Effect of Cu(0) Particle Size on the Kinetics of SET-LRP in DMSO and Cu-Mediated Radical Polymerization in MeCN at 25 °C

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Received August 11, 2008; Revised Manuscript Received October 7, 2008

ABSTRACT: In order to estimate the effect of Cu(0) particle size in SET-LRP, a comparative analysis of Cu(0)/Me_6-TREN-catalyzed polymerization of MA initiated with methyl 2-bromopropionate at 25 °C was performed in DMSO, a solvent that mediates the disproportionation of Cu(I)X, and in MeCN, a solvent in which Cu(I)X does not disproportionate Cu(I)X. Decreasing the Cu(0) particle size results in a marked increase in the apparent rate constant of propagation (k_p^{app}). Decreasing the Cu(0) particle size from 425 to 0.05 μm (50 nm) increases the k_p^{app} by almost an order of magnitude. Regardless of the Cu(0) particle size used, in DMSO a perfect SET-LRP occurs with a first-order polymerization in growing species up to 100% conversion. However, in MeCN the polymerization is not first order in growing species. The results presented here demonstrate that, in addition to the disproportionation of Cu(I)X/L into Cu(0) and Cu(II)X_2/L, the particle size of Cu(0) plays a strong role in the kinetics during the entire polymerization.

Introduction

The ability of Cu(0) and Cu_2O to catalyze the radical polymerization of vinyl monomers initiated with alkyl sulfonyl halides,[1] alkyl halides,[2−4] haloesters,[5,6] and N halides[6] is well established. However, it was only in a recent series of publications that Cu(0) was harnessed in a practical method to perform living radical polymerization without the need of additional Cu^IX activator or $Cu^{II}X_2$ deactivator.[6] In this technique, single-electron transfer living radical polymerization (SET-LRP), bulk Cu(0) and extremely reactive Cu(0) and Cu(II)X_2 species generated in situ through the disproportionation of Cu(I)X in dipolar aprotic solvents (such as DMSO), alcohols,[7] ionic liquids,[8] and H_2O[3,4] in the presence of a diversity of N-containing ligands mediate an ultrafast living radical polymerization of methyl acrylate (MA), methyl methacrylate (MMA), ethyl acrylate (EA),[9] butyl acrylate (BA),[9] and vinyl chloride (VC)[3,4,6] at room temperature or below. SET-LRP is able to rapidly achieve high molecular weights, with excellent control of molecular weight distribution while maintaining perfect retention of chain end functionality.[9] The mechanistic proposal for SET-LRP invokes reversible activation of the dormant polymer chain via a Cu(0)-mediated outer-sphere electron transfer (OSET) process involving heterolytic C−X cleavage.[3,4,6,10,11] Just as crucial, the mechanism suggests that the reaction control needed for living kinetics is achieved through the aforementioned disproportionation of the in situ generated Cu(I)X into Cu(0) activator and Cu(II)X_2 deactivator.[6]

While it was stated in the original publication[6] that the extent of disproportionation of Cu^IX in SET-LRP is highly dependent on ligand[12] and solvent choice, it was only recently that we undertook a thorough examination of the extent of the solvent effect.[13,14] A comparison of SET-LRP of MA in DMSO at 25 °C and an equivalent polymerization in toluene demonstrated that DMSO both accelerates the electron-transfer activation step and that the disproportionation mediated by N-ligands in DMSO is critical for the establishment of first-order kinetics and perfect retention of chain end functionality.[13] In toluene, where disproportionation of Cu(I)X is not favored, the reaction is roughly 16 times slower than in DMSO and plateaus at 60% conversion, and chain end functionality is lost continuously throughout the polymerization. A similar comparison was recently made between SET-LRP in DMSO at 25 °C and an analogous reaction in MeCN, another nondisproportionating solvent, but one more amenable to SET than toluene.[15] This comparison revealed that polymerization in MeCN is still 50% slower than SET-LRP in DMSO, that the conversion still plateaus though in this case at roughly 80%, and that the lack of disproportionation in MeCN prevents the establishment of living behavior indicated by non-first-order kinetics and continuous loss of chain end functionality.

In a recent report, other researchers have suggested that SET-LRP kinetics varies with the age and type of Cu(0) source and that this fact is somehow evidence for Cu(I)-mediated polymerization.[16,17] We present a rigorous analysis of the effect of Cu(0) particle size on the kinetics of SET-LRP of MA initiated with methyl 2-bromopropionate (MBP) and catalyzed by Cu(0)/Me_6-TREN in DMSO at 25 °C as well as in the analogous Cu(0)-mediated radical polymerization in MeCN. Kinetic experiments measured by 500 MHz ^1H NMR spectroscopy were used to demonstrate that a progressive decrease in average Cu(0) particle size results in marked increase in the apparent rate constant of polymerization (k_p^{app}). This trend does not change between SET-LRP in DMSO and Cu-mediated radical polymerization in MeCN. Together, these results strongly suggest that increasing the relative amount of active Cu(0) surface area indirectly modulates the k_p^{app} through an increase in the surface mediated k_{act} and that these trends are conserved in solvents capable of promoting SET.

Results and Discussion

Effect of Particle Size on the Kinetics of SET-LRP in DMSO at 25 °C. Figure 1a−l shows the kinetic experiments for the Cu(0)/Me_6-TREN-catalyzed SET-LRP of MA initiated with MBP in DMSO using Cu(0) powder of different particle sizes (425, 75, 45, 3, 0.1, and 0.05 μm). All polymerization experiments were carried out at 25 °C. The molar ratio between monomer, initiator, catalyst, and ligand were kept constant: $[MA]_0/[MBP]_0/[Cu(0)]_0/[Me_6\text{-TREN}]_0 = 222/1/0.1/0.1$. Regardless of the particle size used all the polymerizations were fast, reaching ~90% monomer conversion in less than 100 min. The slowest polymerization was observed for the largest particle size

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10.1021/ma8018365 CCC: $40.75

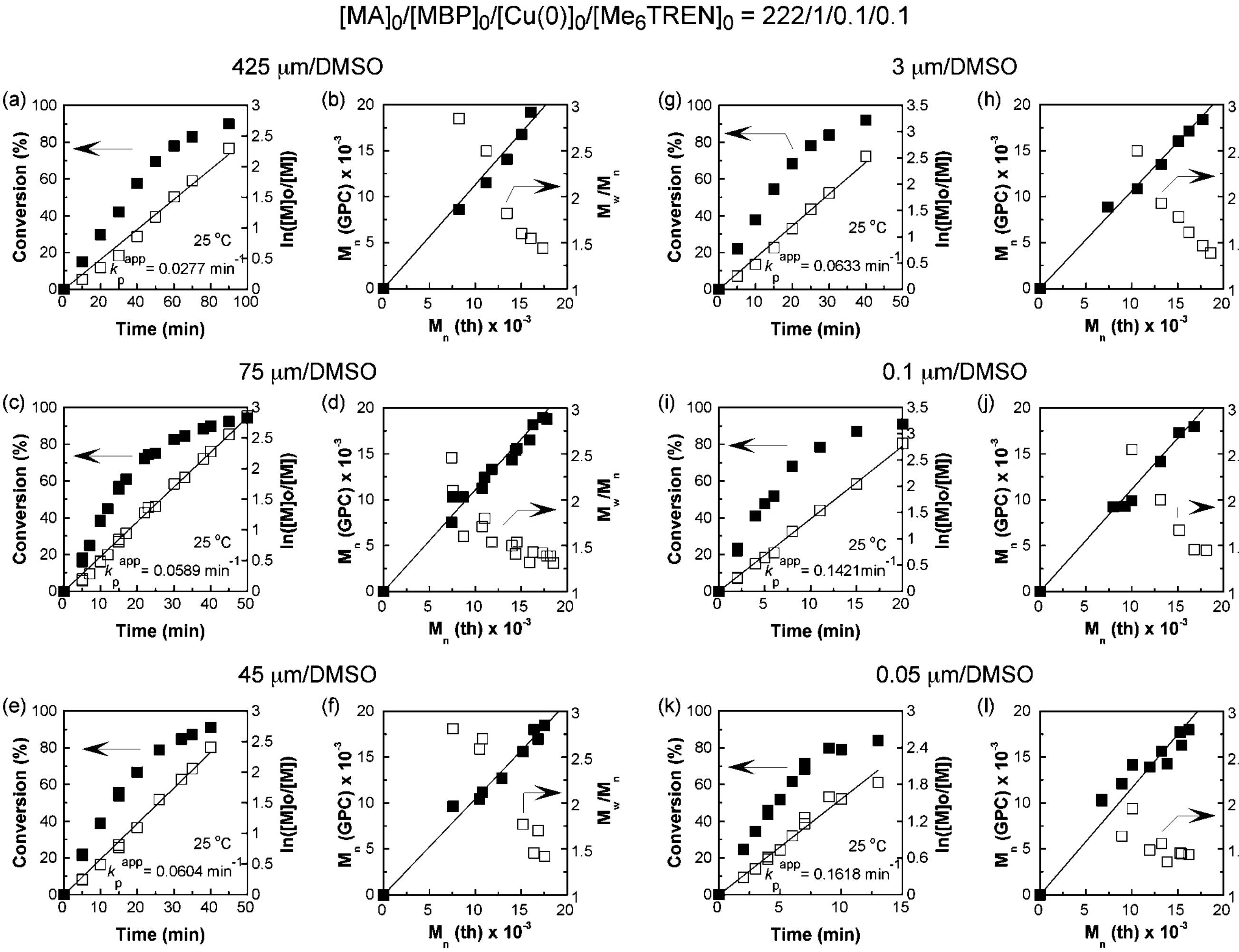


Figure 1. Kinetic plots for the Cu(0)/Me$_6$-TREN-catalyzed SET-LRP of MA initiated with MBP in DMSO at 25 °C using different Cu(0) particle size. (a, b) 425 μm, (c, d) 75 μm, (e, f) 45 μm, (g, h) 3 μm, (i, j) 0.1 μm, and (k, l) 0.05 μm. Polymerization conditions: MA = 1 mL, DMSO = 0.5 mL, $[MA]_0$ = 7.4 mol/L, $[MA]_0/[MBP]_0/[Cu(0)]_0/[Me_6\text{-TREN}]_0$ = 222/1/0.1/0.1.

Table 1. Dependence of k_p^{app} on the Dimensions of the Cu(0) Particle Size during SET-LRP of MA Initiated with MBP in DMSO and Cu-Mediated Radical Polymerization of MA Initiated with MBP in MeCN at 25 °C (Data Collected from Figures 1a−l and 4a−l)

no.	Cu(0) particle size (μm)	solvent	k_p^{app} (min^{-1}) $k^1{}_p{}^{app}$ [a]	$k^2{}_p{}^{app}$ [b]	conv (%)	time (min)	M_w/M_n
1	425	DMSO	0.0277	NA[c]	90	90	1.44
2	75	DMSO	0.0589	NA[c]	92	45	1.39
3	45	DMSO	0.0604	NA[c]	91	40	1.42
4	3	DMSO	0.0633	NA[c]	92	40	1.47
5	0.1	DMSO	0.1421	NA[c]	91	20	1.45
6	0.05	DMSO	0.1618	NA[c]	84	13	1.44
7	425	MeCN	0.0168	0.0052	92	280	1.38
8	75	MeCN	0.0283	0.0026	90	365	1.36
9	45	MeCN	0.0305	0.0018	85	445	1.39
10	3	MeCN	0.0392	0.0007	85	475	1.37
11	0.1	MeCN	0.1301	0.0006	81	630	1.38
12	0.05	MeCN	0.1450	0.0006	65	250	1.40

[a] $k^1{}_p{}^{app}$ is the k_p^{app} for the first kinetic domain (apparent first-order region). [b] $k^1{}_p{}^{app}$ is the k_p^{app} for the second kinetic domain (non-first-order region). [c] Polymerization is living; therefore, there is only one kinetic domain.

(425 μm). This reaction reached 90% conversion in 90 min. On the other hand, the fastest polymerization was observed when Cu(0) nanopowder (50 nm), the smallest particle size investigated, was used as a primary activating species. In this case, PMA of M_n = 18 000 and M_w/M_n = 1.44 was obtained in ~15 min. The details of these kinetic experiments are summarized in Table 1.

SET-LRP catalyzed by Cu(0)/Me$_6$-TREN is believed to be a surface-mediated OSET process.[3,4,6] It is therefore expected that the amount of accessible surface area of the initial copper source should directly affect the rate of the reaction. Figure 2 overlaps the dependence of the conversion and $\ln([M]_0/[M])$ vs time (where [M] is the monomer concentration and $[M]_0$ is the initial monomer concentration) for these six experiments. The values for the k_p^{app} are also listed in Table 1. The evolution of $\ln([M]_0/[M])$ vs time demonstrates that these polymerizations are first order in the monomer concentration as expected for a living radical polymerization process. The k_p^{app} is strongly dependent on the size of the Cu(0) particles used. A continuous increase in k_p^{app} from 0.0277 min^{-1} in the presence of Cu(0) of 425 μm

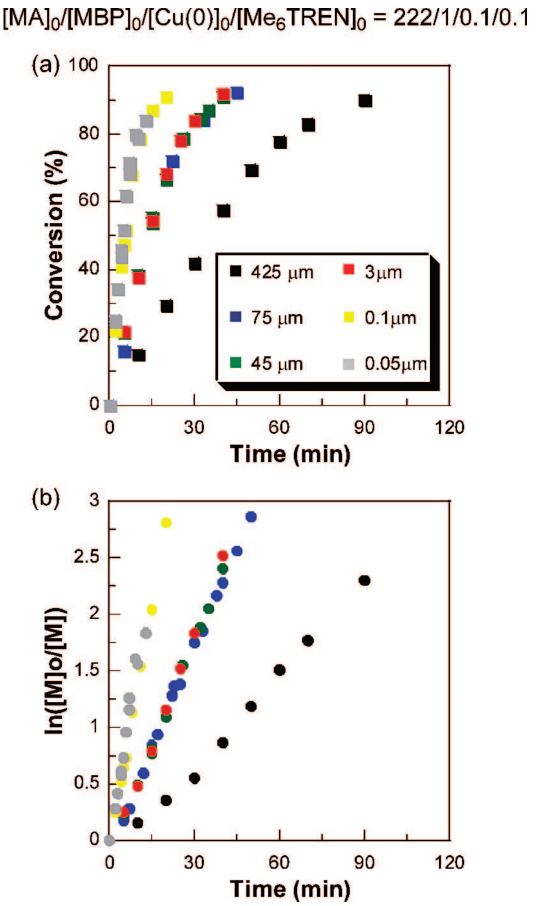


Figure 2. (a) Monomer conversion and (b) $\ln([M]_0/[M])$ vs time for the Cu(0)/Me_6-TREN-catalyzed polymerization of MA initiated with MBP in DMSO at 25 °C using Cu(0) particle size of 425, 75, 45, 3, 0.1, and 0.05 μm. Polymerization conditions: MA = 1 mL, DMSO = 0.5 mL, $[MA]_0 = 7.4$ mol/L, $[MA]_0/[MBP]_0/[Cu(0)]_0/[Me_6\text{-TREN}]_0 = 222/1/0.1/0.1$.

to 0.1618 min^{-1} in the presence of Cu(0) of 0.05 μm was observed. Figure 3a depicts the dependence of measured k_{app} on the average diameter of Cu(0) source. It can be seen that decreasing particle diameter results in a monotonic increase in the observed k_p^{app} (min^{-1}). The exact dependence of particle size on rate is not obvious from this direct representation. One might infer two domains of linear dependence or a global hyperbolic dependence. Previous examination of the kinetics of SET-LRP[6] has suggested a complex external order for Cu(0) of ~0.51. In an ideal living radical polymerization as exemplified by SET-LRP, we assume pseudo-first-order rate dependence in monomer, wherein the concentration of active chains is believed to be constant during the entire polymerization.

$$\text{rate} = k_p^{app}[MA][I]_0 \tag{1}$$

or

$$\text{rate} \propto k_p^{app}[MA] \tag{2}$$

The dependence of the overall rate of the reaction on the amount of Cu(0) utilized is incorporated in k_p^{app}.

$$k_p^{app} \propto [Cu]^{1/2} \tag{3}$$

The work that determined the external order of Cu(0) utilized a single 45 μm Cu source. We now seek to modify this equation to account for Cu(0) particle size. It is most sensible that the effective amount of Cu(0) in the reaction, [Cu], is proportional to the effective surface area of copper. The effective surface area of copper should initially be proportional to the surface area to volume ratio (*SA*/*V*) of the particle. If we assume, rather naively of course, that the Cu(0) particles can be described as spheres, the surface area to volume ratio is 6/*d*,[18] where *d* is the average diameter of the particle. If we introduce this 6/*d* dependence into eq 3, we arrive at a new relationship that depends on the inverse square root of *d*.

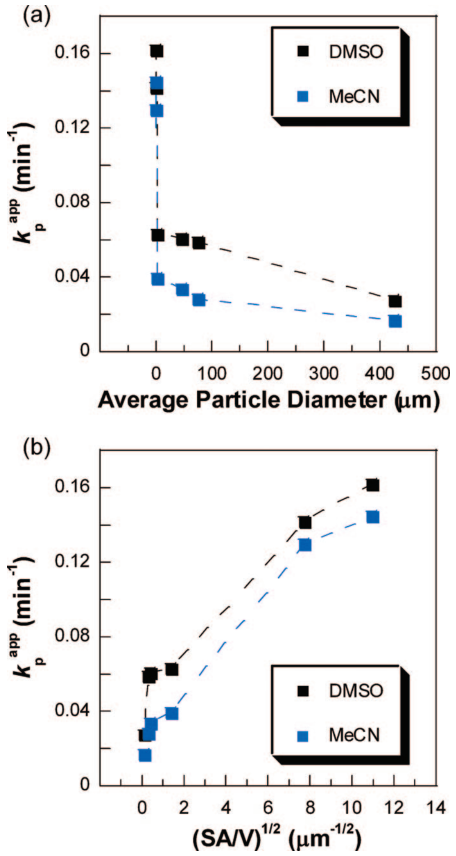


Figure 3. (a) k_p^{app} vs average particle diameter and (b) k_p^{app} vs $(SA/V)^{1/2}$ for the Cu(0)/Me_6-TREN-catalyzed polymerization of MA initiated with MBP in DMSO and MeCN at 25 °C using Cu(0) particle size of 425, 75, 45, 3, 0.1, and 0.05 μm. Polymerization conditions: MA = 1 mL, solvent = 0.5 mL, $[MA]_0 = 7.4$ mol/L, $[MA]_0/[MBP]_0/[Cu(0)]_0/[Me_6\text{-TREN}]_0 = 222/1/0.1/0.1$.

$$k_p^{app} \propto (6/d[Cu])^{1/2} \tag{4}$$

or

$$k_p^{app} \propto (6/d)^{1/2}[Cu])^{1/2} \tag{5}$$

As all experiments in this investigation use the same mass of Cu(0), the proportionality reduces to even greater simplicity.

$$k_p^{app} \propto (6/d)^{1/2} \tag{6}$$

If this relationship between apparent observed rate constant and diameter is correct, we would expect a linear relationship between the k_p^{app} and square root of *SA*/*V* (i.e., 6/*d*). Figure 3b plots the observed k_p^{app} at the various tested particle size versus the corresponding square root of the *SA*/*V*. Indeed, the relationship between the square root of *SA*/*V* and k_p^{app} is roughly linear.

Effect of Particle Size on the Kinetics of SET-LRP in MeCN at 25 °C. The disproportionation of Cu(I)X/L into Cu(0) and $Cu(II)X_2/L$ is the main requirement of SET-LRP, and therefore, the nature of the solvent is expected to exert a strong

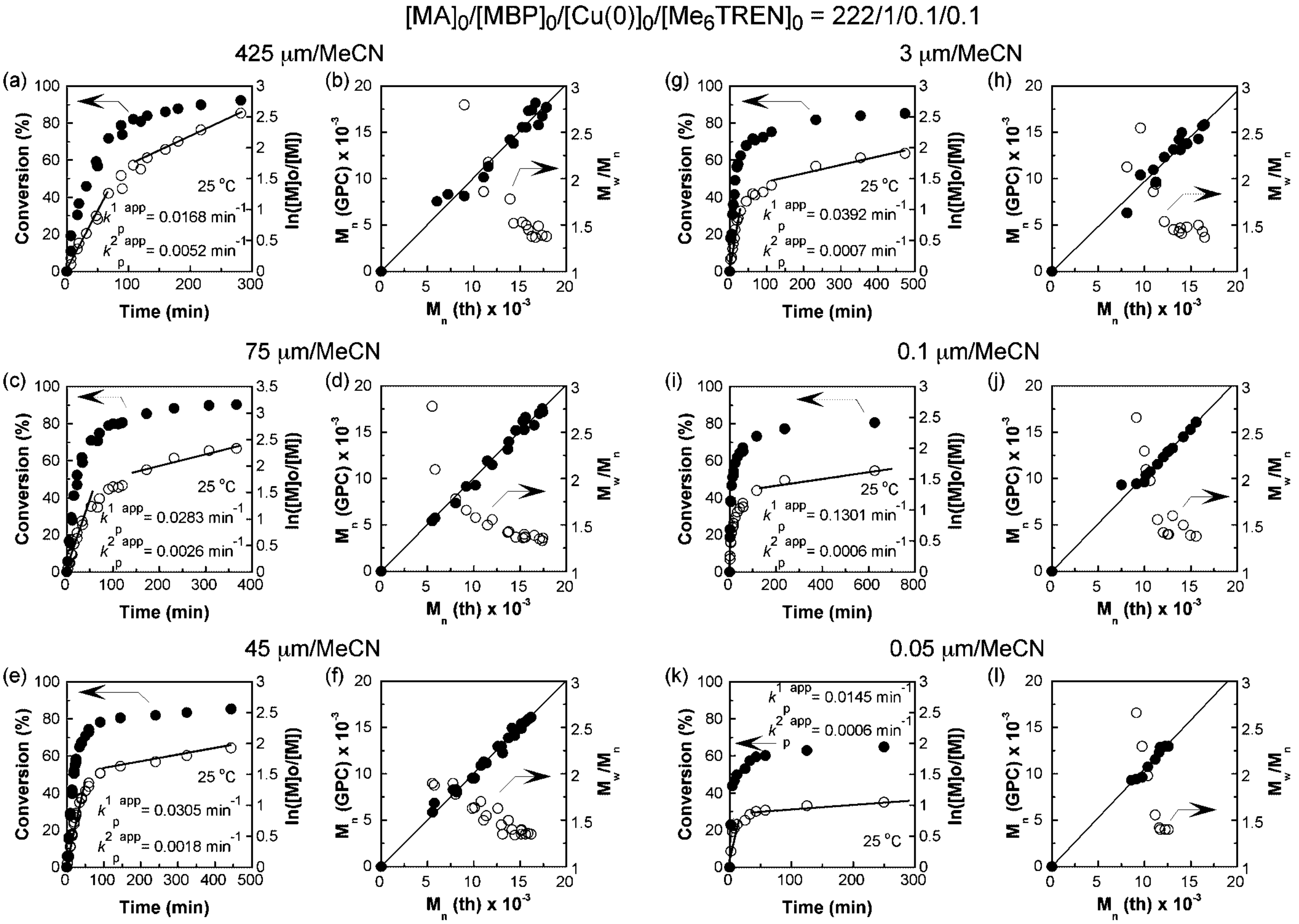


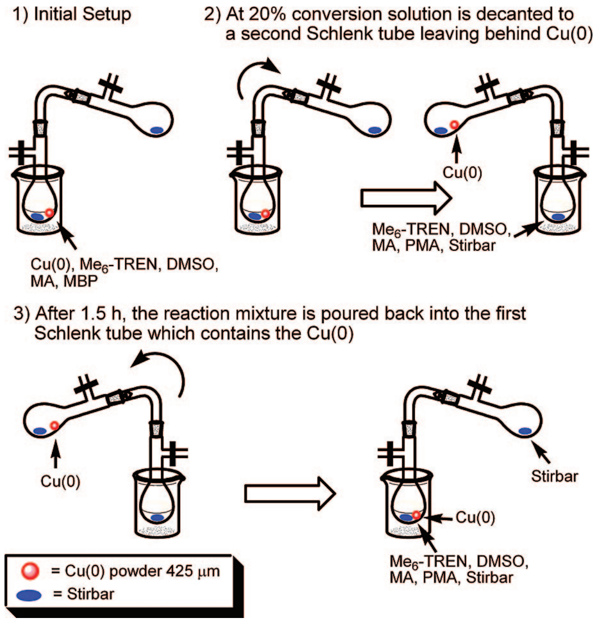
Figure 4. Kinetic plots for the Cu(0)/Me_6TREN-catalyzed polymerization of MA initiated with MBP in MeCN at 25 °C using different Cu(0) particle size: (a, b) 425 μm, (c, d) 75 μm, (e, f) 45 μm, (g, h) 3 μm, (i, j) 0.1 μm, and (k, l) 0.05 μm. Polymerization conditions: MA = 1 mL, MeCN = 0.5 mL, $[MA]_0$ = 7.4 mol/L, $[MA]_0/[MBP]_0/[Cu(0)]_0/[Me_6\text{-TREN}]_0$ = 222/1/0.1/0.1.

influence on this polymerization. DMSO, a solvent that mediates a fast disproportionation of Cu(I)X/L, ensures a living radical polymerization process providing perfect fidelity of the structure of the polymer chain ends, whereas in toluene or MeCN, solvents in which Cu(I)X/L species do not disproportionate, at least at 25 °C, a LRP has not been achieved.[13,14] Regardless of the degree of disproportionation of Cu(I)X/L mediated by the solvent, the initiation step for the Cu(0)/Me_6-TREN-catalyzed polymerization of MA proceeds via activation by OSET.[10,11]

Figure 4a−l shows the kinetic experiments for the Cu(0)/Me_6-TREN-catalyzed SET-LRP of MA initiated with MBP in MeCN using Cu(0) powder of different particle size (425, 75, 45, 3, 0.1, and 0.05 μm). All polymerization experiments were carried under the same conditions reported above. It can be seen that those polymerizations are much slower than those performed in DMSO under identical conditions. The Cu(0) (425 μm)/Me_6-TREN-catalyzed polymerization of MA initiated with MBP in MeCN at 25 °C required 280 min to reach 92% monomer conversion, whereas in DMSO 90% conversion was achieved in 90 min. Moreover it is important to stress that 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 ligand and MeCN solvent does not provide a living radical polymerization.* The same behavior was observed for the other Cu(0) particle sizes investigated (Figure 4a−l). Moreover, the smaller the particle size used, the lower the conversion where the time dependence of $\ln([M]_0/[M])$ deviates from linearity. In accordance with previous results reported from our laboratory,[13,14] the results presented here demonstrate that solvent choice differentiates SET-LRP and Cu-mediated radical polymerization with non-first-order kinetics, and this behavior is independent of the Cu(0) particle size (Figures SF1−SF6 from Supporting Information). Solvents such as DMSO and MeCN are solvents amenable to the OSET process.[19] Since the kinetic experiments performed in MeCN showed nonlinear $\ln([M]_0/[M])$ vs time dependence, only the initial slope was used to calculate k_p^{app} in MeCN as a function of the particle size and compare it with the values obtained in DMSO. These values are listed in Table 1. The values of k_p^{app} in DMSO are higher than those of $k^1{}_p^{app}$ in CH_3CN (Table 1). The k_p^{app} in DMSO are higher than $k^1{}_p^{app}$ in CH_3CN since "nascent" Cu(0) particles created by disproportionation are, due to smaller particle size, much more reactive than the externally added Cu(0) particles. Consequently, even if the activation with "nascent" particles takes place in the presence of excess $Cu(II)X_2$ generated by disproportionation, the resulting k_p^{app} is higher in disproportionating solvents than in nondisproportionating solvents.

For the Cu(0)/Me_6-TREN-catalyzed radical polymerization of MA initiated by MBP in MeCN, the same complex relationship between $k^1{}_p^{app}$ and d (Figure 3a) as well as the more instructive linear relationship between $k^1{}_p^{app}$ and the square root of SA/V (Figure 3b) is observed. Therefore, regardless of the solvent choice and the degree of disproportion in that solvent, it is apparent that the particle size of Cu(0) affects the rate of

Scheme 1. Schematic Description for the Kinetic Experiment Where Reaction Mixture Was Decanted from Cu(0) Powder at ~20% Conversion and Brought Back after 1.5 h[a]



[a] Polymerization conditions: MA = 2 mL, DMSO = 1 mL, $[MA]_0 = 7.4$ mol/L, $[MA]_0/[MBP]_0/[Cu(0)]_0/[Me_6\text{-TREN}]_0 = 222/1/0.1/0.1$, Cu(0) 425 μm.

polymerization according to the same trend, but with higher k_p^{app} in the disproportionating solvent. The results presented here are consistent with a Langmuir−Hinshelwood mechanism, wherein absorption of the initiator or bromine chain end of the dormant polymer precedes an OSET process of heterolytic cleavage to form the propagating macroradical.[20−22]

Role of "Nascent" Cu(0). The originally proposed mechanism for SET-LRP suggests that nascent or "atomic" Cu(0) formed via the disproportionation of Cu(I)X in solution is responsible for the accelerated $k^1{}_p^{app}$ via its enhanced rate of activation of the dormant polymer chains.[3,4,6] This suggestion was supported by the experiments reported in the previous subsection. To determine how "nascent" Cu(0) colloids or clusters mediate the polymerization process, the following experiment was carried out. This experiment was developed to be as close as possible to the procedure used for the general kinetic experiments and is outlined in Scheme 1. A Schlenk tube containing the Cu(0) catalyst 425 μm (red), monomer, ligand, solvent, initiator, and a stirring bar was connected to a second Schlenk tube containing only a stirring bar. After three freeze−pump−thaw cycles the polymerization was performed at 25 °C up to about 20% monomer conversion. Subsequently, the reaction mixture was decanted by tilting the setup from the Schlenk tube containing the catalyst to the one without catalyst. During this process the bulk Cu(0) particles remained in the first Schlenk tube. No polymerization was observed for 1.5 h in the second Schlenk tube. After 1.5 h the reaction mixture was decanted back to the Schlenk tube containing the catalyst, and the polymerization started immediately. Figure 5 shows the kinetic plots for the general kinetic experiment (Figure 5a) and for the experiment where the reaction mixture was decanted from Cu(0) powder after 30 min at 22% conversion (Figure 5b). Figure 5b shows that upon decantation the polymerization ceases. After 1.5 h within experimental error of the kinetic measurements the polymerization did not continue. The reaction mixture was brought back to the original Schlenk tube containing the Cu(0) powder, and the reaction restarted without even a noticeable induction period or change in the k_p^{app} (Figure 5d). Within about 90 min from this transfer the conversion was 92%. This experiment clearly demonstrates that the most active catalyst generated by disproportionation is not freely suspended in the reaction mixture. Other authors have suggested that in SET-LRP low levels of Cu(I)X generated via initiation from Cu(0) are responsible for all secondary activation of the dormant polymer chain.[16] *This experiment demonstrates that the soluble Cu(I)X/N ligand cannot be a major contributor to activation at the levels present in SET-LRP as reaction ceases when the Cu(0) surface is removed.*

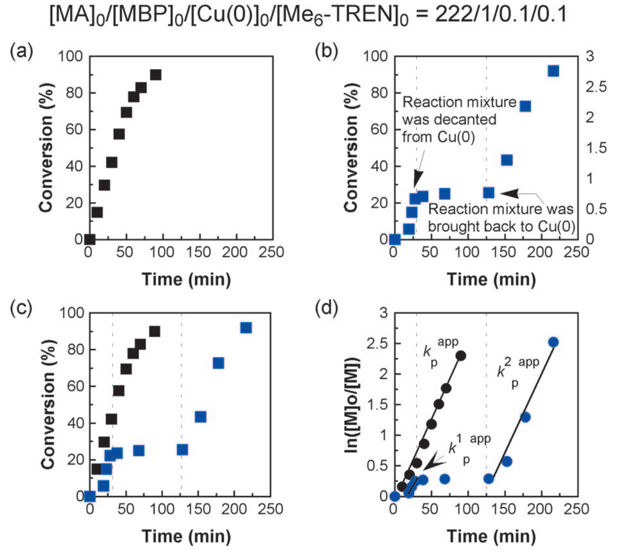


Figure 5. Kinetic plots for the Cu(0)/Me$_6$-TREN-catalyzed SET-LRP of MA initiated with MBP in DMSO at 25 °C. (a) Monomer conversion vs time for a conventional kinetic experiment used as control, (b) monomer conversion vs time for a kinetic experiment where reaction mixture was decanted from Cu(0) powder at ~20% conversion and brought back after 1.5 h, (c) overlapped monomer conversion, and (d) $\ln([M]_0/[M])$ vs time ($k_p^{app} = 0.0277$ min^{-1}, $k^1{}_p^{app} = 0.0253$ min^{-1}, $k^2{}_p^{app} = 0.0261$ min^{-1}) for both experiments. Polymerization conditions: MA = 2 mL, DMSO = 1 mL, $[MA]_0 = 7.4$ mol/L, $[MA]_0/[MBP]_0/[Cu(0)]_0/[Me_6\text{-TREN}]_0 = 222/1/0.1/0.1$, Cu(0) 425 μm.

However, these results still support the assertion that "nascent" Cu(0) derived from disproportionation plays an important role in this reaction. Dynamic light scattering (DLS) studies show that Cu(0) formed from the disproportionation of CuBr/Me$_6$-TREN in DMSO already grow or agglomerate to 100−150 nm *Z*-average diameter within 3 min (Figure 6a). The average particle size continues to grow thereafter. Figure 6b shows the same experiment, but under conditions more akin to the initial setup of a SET-LRP reaction, a 2:1 mixture of MA and DMSO. In this case the size of the agglomerated particles is somewhat larger than in DMSO alone. Figure 6c,d depicts the same experiment, but this time in 10 wt % solution of PMA (M_n = 4900 and M_w/M_n = 1.06) and PMA (M_n = 15 000 and M_w/M_n = 1.09) in DMSO. Here the agglomerated particle size is 5−10 times larger than in the previous cases and agglomerate on the bottom of the quartz cuvette. It should be noted that DLS is only providing data for the dispersed particles. Larger agglomerates precipitate almost immediately in all cases. Further, the results for DLS are based on assumed DMSO viscosity values. The increased viscosity of PMA solutions may account for the larger detected sizes in these cases. The DLS data provide evidence that "nascent" Cu(0) from disproportionation agglomerates at different rates depending upon the solvent and presence of polymer product. Depending upon the ratio between the rate of agglomeration and the rate of activation of bulk Cu(0) and of smaller "nascent" Cu(0) species, part of "nascent" Cu(0) activates the polymerization and the rest deposits on the surface of bulk Cu(0) particles that most probably act as nucleation sites,

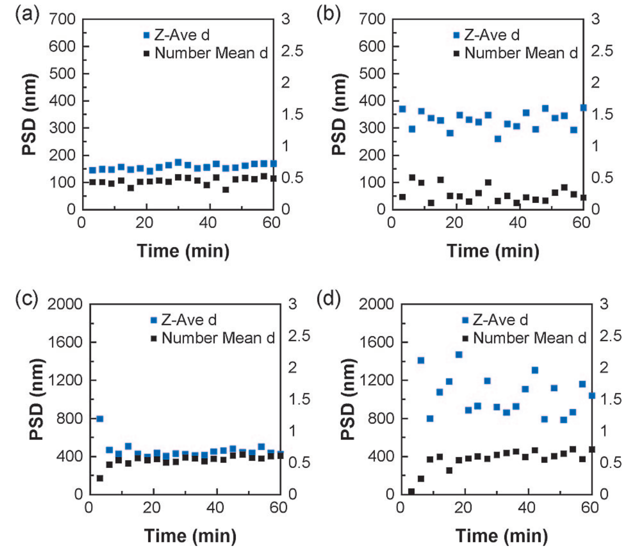


Figure 6. Number-average and *Z*-average particle size diameter (*d*) vs time for the dynamic light scattering (DLS) measurements. (a) CuBr (5×10^{-4} g, 3.49×10^{-3} M) and Me_6-TREN (3.31×10^{-3} M) in 1 mL of DMSO, (b) CuBr (5×10^{-4} g, 2.32×10^{-3} M) and Me_6-TREN (2.21×10^{-3} M) in 1.5 mL of MA/DMSO (2:1 v/v), (c) CuBr (5×10^{-4} g, 3.49×10^{-3} M) and Me_6-TREN (3.31×10^{-3} M) in 1 mL of DMSO with PMA-Br (10 wt %, $M_n = 4900$, $M_w/M_n = 1.06$), and (d) CuBr (5×10^{-4} g, 3.49×10^{-3} M) and Me_6-TREN (3.31×10^{-3} M) in 1 mL of DMSO with PMA-Br (10 wt %, $M_n = 15\,000$, $M_w/M_n = 1.09$). Viscosity of DMSO ($\eta = 2.24$ cP) was used in all DLS experiments for the analysis of particle diameter.

and therefore, no active Cu(0) particles created by disproportionation will be transferred in the second Schlenk tube. The deposition of smaller particulates on the bulk surface may explain the enhanced rate of reactivity in SET-LRP, while still providing the same relationship between initial *SA*/*V* and $k^1{}_p{}^{app}$ with higher values in DMSO. One final possibility is that activation of the dormant polymer chain occurs via an atom-leaching mechanism, wherein “atomic” Cu(0) is released from the surface of Cu and provides enhanced reactivity.[23] This mechanism is also consistent with the observed *SA*/*V* ratio vs $k^1{}_p{}^{app}$ trend. Finally, the thermodynamics of nucleation and agglomeration of Cu(0) may also play a role in driving disproportionation.

Conclusions

The effective amount of Cu(0) surface area utilized directly effects the $k_p{}^{app}$ in SET-LRP of MA in DMSO. Moving from 425 to 0.05 μm copper powder, the rate of the reaction can be modulated by almost an order of magnitude. Changing solvent from the disproportionating DMSO to the nondisproportionating MeCN, while eliminating the living behavior of the polymerization, produces a Cu(0)-mediated radical polymerization that replicates the same trend, though with up to a 50% reduction in $k^1{}_p{}^{app}$. The simplest explanation for these observations is that when Cu(0) is used as the sole Cu source, it is the surface of the Cu(0) that is responsible for reversible OSET activation and that the greater the total active surface area provided the faster the polymerization. The amount of total surface can be modulated through increased Cu loading levels or through modulation of the particle of size, shape, and surface quality of Cu(0). These results and the subsequent filtration experiment confirm Cu(0) as the primary activating agent in SET-LRP and Cu(0)-mediated nonliving radical polymerization in nondisproportionating solvents and demonstrates the transition from nonliving to LRP mediated by disproportionating solvents. While the dynamics of “nascent” Cu(0) formation and the potential aggregation on existing Cu(0) is not well-understood, the results presented here demonstrated that the characteristics of the bulk Cu(0) play a strong role in the kinetics during the entire time course of the polymerization.

Experimental Section

Materials. Methyl acrylate (MA) (99%, Aldrich), copper (99.5%, <425 μm powder, Aldrich), copper (99%, <75 μm powder, Aldrich), copper (99%, ∼45 μm powder, Across), copper (99.7%, ∼3 μm powder, dendritic), copper (99.8%, ∼0.1 μm powder, Aldrich), copper (99.9+%, <0.05 μm powder, Aldrich), copper(I) bromide (99.999%, Aldrich), methyl 2-bromopropionate (MBP) (98%, Aldrich), acetonitrile (MeCN) (99.9%, Fisher), and dimethyl sulfoxide (DMSO) (99.9%, Fisher) were used as received. Hexamethylated tris(2-aminoethyl)amine (Me_6-TREN) was synthesized as described in the literature.[24]

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 104 Å, 5 μm) columns. THF (Fisher, HPLC grade) was used as eluent at a flow rate of 1 mL/min. The number-average (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. Dynamic light scattering measurements were performed using a Malvern Zetasizer Nano Series running DTS software and operating a 4 mW He−Ne laser at 633 nm. Analysis was performed at an angle of 90° and a constant temperature of 25 °C. Dilute particle concentrations ensure that multiple scattering and particle−particle interactions can be considered negligible during data analysis.

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. 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 ^{1}H 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 (about 0 °C) with stirring. Methanol was removed by decantation, and the final colorless polymer was dried under vacuum until constant weight was reached.

Procedure for the Kinetic Experiment Interrupted/Reinitiated by Decanting the Reaction Mixture from Cu(0) Powder. The monomer (MA, 2 mL, 22.2 mmol), solvent (DMSO, 1 mL), initiator (MBP, 11.2 μL, 0.1 mmol), catalyst (Cu(0) 425 μm, 0.64 mg, 0.01 mmol), and ligand (Me_6-TREN, 2.3 mg, 0.01 mmol) were added to a 25 mL Schlenk tube in the following order: Cu(0), monomer, ligand, solvent, initiator. A second Schlenk tube was connected to the first one through a V-glass joint. After three freeze−pump−thaw cycles, the system was filled with nitrogen, and the reaction mixture was placed in an oil bath thermostated at 25 ± 0.1 °C with stirring. After 30 min (22% monomer conversion) the polymerization mixture was transferred by tilting the Schlenk tube to the second Schlenk tube leaving behind Cu(0) powder

(Scheme 1). The mixture was stirred in the second Schlenk tube. After 90 min (24% monomer conversion), the polymerization mixture was transferred, by tilting the Schlenk tube, back into the first Schlenk tube containing the Cu(0) powder. During all steps, the monomer conversion was determined by ^{1}H NMR as in the case of conventional kinetic experiments. The side arm of the corresponding tube was purged with nitrogen before it was opened for samples to be removed at predetermined times, with an airtight syringe.

Typical Procedure for Dynamic Light Scattering (DLS) Measurements. Copper(I) bromide (CuBr) (5×10^{-4} g, 2.32×10^{-3} M) was added to a quartz cuvette and fitted with a rubber septum. The cell was then purged with an argon stream for 15 min. A Schlenk flask was charged with 0.5 mL of a stock solution of Me_6-TREN in DMSO (0.01524 g in 10 mL, 2.21×10^{-3} M) and when needed also methyl acrylate (1 mL, 7.36 M) and purged with argon for 15 min. The solution was then transferred via a gastight syringe to the quartz cuvette and swirled to homogenize. Once homogeneous the cuvette was placed into the DLS and measured 15 times at every 3 min at 25 °C.

Acknowledgment. Financial support by the National Science Foundation (DMR-0548559 and DMR-0520020) and the P. Roy Vagelos Chair at Penn is gratefully acknowledged. B.M.R. gratefully acknowledges funding from a NSF Graduate Research Fellowship.

Supporting Information Available: Overlapped monomer conversion and ln([M]$_0$/[M]) vs time plots for the kinetic experiments performed in DMSO and MeCN using different Cu(0) particle sizes. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA8018365