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Solvent Choice Differentiates SET-LRP and Cu-Mediated Radical Polymerization with Non-First-Order Kinetics

Gerard Lligadas, Brad M. Rosen, Michael J. Monteiro, and Virgil Percec*

Roy & Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

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ABSTRACT: In order to assess the role of the solvent mediating the disproportionation of Cu(I)X into Cu(0) and Cu(II)X_2 during SET-LRP, a series of polymerizations of methyl acrylate initiated with methyl 2-bromopropionate and catalyzed by Cu(0)/Me_6-TREN at 25 °C in DMSO, MeCN, and their mixtures were investigated. These polymerizations proceed in a dissimilar manner. SET-LRP of MA in DMSO, a solvent that mediates disproportionation, was exemplary of "ultrafast living radical polymerization" with complete conversion in 45 min following the expected first-order kinetics and providing perfect fidelity of the structure of the polymer chain ends. When the polymerization was performed in MeCN, a solvent in which Cu(I)X species do not disproportionate, it displayed nonlinear first-order kinetics with a poor retention of the bromine chain end functionality. The lack of first-order kinetics and decrease of chain end functionality with conversion indicate a nonliving polymerization in MeCN. Increasing the concentration of DMSO in DMSO/MeCN mixtures provided a continuous transition from a nonliving to a living polymerization. The incompatibility of MeCN with SET-LRP lends support that disproportionation of Cu(I)X/N ligand to Cu(0) and Cu(II)X_2/N ligand is the key step in SET-LRP.

Introduction

Single-electron tranfer living radical polymerization (SET-LRP)[1a] wherein extremely reactive Cu(0) and Cu(II)X_2 species, obtained by disproportionation of Cu(I)X species in dipolar aprotic solvents such as DMSO,[1a,b] alcohols,[2] ethylene and propylene carbonate, ionic liquids, and H_2O[3,4] in the presence of a diversity of N-containing ligands,[1,5] mediate an ultrafast living radical polymerization of methyl acrylate (MA), methyl methacrylate (MMA), ethyl acrylate (EA),[6] butyl acrylate (BA),[6] and vinyl chloride (VC)[1,3,4] at room temperature or below. SET-LRP is able to rapidly achieve high molecular weights, with excellent control of molecular weight distribution, with perfect retention of chain end functionality.[1b,7] Among the many tenants of the proposed mechanism of SET-LRP, the two most notable are that reversible activation of dormant polymer chain is achieved through a Cu(0) mediated outer-sphere electron transfer (OSET) process of heterolytic C−X bond dissociation[8,9] and that Cu(0) activator and Cu(II)X_2 deactivator are continuously regenerated via ligand/solvent mediated disproportionation of in situ generated Cu(I)X.[5]

Since the disproportionation of Cu(I)X to Cu(0) and Cu(II)X_2/N ligand is a key control process in SET-LRP, the nature of the solvent and the presence of complexing agents are expected to exert a strong influence on this polymerization. In pure DMSO, the primary choice for SET-LRP, Cu(I) is markedly stabilized relative to Cu(II) and metallic Cu(0) due to the stronger solvation of this oxidation state. However, the equilibrium for disproportionation of Cu(I) is dramatically altered by the presence of other complexing agents, such as N ligands, that stabilize Cu(I) and Cu(II) in a different manner.[5] A UV−vis spectroscopy study reported from our laboratory showed that, in pure DMSO and without any ligand, the disproportionation of Cu(I) is both slow and thermodynamically disfavored. However, disproportionation was observed in DMSO in the presence of Me_6-TREN.[1,5] These observations are supported by a recent density functional theory (DFT) computational study[5] that demonstrated that certain N ligands such as Me_6-TREN and TREN, which were previously shown to mediate an effective SET-LRP,[1,3,4] form stronger complexes with Cu(II) than with Cu(I). This results in an increased propensity for disproportionation of Cu(I) into Cu(II) and Cu(0). On the other hand, in a solvent such as MeCN, Cu(I)X species are known to be stable at least at 25 °C even in the presence of the same N ligands.[1]

Other researchers have suggested that Cu(0)/Me_6-TREN-catalyzed polymerization of MA initiated by methyl 2-bromopropionate (MBP) at 25 °C in DMSO and an analogous polymerization performed in MeCN exhibit both nonlinear fist-order kinetics and display an "astonishingly similar" level of control and overall rate.[10] These results might lead one to believe that, contrary to the prevailing body of evidence, disproportionation does not play a critical roll in the enhanced rate, control, and chain end fidelity associated with SET-LRP.

The goal of this publication is to compare our data for the Cu(0)/Me_6-TREN-catalyzed polymerization of MA initiated by MBP at 25 °C in DMSO with that in MeCN and in various DMSO/MeCN mixtures, with the data reported previously,[10] and demonstrate by a combination of kinetic experiments and chain end analysis by 500 MHz ^{1}H NMR spectroscopy that the solvent choice differentiates SET-LRP and Cu-mediated radical polymerization with non-first-order kinetics. These results demonstrate that the presence of a solvent/ligand pair that mediates the disproportionation of Cu(I)X species into Cu(0) and Cu(II)X_2 is a requirement to ensure the achievement of a radical polymerization process that is truly living.

Results and Discussion

The Cu(0)/Me_6TREN-catalyzed polymerization of MA was carried out at 25 °C in DMSO and in MeCN using MBP as an initiator under the following conditions: $[MA]_0/[MBP]_0/[Cu(0)]/[Me_6\text{-TREN}]_0 = 222/1/0.1/0.1$, $[MA]_0 = 7.4$ mol/L. Cu(0) powder with a particle size <75 μm was used as the primary activating species.

Figure 1a,b summarizes the kinetic data for the Cu(0)/Me_6-TREN-catalyzed SET-LRP of MA initiated with MBP in

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* To whom correspondence should be addressed: e-mail percec@sas.upenn.edu.

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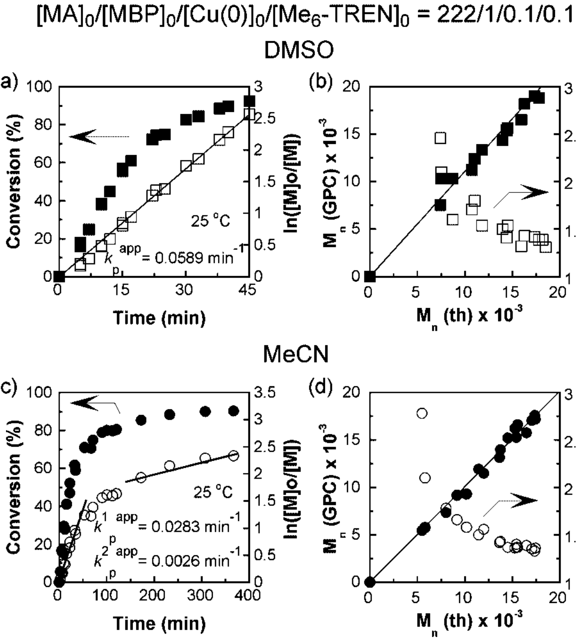

Figure 1. Kinetic plots for the Cu(0)/Me$_6$-TREN-catalyzed SET-LRP of MA initiated with MBP at 25 °C in (a, b) DMSO and (c, d) MeCN. Polymerization conditions: MA = 1 mL, solvent = 0.5 mL, $[MA]_0$ = 7.4 mol/L, $[MA]_0/[MBP]_0/[Cu(0)]_0/[Me_6\text{-}TREN]_0 = 222/1/0.1/0.1$, and Cu(0) < 75 mm.

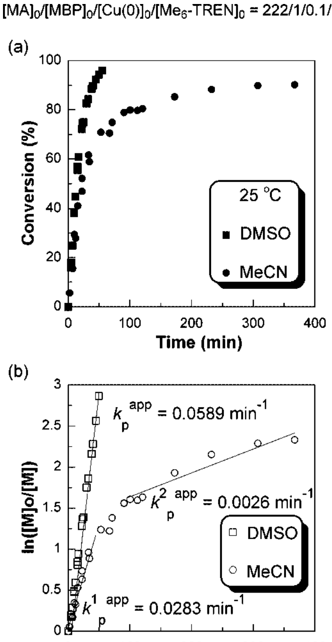

Figure 2. (a) Monomer conversion and (b) $\ln([M]_0/[M])$ vs time for the Cu(0)/Me$_6$-TREN-catalyzed polymerization of MA initiated with MBP at 25 °C in DMSO and MeCN. Polymerization conditions: MA = 1 mL, solvent = 0.5 mL, $[MA]_0$ = 7.4 mol/L, $[MA]_0/[MBP]_0/[Cu(0)]_0/[Me_6\text{-}TREN]_0 = 222/1/0.1/0.1$, and Cu(0) < 75 mm.

Table 1. Apparent Rates Constants of Propagation (k_p^{app}) for the Cu(0)/Me$_6$-TREN-Catalyzed SET-LRP of MA Initiated with MBP at 25 °C in DMSO, MeCN, and Different Mixtures of Both Solvents[a]

solvent	$k^1{}_p^{app}$ (min^{-1})[a]	$k^2{}_p^{app}$ (min^{-1})[b]
DMSO	0.0589	NA[c]
DMSO:MeCN (70:30)	0.0541	0.0392
DMSO:MeCN (50:50)	0.0467	0.0262
DMSO:MeCN (30:70)	0.0289	0.0088
MeCN	0.0283	0.0026

[a] $k^1{}_p^{app}$ is the k_p^{app} or the first kinetic domain (apparent first-order region). [b] $k^2{}_p^{app}$ is the k_p^{app} for the second kinetic domain (non-first-order region). [c] Polymerization is living; therefore, there is only kinetic one domain. [a] Polymerization conditions: MA = 1 mL, solvent = 0.5 mL, $[MA]_0$ = 7.4 mol/L, $[MA]_0/[MBP]_0/[Cu(0)]_0/[Me_6\text{-}TREN]_0 = 222/1/0.1/0.1$, and Cu(0) < 75 μm.

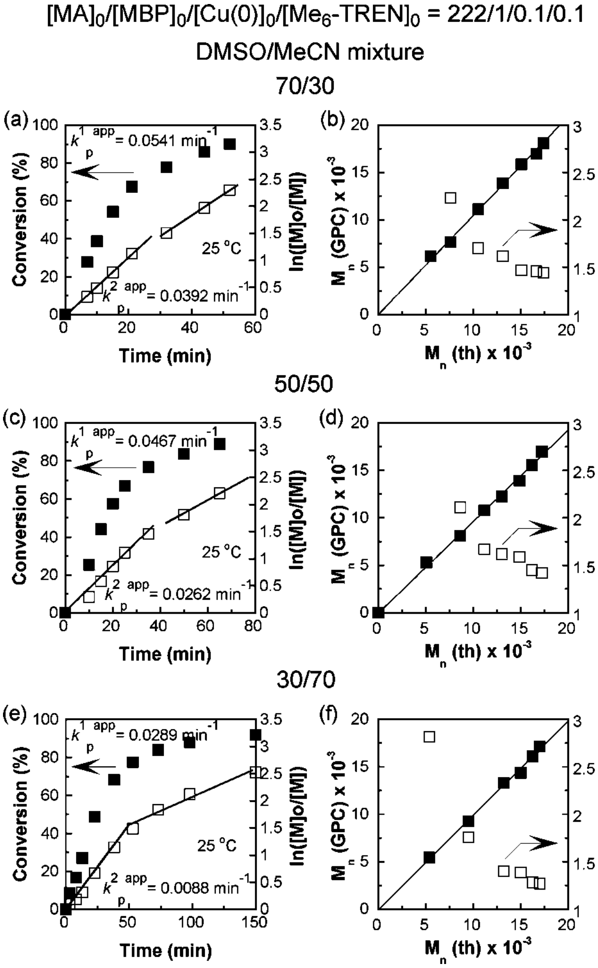

Figure 3. Kinetic plots for the Cu(0)/Me$_6$-TREN-catalyzed SET-LRP of MA initiated with MBP at 25 °C in DMSO/MeCN mixtures (v/v): (a, b) 70/30, (c, d) 50/50, and (e, f) 70/30. Polymerization conditions: MA = 1 mL, solvent = 0.5 mL, $[MA]_0$ = 7.4 mol/L, $[MA]_0/[MBP]_0/[Cu(0)]_0/[Me_6\text{-}TREN]_0 = 222/1/0.1/0.1$, and Cu(0) < 75 mm.

DMSO. The data obtained from three repetitions of the same experiment are plotted together. Plots of conversion and $\ln([M]_0/[M])$ vs time demonstrate that this is a LRP process. The polymerization is fast and reaches 90% conversion in 45 min. The time dependence of $\ln([M]_0/[M])$ is linear, which indicates a first-order rate of propagation in both growing radicals and monomer concentrations and that the concentration of active species is constant during the polymerization. These observations in addition to the linear dependence of M_n vs theoretical molecular weight (M_n^{th}) support a living polymerization mechanism for the Cu(0)/Me$_6$-TREN-catalyzed SET-LRP of MA initiated with MBP in DMSO.

Figure 1c,d shows the data obtained from three repetitions of the same experiment performed in MeCN. Based on the experiments carried out in our laboratories when the same polymerization was performed in MeCN, the kinetic data display a completely different behavior. It can be seen that in this case the polymerization is much slower reaching 90% conversion only after 6 h. Incidentally, the monomer conversion where the kinetics loses the linear behavior is strongly dependent on the Cu(0) particle size used. This trend will be analyzed in a

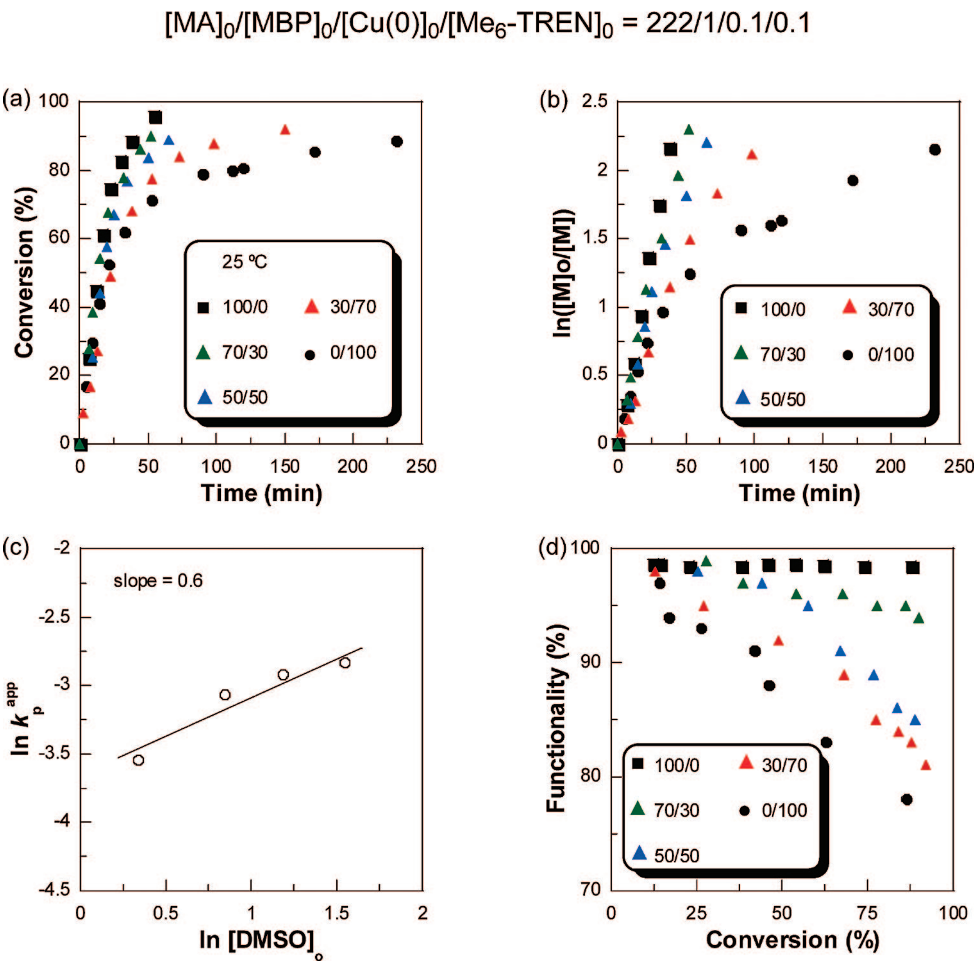

Figure 4. (a) Monomer conversion, (b) $\ln([M]_0/[M])$ vs time, (c) $\ln k_p^{app}$ vs $[DMSO]_0$, and percentage of bromine-functionalized chain vs conversion (%) for the Cu(0)/Me_6-TREN-catalyzed polymerization of MA initiated with MBP at 25 °C in pure DMSO, MeCN, and DMSO/MeCN mixtures (v/v 70/30, 50/50, and 30/70). Polymerization conditions: MA = 1 mL, solvent = 0.5 mL, $[MA]_0 = 7.4$ mol/L, $[MA]_0/[MBP]_0/[Cu(0)]_0/[Me_6\text{-TREN}]_0 = 222/1/0.1/0.1$, and Cu(0) < 75 mm.

forthcoming publication. When comparing both experiments, it is important to carefully examine the evolution of both conversion and $\ln([M]_0/[M])$ vs time. It can be seen that in MeCN the time dependence of $\ln([M]_0/[M])$ is linear only up to ~65% monomer conversion, after which a linear behavior of the semilogarithmic plot is no longer observed. The deviation from linearity indicates that in this case the concentration of the active species is not constant during the polymerization process. Therefore, the combination of Me_6-TREN as ligand and a solvent such as MeCN is not sufficient to mediate a rapid enough disproportionation of Cu(I)X/L species required for a living radical polymerization.

It was previously claimed that these two polymerizations display an astonishingly similar overall rate.[10] Figure 2 overlaps the evolution of conversion and $\ln([M]_0/[M])$ vs time for both experiments and demonstrates that the kinetics of the two polymerizations are different. The same behavior was observed when the kinetic data were obtained from an experiment that was scaled up to 9 mL of MA (solvent = 4.5 mL, $[MA]_0 = 7.4$ mol/L, $[MA]_0/[MBP]_0/[Cu(0)]_0/[Me_6\text{-TREN}]_0 = 222/1/0.1/0.1$, and Cu(0) < 75 μm). From the data reported here, a direct comparison of the apparent rate constant of propagation (k_p^{app}) for these two polymerizations can be obtained. As the kinetic experiment in MeCN showed a nonlinear $\ln([M]_0/[M])$ vs time dependence, only the initial slope was used to calculate $k^1{}_p^{app}$ in MeCN and compare it with k_p^{app} in DMSO. These values for the apparent rate constant of propagation (k_p^{app}) are shown on the kinetic plots presented in Figures 2 and in Table 1. For the Cu(0) particle size reported here, it can be seen that while the initial k_p^{app} in MeCN ($k^1{}_p^{app} = 0.0283$ min^{-1}) is about 2 times smaller than the k_p^{app} measured in DMSO ($k_p^{app} = 0.0589$ min^{-1}), it is ~22 times larger than the same k_p^{app} measured in toluene ($k_p^{app} = 0.0027$ min^{-1}) under the same reaction conditions.[11] According to the OSET model for the activation step in SET-LRP, while the reduced k_p^{app} in toluene is partially and perhaps solely attributable to the diminished rate of electron transfer in toluene, the similarity in rate observed between MeCN and DMSO confirms that both solvents are amenable to the OSET process.[12]

In order to monitor the transition from a Cu(0)/Me_6-TREN-catalyzed SET-LRP to a Cu(0)/Me_6TREN-catalyzed radical polymerization, the polymerization experiments reported above were also performed in different MeCN/DMSO mixtures. Figure 3 shows the kinetic plots for the Cu(0)/Me_6-TREN-catalyzed polymerization of MA initiated with MBP at 25 °C in different MeCN/DMSO mixtures (70/30, 50/50, and 30/70 v/v). It can be seen that the higher the amount of DMSO, the faster the polymerization. Figure 4a,b presents the kinetic plots of the experiments performed in solvent mixtures overlapped with the kinetic plots in pure DMSO and MeCN. It can be seen that increasing the amount of DMSO reduces the curvature of the semilogarithmic plot and increases the tendency toward a first-order reaction. This trend can also be observed from the k_p^{app} reported in Table 1. The values of $\ln k^1{}_p^{app}$ from Table 1 are plotted Figure 4c as a function of $\ln [DMSO]_0$. They show a non-first-order external order of reaction in DMSO. These results

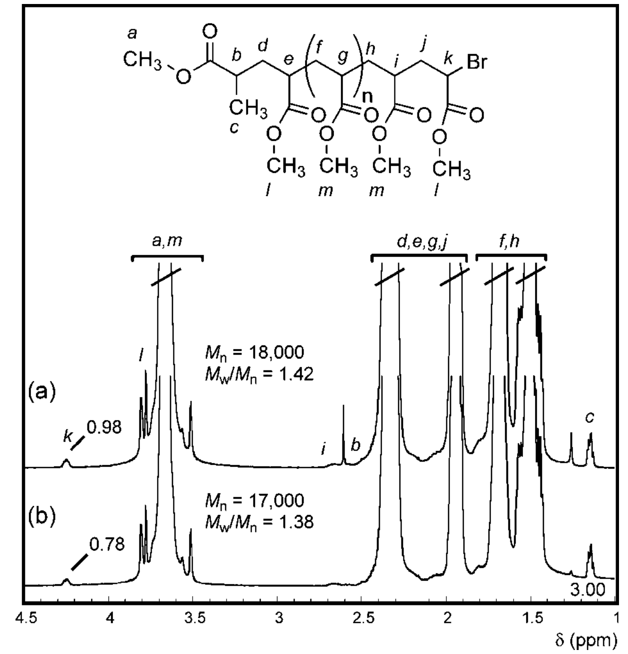

Figure 5. 500 MHz ^{1}H NMR spectra ($CDCl_3$) of PMA obtained by Cu(0)/Me_6-TREN-catalyzed polymerization of MA initiated with MBP at 25 °C in (a) DMSO ($M_n = 18\,000$ and $M_w/M_n = 1.42$, after 40 min at 88% monomer conversion) and (b) MeCN ($M_n = 17\,000$ and $M_w/M_n = 1.38$, after 4 h at 86% monomer conversion). Polymerization conditions: MA = 1 mL, solvent = 0.5 mL, $[MA]_0 = 7.4$ mol/L, $[MA]_0/[MBP]_0/[Cu(0)]_0/[Me_6\text{-TREN}]_0 = 222/1/0.1/0.1$, and Cu(0) < 75 mm.

further demonstrate that Cu(0)/Me_6-TREN polymerization of MA under the reported conditions does not proceed in a similar manner in both DMSO and MeCN. Rather, DMSO is the only solvent of these two that mediates truly first-order kinetics that supports a living radical polymerization.

The evolution of the percentage of functionality (*f*) was monitored during the five polymerizations studied in this communication through the withdrawal of samples from the polymerization mixture at different times followed by their analysis by 500 MHz ^{1}H NMR. Figure 5 shows the 500 MHz ^{1}H NMR spectrum together with its proton assignments of two isolated PMA samples obtained from the Cu(0)/Me_6-TREN-catalyzed polymerization of MA at 25 °C in (a) DMSO ($M_n = 18\,000$ and $M_w/M_n = 1.42$, after 40 min at 88% monomer conversion) and in (b) MeCN ($M_n = 17\,000$ and $M_w/M_n = 1.38$, after 4 h at 86% monomer conversion). The signals of the protons of the main chain ($-CH_2-$ and $-CH-$) are present in the region 1.30−2.70 ppm. The signal of $-OCHH_3$ side group appears at around 3.7 ppm. The percentage of chain-end functionality can be estimated by a comparison of the integrals of the peaks H_c (corresponding to the initiator CH_3-CH groups) and H_k (proton CH located in the α-position of the bromine chain end) (eq 1).

$$\%\ \text{functionality} = [H_k/(H_c/3)] \times 100 \qquad (1)$$

This value, measured by NMR, is the fraction of initiated chains that are effectively capped with a bromine atom. In an ideal living polymerization with no bimolecular termination or other chain breaking reactions, this value should be 100%. The integration of signal H_c (corresponding to the initiator CH_3-CH groups) vs H_k (proton CH located in the α-position of the bromine chain end) in Figure 3 indicates that a significant percentage of bromine end groups (22% at 86% monomer conversion) are lost. On the other hand, the PMA isolated from the polymerization performed in DMSO shows a much better fidelity of the structure of the bromine chain ends. Figure 4d shows the evolution of *f* versus the conversion for the experiments performed in pure DMSO and MeCN and in mixtures of both solvents. The most relevant result is the ≥98% bromine functionality observed through the Cu(0)/Me_6-TREN-catalyzed SET-LRP of MA in DMSO. This is in agreement with the mechanism proposed for SET-LRP mechanism.[1] In SET-LRP activation of alkyl halides is produced by Cu(0) species while deactivation is generated by the $Cu(II)X_2$ species produced by the disproportionation of Cu(I)X into Cu(0) and $Cu(II)X_2$. This mechanism does not require the persistent radical effect,[13,14] which is created by irreversible bimolecular termination, or if it does, it is negligible by comparison with the case of the polymerization carried out in MeCN. On the other hand, progressive decrease in the percentage of bromo terminal functionality was observed in the polymerization of MA carried out in MeCN. In this case, the percentage of bromine chain ends decreases through the polymerization and is ~80% at 86% monomer conversion. These observations are in agreement with the non-first-order kinetics and indicate that in MeCN the lack of disproportionation is balanced by a large extent of bimolecular termination that creates the persistent radical effect[13,14] throughout the polymerization process. This phenomenon accumulates $Cu(II)X_2$ species, reduces the amount of Cu(0), and consequently slows down the polymerization. The evolution of *f* versus the conversion for the experiments performed in DMSO/MeCN mixtures shows the expected trend. These results demonstrate that disproportionation is the crucial step for the successful SET-LRP of MA at 25 °C.

In conclusion, the kinetic and chain-end analysis reported here for the Cu(0)/Me_6TREN-catalyzed SET-LRP of MA initiated with MBP at 25 °C in DMSO, a solvent that mediates the disproportionation of Cu(I)X, in MeCN, a solvent in which Cu(I)X species do not undergo disproportionation at least at 25 °C, and in their mixtures demonstrates that while DMSO is able to provide a living radical polymerization with first-order kinetics and a nearly complete retention of the bromine chain ends, MeCN does not.

Experimental Section

Materials. Methyl acrylate (MA) (99%, Aldrich), copper (<75 μm powder 99%, Aldrich), methyl 2-bromopropionate (98%, Aldrich), dimethyl sulfoxide (DMSO) (99.9%, Fisher), and acetonitrile (MeCN) (99.9%, Fisher) were used as received. Hexamethylated tris(2-aminoethyl)amine (Me_6-TREN) was synthesized as described in the literature.[15]

Techniques. 500 MHz ^{1}H NMR spectra were recorded on a Bruker DRX500 NMR instrument at 20 °C in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Gel permeation chromatographic (GPC) analysis of the polymer samples were done on a Perkin-Elmer Series 10 high-performance liquid chromatograph, equipped with an LC-100 column over (40 °C), a Nelson Analytical 900 Series integration data station, a Perkin-Elmer 785A UV−vis detector (254 nm), a Varian star 4090 refractive index (RI) detector, and two AM gel (500 Å, 5 μm and 10^4 Å, 5 μm) columns. THF (Fisher, HPLC grade) was used as eluent at a flow rate of 1 mL/min. The number (M_n) and weight-average (M_w) molecular weights of the PMA samples were determined with PMMA standards purchased from American Polymer Standards. Since the hydrodynamic volume of PMA is the same as PMMA, no correction is needed in the determination of M_n.

Typical Procedure for Polymerization Kinetics. The monomer (MA, 1 mL, 11.1 mmol), solvent (DMSO, 0.5 mL), initiator (MBP, 5.6 μL, 0.05 mmol), catalyst (Cu(0), 0.32 mg, 0.005 mmol), and ligand (Me_6-TREN, 1.15 mg, 0.005 mmol) were added to a 25 mL Schlenk tube in the following order: Cu(0), monomer, ligand, solvent, initiator. When a mixture of DMSO/MeCN was used as a solvent, it was previously prepared at a desired ratio. After three freeze−pump−thaw cycles, the tube was filled with nitrogen, and the reaction mixture was placed in an oil bath thermostated at 25 ± 0.1 °C with stirring. The side arm of the tube was purged with nitrogen before it was opened for samples to be removed at predetermined times, with an airtight syringe. Samples were dissolved in $CDCl_3$, and the conversion was measured by ^1H NMR spectroscopy. The M_n and M_w/M_n values were determined by GPC with PMMA standards (conversion: 88% (40 min), $M_n^{GPC} = 18\,000$, $M_w/M_n = 1.42$). The polymerization mixture was dissolved in 5 mL of CH_2Cl_2 and passed through a small basic Al_2O_3 chromatographic column to remove unreacted Cu(0) catalyst and Cu(II) compounds, and the resulting solution was precipitated twice in 60 mL of cold methanol with stirring. Methanol was removed by decantation, and the final colorless polymer was dried under vacuum until constant weight was reached.

Chain-End Analysis of PMA. The evolution of the percentage of functionality (*f*) of the PMA was monitored during the five polymerizations studied in this communication through the withdrawal of samples from the polymerization mixture at different times followed by their analysis by 500 MHz ^1H NMR. In the ^1H NMR spectra of all the PMA, the signals of the protons of the main chain (methyne and methylene) are present in the region 1.30−2.70 ppm. The signal of OCH_3 side groups appears at around 3.7 ppm. Of special interest are the signals associated with the chain ends. The signal at 4.24 ppm corresponds to the proton −CH− located in the α-position of the bromine chain end H_k, whereas the signal at 1.14 ppm (H_c) is associated with the initiator $-CH-CH_3$ groups. The percentage of chain-end functionality of PMA can be estimated from the integral ratio between these two signals (eq 1). This value is the fraction of initiated chains that are effectively capped by a bromine atom.

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