolar aprotic as well as protic solvents facilitate fast SET reactions between electron donors (including Cu(0)) and various halogen-containing compounds (including haloforms and tetrahalomethanes).[14,23]

A series of quantum chemical calculations[13a] was performed on model systems to verify the path that best describes the

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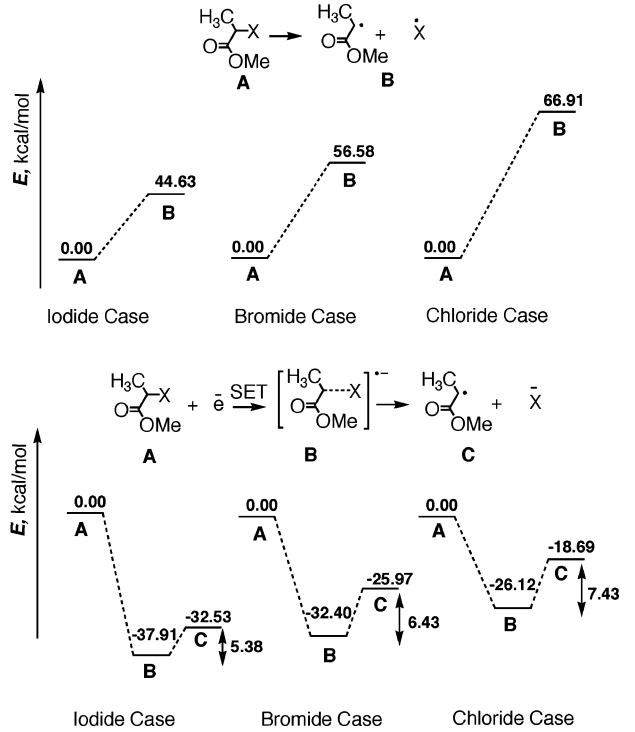
(23) (a) Pause, L.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2000**, *122*, 9829−9835. (b) Cardinale, A.; Isse, A. A.; Gennaro, A.; Rosset, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2002**, *124*, 13533−13539. (c) Costentin, C.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2003**, *125*, 10729−10739.

Scheme 2. Relative C−X Bond Dissociation Energies in Methyl 2-Halopropionates[a]



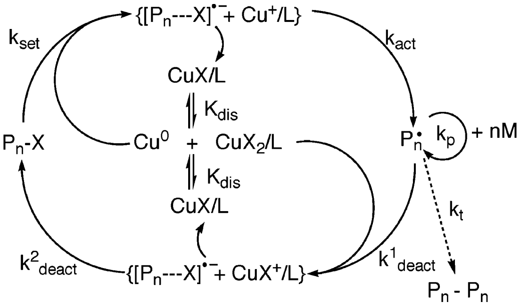
[a] Homolytic bond dissociation (top diagram) and formation and decomposition of anion−radicals formed by an SET process (bottom diagram) calculated using (U)B3LYP/6-31+G*//(U)B3LYP/6-31+G* (for Cl and Br case) or (U)B3LYP/LACVP+*// (U)B3LYP/LACVP+* (for I case) methods.

experimental observation that the nature of the halogen does not affect the rate of polymerization of MA when Cu(0) catalyst is used under similar conditions. The details of the quantum chemical calculations performed are described in the Supporting Information, and the results are shown in Scheme 2.

It is obvious that the homolytic C−X bond dissociation energy (BDE) in the initiators MCP (X = Cl), MBP (X = Br), and MIP (X = I) (Supporting Scheme SS2) strongly depends on the nature of the halogen and usually increases in the following order: Cl > Br > I (Scheme 2, top diagram). The calculated BDEs are in good agreement with previously calculated values obtained for the same methyl 2-halopropionate systems.[13b] The C−X bond dissociation energy depends very little on the nature of the halogen (X) if it occurs through the decomposition of the radical−anion formed via a SET process (Scheme 2, bottom diagram). The generalized catalytic cycle of SET-LRP is depicted in Scheme 3.

The reaction starts with an SET reaction between Cu(0) species and the halogen-containing substrate (initiator or halogen-terminated polymeric chain end). Any polar solvent, including DMSO, facilitates the decrease of interaction between the anion (X^-) and the electrophilic radical ($R^\bullet$) from the radical−anion pair.[23] The radical−anion cluster and Cu/L^+ countercation must be in close proximity in the so-called caged ion pair, thus further facilitating decomposition of the radical−anion into the electrophilic radical and the anion (X^-). The reaction between a radical and the deactivator CuX_2/ligand in polar media is a more complex process. One of the possible mechanisms may involve the transfer of the halide anion X^- from the deactivator to the propagating macroradical $R^\bullet$, leading to a similar ion cage composed of a radical−anion $[R\text{- - -}X]^{\bullet-}$ and a CuX/L^+ countercation. The mechanism depicted in Scheme 3 was simplified in order to facilitate the understanding of the main chemical events that might be involved in this catalytic process. However, the goal of this report was not to provide a complete mechanistic explanation of the SET-LRP process mediated by nascent Cu(0) species but rather to develop the SET-LRP synthetic method and to compare it with that based on the inner-sphere process. More experimental and theoretical studies are necessary to elucidate the hypothetic mechanism outlined in Scheme 3. Investigations in this direction are in progress and will be reported in due time. Nevertheless, the SET-LRP reported here, together with its mechanistic hypothesis, explains numerous literature examples in which an acceleration of the "Cu(I)X"-catalyzed LRP initiated with alkyl halides, sulfonyl halides, and *N*-halides was observed in H_2O,[24a−f] alcohols,[24g−j] ethyleneglycol,[15a,21j,k] DMSO,[24l−q] DMF,[24p] and ionic liquids,[4a] including a recent example of high molar mass polymethacrylate.[24s] This reaction will also facilitate access to complex organic synthesis by radical reactions performed under mild conditions.[25] Research along this line will be reported.

Scheme 3. Proposed Catalytic Cycle of SET-LRP Mediated by Cu(0) Species in Polar Media



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Conclusions

The disproportionation of Cu(I)X species into Cu(0) and Cu(II)X_2 species in alcohols, dipolar aprotic solvents, ethylene and propylene carbonate, and ionic liquids in the presence of a diversity of *N*-containing ligands is reported. This discovery complements the well-known disproportionation of Cu(I)X in H_2O. In water, alcohols, dipolar aprotic solvents, ethylene and propylene carbonate, and ionic liquids, Cu(0) and its alloys as powder, wire, or any other form (Figure 11, SF50), Cu_2Se, Cu_2Te, Cu_2S, and Cu_2O and the nascent, extremely reactive atomic Cu(0) and Cu(II)X_2 species obtained by disproportionation all mediate an ultrafast LRP of acrylates, methacrylates, and vinyl chloride at room temperature and below, initiated with alkyl halides, sulfonyl halides (Figure 9 and SF47), and *N*-halides (SF47). This polymerization proceeds by an outer-sphere SET mechanism in which Cu(0) species act as electron donors, and the dormant initiator and propagating R−X species act as electron acceptors. By contrast with other metal-catalyzed LRPs, including ATRP, in which excess Cu(II)X_2 species are created by the undesired radical dimerization, here, the Cu(II)X_2 species responsible for the reversible deactivation of the radicals are formed by the disproportionation of Cu(I)X. The previously reported metal-catalyzed LRP, including ATRP, generate radicals by an inner-sphere process that requires a high activation energy. The outer-sphere SET process involved in this new polymerization has a very low activation energy. Therefore, SET-LRP involves very fast activation and deactivation steps and negligible bimolecular termination at room temperature. Since activation takes place at room temperature in the presence of excess Cu(II)X_2, an extremely good control of the reaction is accomplished with only a very small amount of catalyst. This provides an ultrafast polymerization of both activated and nonactivated functional monomers containing electron-withdrawing groups. Without optimization, polymers with M_n in the range of 1.5×10^6 with a narrow molecular weight distribution are obtained in a short reaction time with no purification. This reaction also applies to the polymerization of a diversity of functional monomers and is expected to facilitate the rapid synthesis of complex macromolecular[7] and organic[25] compounds under mild conditions. Since activation and deactivation steps in SET-LRP are expected to be faster than chain transfer to initiators and/or dormant species of the general structure R−X with X = Cl, Br, I, all these initiators can be used without competition with degenerative chain transfer. Preliminary simulations of the SET-LRP kinetic experiments demonstrated that, under suitable reaction conditions, the extent of bimolecular termination is below the level detectable by any available analytical method. Recently, accelerated methods for the inner-sphere metal-catalyzed ATRP process were also reported.[26]

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Supporting Information Available: Experimental section containing materials, techniques, synthesis, structural analysis, additional kinetic experiments, and method used in the quantum chemical calculations. Also complete ref 13a. This material is available free of charge via the Internet at http://pubs.acs.org.

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