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Optimization of Atom Transfer Radical Polymerization Using Cu(I)/Tris(2-(dimethylamino)ethyl)amine as a Catalyst

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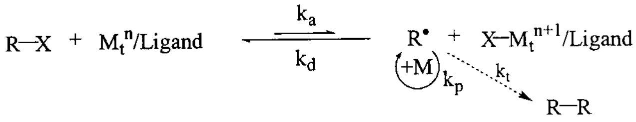
ABSTRACT: The optimization of the synthesis of homopolymers from *n*-butyl acrylate (BA), styrene (Sty), and methyl methacrylate (MMA), using copper-based atom transfer radical polymerization (ATRP) with tris(2-dimethylaminoethyl)amine (Me_6-TREN) as a ligand is reported. Catalyst concentration (copper bromide complexed with 1 equiv of Me_6-TREN) as low as 1% relative to initiator (50 ppm in the reaction mixture) was sufficient to successfully prepare well-defined poly(*n*-butyl acrylate) in bulk. With 50% catalyst to initiator, styrene was polymerized in bulk. The deactivator species had poor solubility in nonpolar solvents. Finally, the polymerization of methyl methacrylate with CuBr/Me_6-TREN required the use of a high concentration of catalyst and the addition of Cu(II)Cl_2 at the beginning of the reaction; the resulting polymers were of higher molecular weight than predicted by theory and had relatively broad molecular weight distributions.

Introduction

Radical polymerization has been the subject of keen interest. The large range of monomers available, the relatively simple experimental conditions, and the ability to conduct the polymerization in bulk, solution, suspension, and emulsion, albeit with the absence of oxygen, have made radical polymerization one of the most practical polymerizations. Nevertheless, free radical polymerization is limited by the inevitable, fast, and irreversible termination of the growing radicals by coupling and disproportionation reactions, leading to poor control of the reaction and a high polydispersity of the resulting polymer. Thus, much research has been devoted to developing a controlled radical polymerization to synthesize well-defined polymers with narrow molecular weight distributions and complex architectures.[1,2] One of the most successful methods has been atom transfer radical polymerization (ATRP), which is a catalytic process where a transition metal complex reversibly activates the dormant polymer chains via a halogen atom transfer reaction.[3−7]

In this system, the transition metal catalyst (M_t^n/ligand) reacts with an alkyl halide initiator, generating a radical and a transition metal complex by transfer of the halogen (X) to the catalyst (Scheme 1). As the radical propagates by reaction with monomer (M), it is rapidly deactivated by reaction with the oxidized transition metal halide ($X-M_t^{n+1}$/Ligand), to re-form the original catalyst and an oligomeric alkyl halide. This process repeats itself, with all chains growing in short, controlled steps, resulting in polymers with molecular weights defined by $DP_n = \Delta[M]/[I]_0$, where $[I]_0$ is the original initiator (alkyl halide) concentration, and narrow molecular weight distributions, $M_w/M_n < 1.5$. Indeed, a wide range of monomers including styrene and its derivatives, (meth)acrylates, acrylamide, and acrylonitrile, have been polymerized in a well-controlled manner.[5,6]

Scheme 1



The activity of the catalyst is correlated to the equilibrium constant (K_{eq}) defined by the ratio $K_{eq} = k_a/k_d$, where k_a and k_d are respectively the activation and deactivation rate constants. To obtain good control of the polymerization, the equilibrium must be strongly shifted toward the dormant species, so as to limit termination between active species (k_t). Second, deactivation of the active species must be fast enough, in comparison with propagation (k_p), to provide the same rate of growth for all chains and lead to controlled/"living" behavior.[8] By fine-tuning the catalyst structure, through adjustment of the equilibrium constant, it is possible to reduce the amount of catalyst needed for reasonable rates yet still maintain sufficient control of the polymerization.

The catalyst reactivity can be adjusted by changing either the ligand, counterion, or transition metal itself. Catalyst systems employing copper seem to be the most reactive catalyst systems when compared to other metal centers such as iron,[9,10] nickel,[11,12] or ruthenium.[4] Although other catalyst systems have used nonhalogen counterions, such as acetates,[13] hexafluorophosphate,[14] triflate,[15] or atomic oxygen,[16] for simplicity we focus here on the use of copper halides. To fine-tune the catalyst system, a variety of ligands have been developed that attenuate either the solubility of the catalyst, the reactivity of the catalyst, or both. For example, the use of 4,4′-alkyl-substituted bipyridynes has resulted in the preparation of polymers with very low polydispersities ($M_w/M_n < 1.1$).[17] Recently, linear aliphatic amines,[18] terpyridyl,[19] and picolyl[20] ligands provided catalysts that are more reactive than the 2,2′-bipyridyne (bpy) ligands originally employed.[3] Branched, aliphatic amine ligands were so reactive that the polymerization of methyl acrylate was extremely fast, requiring a significant reduction in catalyst concentration, even at room tem-

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perature;[21] in comparison, the polymerizations using *N*,*N*,*N'*,*N''*,*N''*-pentamethyldiethylenetriamine or bpy were conducted at ≥80 °C.

The polymerization of methyl acrylate (MA) using 0.1 equiv of the catalyst Cu(I)Br/tris(2-(dimethylamino)-ethyl)amine (Me_6-TREN) relative to initiator (methyl 2-bromopropionate) reached 41% conversion within 1 h at room temperature to yield poly(methyl acrylate) (PMA) of $M_{n,\,SEC} = 8200$ ($M_{n,Th} = 9100$) and $M_w/M_n = 1.09$.[21] The Cu(I)/Me_6-TREN catalyst is the most efficient ATRP catalyst that has been reported to date.

In subsequent studies, we optimized the use of this catalyst system for acrylates, methacrylates, and styrene. One of our original goals was to determine the lowest concentration of the catalyst that would still provide good rates of polymerization, good agreement with predicted molecular weights, and polymers with narrow polydispersities. Toward this end, we set arbitrary limits for these criteria. Acceptable rates were considered to be ~90% conversion in 8 h or less, molecular weights that were within 10% of that predicted for $DP_n = \Delta[M]/[I]_0$, and low polydispersities, $M_w/M_n < 1.3$. The degree of polymerization was also arbitrarily set at 200, i.e., $[M]_0/[I]_0 = 200$.

Experimental Section

Materials. Styrene (Sty), *n*-butyl acrylate (BA), and methyl methacrylate (MMA) (all 97% from Aldrich) were vacuum-distilled from CaH_2 and stored under a nitrogen atmosphere at 5 °C. Ethylene carbonate, hexadecane, anisole, methanol, and 1,4-dimethoxybenzene (DMB, 99%) from Aldrich were used without further purification. CuBr (98%, Aldrich) and CuCl (98%, Aldrich) were purified by stirring in acetic acid, washing with ethanol, and then drying under vacuum. The monomers and solvents were bubbled with dry nitrogen for 1 h immediately before the polymerization. The initiators methyl 2-bromopropionate (MBP, 99%, Acros), ethyl 2-bromoisobutyrate (EBiB, 98%, Acros), and *p*-toluenesulfonyl chloride (*p*-TsCl, 99%, Acros) and the metal compounds $Cu(II)Br_2$ (98%, Aldrich), $Cu(II)Cl_2$ (97%, Aldrich), and Cu^0 (turning and powder 99%, Aldrich) were used without any further purification.

Tris(2-(dimethylamino)ethyl)amine (Me_6-TREN) Synthesis. The following was adapted from Ciampolini.[22] A mixture of formaldehyde (37% (w/w) Aldrich) and formic acid (90% (w/w) Aldrich) was stirred at 0 °C. Over a period of an hour, a solution of TREN and deionized water was added dropwise. The mixture was gently refluxed overnight at 95 °C. After cooling to room temperature, the volatile fractions were removed by rotary evaporation. The distinctly brown residue was treated with a saturated sodium hydroxide aqueous solution until pH > 10, producing an oil layer, which was extracted into methylene chloride. The organic phase was dried over magnesium sulfate and evaporated to produce a yellow oil. The yield was 70%. Purity was >95% by NMR; signals from the starting TREN were below 1% with respect to Me_6TREN. ^1H NMR ($CDCl_3$) δ: 2.58 (dd, 12H); 2.36 (dd, 12H); 2.21 (s, 18H) ppm.

Polymerization Procedures. The polymerizations were conducted in a predried Schlenk flask. The solids (Cu^IBr, $Cu^{II}Br_2$, Cu^ICl, $Cu^{II}Cl_2$, Cu^0 (turning or powder), solid solvents or internal standards) and a stirring bar were added, and then the flask was tightly sealed with a rubber septum. Oxygen was removed from the flask by applying vacuum and back-filling with nitrogen (three cycles). The sparged monomer, the ligand, and the solvents were added via syringe. The mixture was stirred for 20−30 min to dissolve the catalyst. Finally, the initiator was added to the mixture. A first sample was removed as reference and the flask immersed in an oil bath held by thermostat at the desired temperature or in a water bath for the experiments conducted at room temperature (RT). At timed intervals, samples were removed from the flask with degassed syringes, dissolved in THF, and stored at 5 °C. After the end of the polymerization, the flask was removed from the oil bath, and the reaction mixture was diluted with THF. The solution was filtered through neutral alumina (80−200 mesh) to remove the catalyst. The solution was then concentrated by rotary evaporation, and the polymer was dried under vacuum overnight. The precise concentrations for each experiment are included in the figure captions; cf. also the extension polymerization experiment described below.

Poly(*n*-butyl acrylate) Macroinitiator Purification. The polymer was dissolved in acetone. The solution was then purified by stirring with DOWEX MSC-1 macroporous ion-exchange resin (20−50 mesh) to remove the colored copper salts and filtered through neutral alumina. The poly(*n*-butyl acrylate) (pBA) was precipitated into an aqueous solution of methanol (50 vol %). After decantation, the polymer was dissolved in acetone before being concentrated by rotary evaporation and dried under vacuum overnight.

Extension Polymerization. The Br-terminated PBA macroinitiator ($M_n = 2.1 \times 10^4$, $M_w/M_n = 1.22$, 5.0 g, 0.23 mmol) was introduced to a predried Schlenk flask with a stirring bar. The Schlenk flask was tightly closed with a rubber septum and degassed overnight and back-filled with nitrogen. Half of the BA (16.0 mL) was added via syringe to dissolve the macroinitiator. Hexadecane (0.3 mL, internal standard for the conversion measurements by GC) was added to the solution. The Cu(I)Br (3.3 mg, 0.023 mmol) was added to a second, predried, round-bottom flask. The oxygen was removed by vacuum and back-filled with nitrogen (three cycles of 30 min). The other half of the monomer (17. 5 mL, total BA: 33.5 mL, 30.0 g, 234 mmol) and the TREN-Me_6 (5.3 mg, 0.023 mmol) were added via syringe to the round-bottom flask. The mixture was stirred and heated at 60 °C for 20−30 min to dissolve the catalyst. Then, the solution containing the catalyst complex was added to the macroinitiator via cannula, and a first sample was removed as a reference. The Schlenk flask was immersed in an oil bath held by thermostat at 60 °C. After 3 h, the reaction was stopped and the mixture analyzed by GC (conversion = 0.28) and GPC ($M_n = 5.4 \times 10^4$, $M_w/M_n = 1.15$, $M_{n,\,th} = 5.7 \times 10^4$).

Characterization. Conversion was determined from the concentration of the residual monomer by gas chromatography (GC), with hexadecane as an internal standard. The sample was filtered through neutral alumina and a 0.2 μm filter for determination of the molecular weight by size exclusion chromatography (SEC). A sample of the final, purified polymer was dissolved in $CDCl_3$ for ^1H NMR measurement. Kinetic measurements were performed on a Shimadzu GC-14A, using a J&W Scientific DB-WAX 30 m column: injector temperature, 250 °C; detector, 250 °C; temperature program, 2 min 40 °C, 40 °C/min until 180 °C, 2 min 180 °C. Molecular weights (relative to linear polystyrene standards) were measured using a Waters SEC equipped with 10^2, 10^3, and 10^5 Å PSS columns and a Waters 410 refractive index detector, using toluene as an internal standard and THF as the eluent at 35 °C with the flow rate 1 mL/min. ^1H NMR spectra were recorded on a Bruker AC 300 (300 MHz) NMR in $CDCl_3$.

Results

Effect of Reaction Conditions on ATRP of Acrylates. As the goal of these experiments was to determine what minimum level of copper catalyst could be employed while maintaining sufficiently fast polymerizations and control of molecular weights, several parameters were varied to influence the equilibrium between active and dormant species and thus the radical concentration. By adjustment of the equilibrium, the radical concentration could be elevated to increase the rate of polymerization or lowered to suppress termination between growing chains. The parameters that were used to control radical concentration include temperature, catalyst concentration, and use of zerovalent metals.

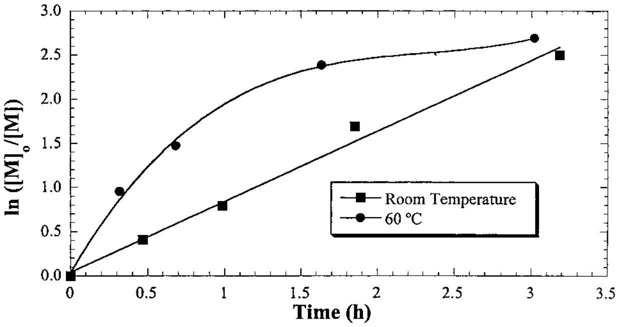

Figure 1. First-order kinetic plot for the polymerization of BA at room temperature and 60 °C with 10 mol % catalyst relative to initiator (~500 ppm). $[BA]_0 = 6.97$ M; $[MBP]_0 = 0.035$ M; $[Cu(I)Br]_0 = [Me_6\text{-TREN}]_0 = 0.0035$ M.

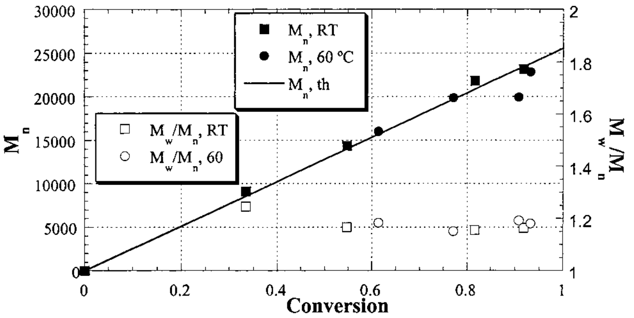

Figure 2. M_n and M_w/M_n versus conversion for the BA polymerization at room temperature and 60 °C with 10 mol % catalyst relative to initiator (~ 500 ppm).

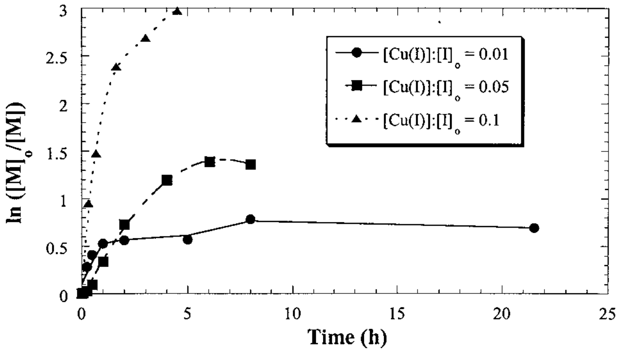

Figure 3. First-order kinetic plot for the polymerization of BA at various levels of Cu(I)/Me$_6$-TREN. $[BA]_0 = 6.97$ M; $[MBP]_0 = 0.035$ M; 60 °C.

Temperature. BA was initially polymerized at room temperature using 10 mol % catalyst relative to the initiator, MBP. The polymerization was also performed at 60 °C to confirm that increasing the temperature leads to a faster polymerization, as should be expected. The first-order kinetic plots of the two polymerizations are shown in Figure 1. As can be seen, there was an increase in the rate of polymerization at higher temperature, but a nonlinear plot was observed, indicating a higher contribution of termination. However, there was no significant difference between the two reactions in terms of molecular weight control (Figure 2). Apparently, the proportion of terminated chains could not exceed the concentration of the catalyst, e.g., 10%.

Catalyst Concentration. At 60 °C, the concentration of the catalyst was reduced from 10% to 5% and 1%, relative to initiator (Figure 3). As expected, the polymerization was slower with less catalyst. With 5% catalyst relative to initiator, the system seems to reach a conversion of 75%. With 1% of catalyst the reaction led to an apparently limited conversion of ~50%.

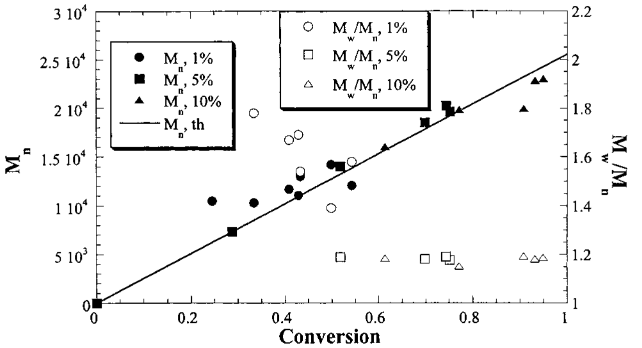

Figure 4. Dependence of molecular weights and polydispersities with conversion for the polymerization of BA using various amounts of catalyst. See Figure 3 for reaction conditions.

When the molecular weight data from these polymerizations were analyzed (Figure 4), the number-average molecular weight values were in agreement with predicted values, and polydispersities were narrow (except with 1% catalyst). This may be assigned to slower deactivation processes (cf. eq 3). The maximum number of lost end groups by termination reactions was determined by the relative amount of catalyst, i.e., 10, 5, or 1% of the chains.

The polymerization was conducted with 1% catalyst relative to initiator, corresponding to roughly 50 ppm relative to monomer. Such low concentrations of catalyst can be poisoned by trace amounts of oxygen, or other impurities, leading to limited conversions. The monomer was purged by nitrogen to remove oxygen; we did not apply more sophisticated methods to purify the system, as we wanted to see the limits of the catalyst system with a simple polymerization set up as opposed to one more complicated, e.g., as in anionic polymerization systems. Additionally, in controlled radical polymerizations governed by the persistent radical effect,[23] the system requires that some termination occur, leading to formation of deactivator at levels greater than the concentration of free radicals. The amount of spontaneously formed deactivator that was generated by the persistent radical effect is governed by K_{eq} of the catalyst/monomer pair as well as by the relative concentrations of the reagents used. For example, in the bulk polymerization of styrene using Cu(I)Br/2bpy with a $[M]_0/[I]_0 = 100$ and $[I]_0:[Cu(I)]_0 = 1:1$ at 110 °C, approximately 5% of the Cu(I), and the initiator as well, was transformed into Cu(II) or termination products;[24] similarly, for MMA (in 50% solution) the amount was 5−6%, while for MA (bulk) it was ~3%.[25]

Use of Copper Metal. Zerovalent metals can be used to enhance the rate of polymerization in ATRP reactions by reduction of the deactivator (Cu(II) or Fe(III))[26] and also to allow for ATRP to occur in vessels that contain a finite amount of oxygen[27] where the catalyst system consumes the oxygen by oxidation of the Cu(I) by oxygen and the Cu^0 reduces it back to an active form. Cu^0 was employed in the polymerization using 1% Cu(I)/Me$_6$-TREN to regenerate an active catalyst and obtain higher conversions in the polymerization of BA.

As Cu^0 was insoluble and the Cu(II)/Me$_6$-TREN complex was soluble, the rate of reaction between the two should be affected by the surface area of the Cu^0. To this end, we used a fine powder (200 mesh) and a large copper turning; the kinetic data are presented in

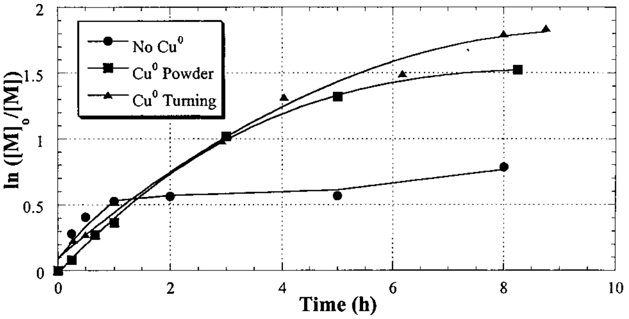

Figure 5. First-order kinetic plots for the polymerization of BA using 1% Cu(I)Br/Me$_6$-TREN with and without added Cu^0. $[BA]_0 = 6.97$ M; $[MBP]_0 = 0.035$ M; $[Cu(I)/Me_6\text{-TREN}]_0 =$ 0.000 35 M, 60 °C.

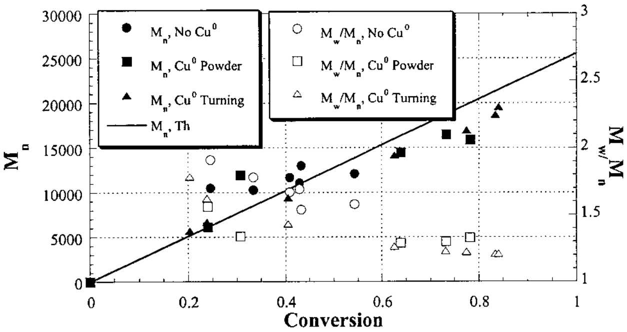

Figure 6. Molecular weight dependence for the polymerization of BA using 1% Cu(I)Br/Me$_6$-TREN with and without added Cu^0. See Figure 5 for reaction conditions.

Figure 5. The rate of polymerization using either the powder or turning was approximately the same, and the overall conversion was improved in both cases.

The molecular weight of the resulting polymer was in good agreement with that predicted by $\Delta[M]/[I]_0$, and the polydispersities remained low (Figure 6). This control suggests that the use of small amounts of Cu^0 can increase the rate of polymerization and overall conversion, without adversely affecting the number of growing chain ends. That is, only a small fraction of the chain ends are lost by radical−radical termination during the polymerization.

Effect of Ligand Concentration. When Cu^0 is used to enhance the rate of the polymerization, the Cu(II)/L in solution should be reduced by electron transfer from the Cu^0, resulting in the formation of Cu(I)/L in solution and Cu(I) on the surface of the Cu^0. This newly formed Cu(I) should not be soluble in the reaction medium unless it is complexed with a suitable ligand. If the amount of ligand is sufficient only to coordinate and form complexes with the original Cu(I), then the Cu^0 should eventually be coated with Cu(I). This may have two effects on the reaction. First, the rate of reduction of the Cu(II)/L in solution may be slower, and second, there would be no enhancement of the polymerization rate expected for higher [Cu(I)/L]. To solublize the extra Cu(I) formed, additional ligand should be introduced to the reaction mixture. We added excess of Me$_6$-TREN (1.5 or 2 equiv) to see whether there would be any effect on the rate and/or molecular weight.

As shown in Figure 7, there was minor difference in the initial rate of polymerization (all reach about 80% conversion after 4 h), but higher overall conversions were obtained using 1.5 and 2 equiv of Me$_6$-TREN relative to the initial Cu(I)Br. The molecular weight behavior was virtually identical for all ratios of Cu(I)Br/Me$_6$-TREN (Figure 8). The small change in soluble catalyst concentration (1−2% relative to initiator) allowed for the higher final conversions but resulted in negligible differences in the number of active chain ends.

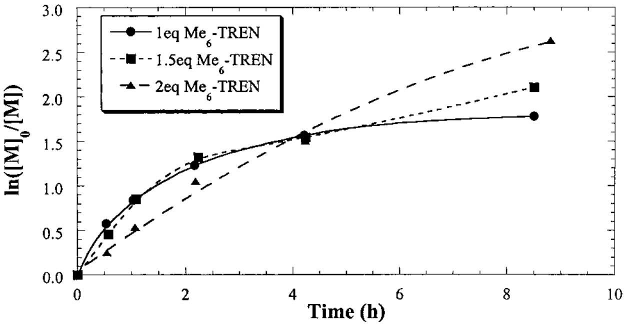

Figure 7. Conversion versus time and first-order kinetic plots for the BA polymerization with Cu^0 and various concentration of ligand $[Me_6\text{-TREN}]_0 = 0.000$ 35, 0.000 52, and 0.0007 M; $[BA]_0 = 6.97$ M; $[CuBr]_0 = 0.000$ 35 M; $[MBP]_0 = 0.035$ M; 60 °C.

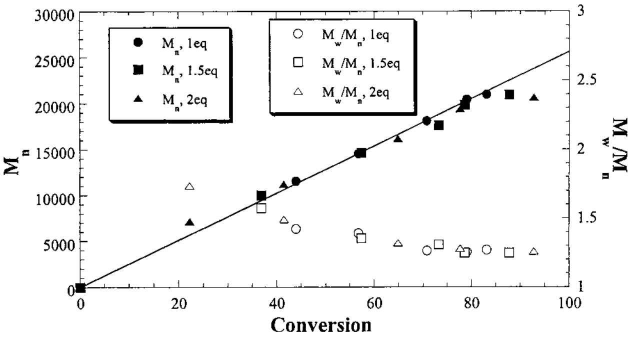

Figure 8. Evolution of M_n and M_w/M_n versus conversion for the BA polymerization with Cu^0 and various concentration of ligand $[Me_6\text{-TREN}]_0 = 0.000$ 35, 0.000 52, and 0.0007 M; $[BA]_0 = 6.97$ M; $[CuBr]_0 = 0.000$ 35 M; $[MBP]_0 = 0.035$ M; 60 °C.

Preservation of End Groups. Since a high degree of functionality is crucial for the preparation of well-defined polymers (block copolymers, telechelics, etc.), it is of interest to know the percentage of chain ends that are lost during the polymerization process, i.e., the extent of irreversible termination. Since the total number of dead chains cannot exceed the amount of catalyst added, the use of Me$_6$-TREN (1−10% catalyst) should afford polymer with high degrees of functionality. Indeed, when a poly(*n*-butyl acrylate)-Br, $M_n = 2.1 \times 10^4$, $M_w/M_n = 1.22$, prepared using the Cu(I)/Me$_6$-TREN catalyst was used as a macroinitiator for BA, again using the Cu(I)/Me$_6$-TREN catalyst, SEC analysis showed that the resulting polymer ($M_n = 5.4 \times 10^4$, $M_w/M_n =$ 1.15) had very little residual macroinitiator, and its molecular weight distribution narrowed, indicating that the macroinitiator and subsequent polymer retained a high degree of functionality (Figure 9). The number distribution (obtained by dividing the RI signal by molecular weight) does not exhibit any bimodality indicating the efficient extension.

Styrene Polymerization. Previously reported styrene polymerizations employing the Cu(I)Br/Me$_6$-TREN catalyst were conducted in bulk.[28] As an example, styrene was polymerized using 1-phenylethyl bromide as the initiator ($[M]_0/[I]_0 = 400$) with $[Cu(I)]/[I]_0 = 1$ and after 380 min at 110 °C, 63% conversion was obtained with $M_n = 2.7 \times 10^4$ ($M_{n,th} = 2.6 \times 10^4$); $M_w/M_n = 1.36$.

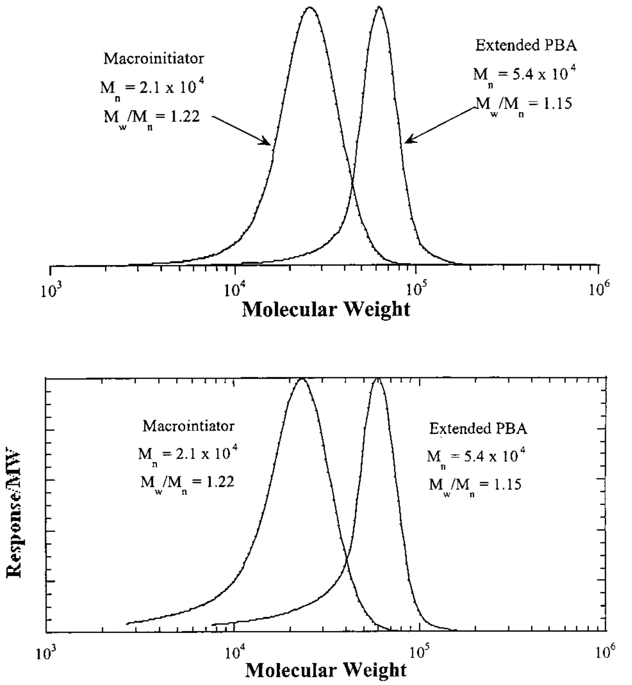

Figure 9. SEC traces of pBA macroinitiator and the extended macroinitiator polymer.

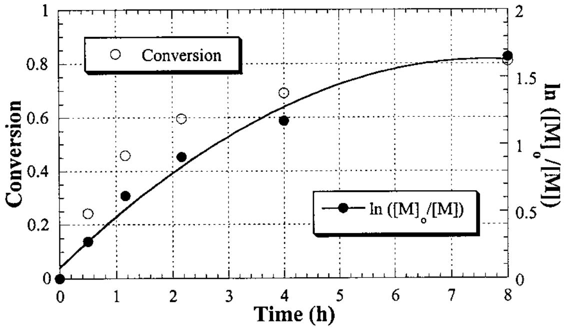

Figure 10. Kinetic plots for the polymerization of Sty using Me$_6$-TREN. [Sty]$_0$ = 8.73 M; [CuBr]$_0$ = [Me$_6$-TREN]$_0$ = 0.022 M; [MBP]$_0$ = 0.044 M; 110 °C.

In this work, the polymerization of styrene was performed using a half equivalent of catalyst relative to initiator. As the reaction progressed, some of the catalyst appeared to become insoluble, and a green precipitate was observed (presumably Cu(II) species). The reaction was reasonably fast (Figure 10), faster than that reported previously for bipyridine,[29] and appeared to be even faster than when using the aliphatic amine ligands[18] (when taking into account the differences in initiator and catalyst concentrations). The obtained molecular weights agreed with those predicted by theory, and the polydispersities were relatively low, although they increased slightly with conversion (M_w/M_n = 1.15−1.2) (Figure 11). Although the Cu(II)/Me$_6$-TREN complex was poorly soluble in the styrene monomer (its precipitation resulted in lower deactivator concentrations), there remained a sufficient amount to provide control, yet not at levels required to produce the very low polydispersities seen with the alkylated bipyridynes.[17]

Using 0.1 equiv of catalyst relative to initiator resulted in a polymerization that reached only approximately 20% conversion. Addition of solvent, i.e., toluene, did not improve the solubility of the catalyst. The use of polar solvents such as ethylene carbonate at 110 °C yielded homogeneous solutions but resulted in very low conversions, low molecular weights, and broad molecular weight distributions. A likely cause for this behavior could be elimination of HBr from the chain end by an E1 process in the polar reaction medium and leading to unsaturated chain ends.[30]

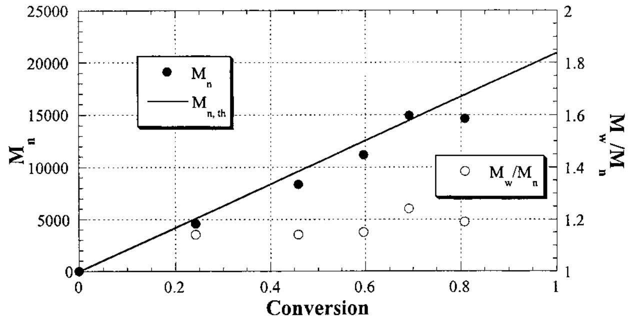

Figure 11. Evolution of M_n and M_w/M_n versus conversion for the polymerization of Sty. [Sty]$_0$ = 8.73 M; [Cu(I)Br/Me$_6$-TREN]$_0$ = 0.022 M; [MBP]$_0$ = 0.044 M; 110 °C.

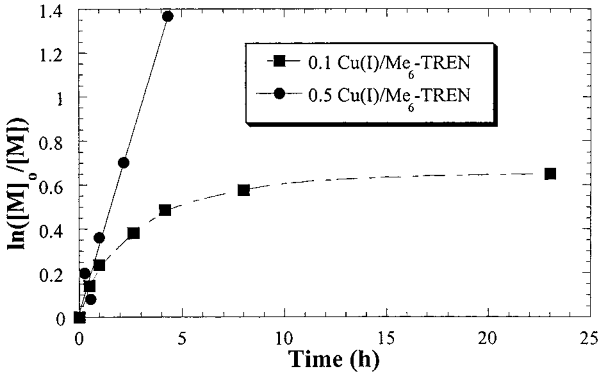

Figure 12. Conversion versus time and first-order kinetic plots for the styrene polymerization with Cu^0 turning and various concentrations of catalyst concentration: [Sty]$_0$ = 8.73 M; [CuBr]$_0$ = [Me$_6$-TREN]$_0$ = 0.022 and 0.0044 M; [MBP]$_0$ = 0.044 M; 110 °C.

To enhance the rate of polymerization, the addition of Cu^0 was attempted. For the polymerization using 0.5 equiv of catalyst relative to initiator, the reaction was fast enough to meet the originally established criteria, but the use of 0.1 equiv of catalyst resulted in polymerizations which reached only limited conversions ($\sim$50%) (Figure 12). Further, the evolution of molecular weight with conversion was much less controlled than for BA. Using 0.5 equiv of catalyst resulted in molecular weights higher than predicted, and polydispersities increased with conversion (Figure 13). The use of 0.1 equiv of catalyst in the presence of Cu^0 resulted in polymers with molecular weights closer to theoretical, but with relatively high polydispersities (M_w/M_n > 1.5).

MMA Polymerization. The polymerization of MMA using Me$_6$-TREN as a ligand for Cu(I) was less successful. Initially, the catalyst precipitated as for styrene, and conversions were less than 10% even after prolonged reaction times. For MMA, the use of the polar solvent ethylene carbonate was feasible (the E1 reaction is less favored for the 2-bromoisobutyrate end group), but the reaction mixture turned dark green, almost immediately. Very low (<10%) conversions were obtained for 0.5 and 0.1 equiv of catalyst versus initiator; only when a 1:1 ratio was used did the polymerization progress to higher conversions (Figure 14).

The molecular weights increased with conversion (Figure 15) but were much higher than predicted by

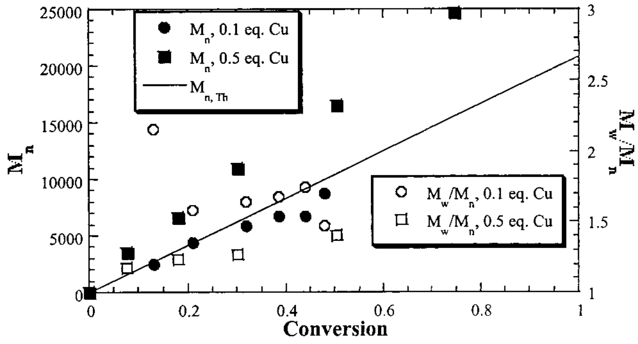

Figure 13. Evolution of M_n and M_w/M_n versus conversion for the styrene polymerization in the presence of Cu^0. $[Sty]_0$ = 8.73 M; $[CuBr]_0 = [Me_6\text{-}TREN]_0$ = 0.022 and 0.0044 M; $[MBP]_0$ = 0.044 M; 110 °C.

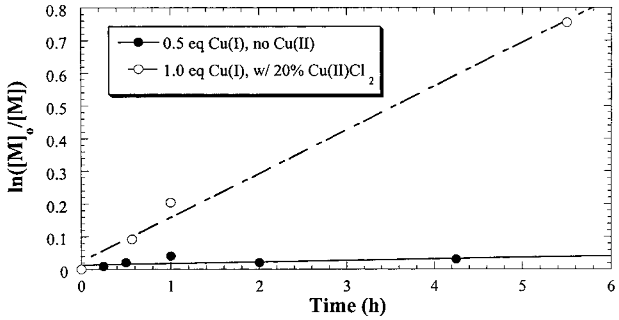

Figure 14. Kinetics of the polymerization of MMA using various amounts of Cu(I)/Me$_6$-TREN. 50% MMA in ethylene carbonate, $[MMA]_0$:$[EBiB]_0$ = 200:1, 60 °C.

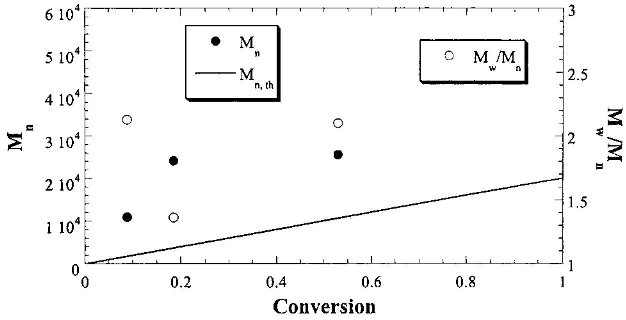

Figure 15. Molecular weight behavior for the polymerization of MMA using Cu(I)Cl/Me$_6$-TREN in ethylene carbonate with 20% Cu(II)Cl$_2$ (relative to Cu(I)Cl) added.

theory, suggesting that a significant portion of the initial initiator was lost due to termination reactions at the beginning of the polymerization, resulting in a reduced initiator efficiency. Even with the addition of 20 mol % Cu(II)Cl$_2$/Me$_6$-TREN at the beginning of the reaction, the SEC chromatograms (Figure 16) of the resulting polymers displayed broad molecular weight distributions due to significant low molecular weight tailing, indicative of termination reactions occurring throughout the polymerization.

Discussion

In ATRP, the catalyst plays a significant role in determining the rate of the polymerization and the extent of control of the resulting polymers. Consequently, there has been considerable effort in developing new catalysts for a variety of reasons. These include the development of catalysts that have higher equilibrium constants (which enables a reduction in the amount of catalyst required for reasonable polymerization times),

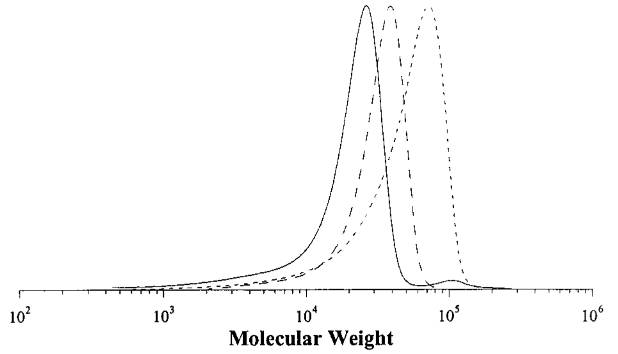

Figure 16. SEC chromatograms from the polymerization of MMA using Cu(I)Cl/Me$_6$-TREN in ethylene carbonate with 20% Cu(II)Cl$_2$ (relative to Cu(I)Cl) added.

catalysts that are less expensive than current ones, catalysts that allow ATRP to be expanded into nonorganic polymerization media (aqueous suspensions/emulsions,[31,32] CO$_2$,[33] etc.), allow for easier removal of the catalyst,[34−36] and to extend ATRP to new monomers that could not be polymerized using the original Cu(I)/bpy catalysts, such as vinyl acetate, ethylene, acrylamides, etc. Although the development of the Cu(I)/Me$_6$-TREN catalyst has allowed for the polymerization of some new monomers (4-vinylpyridine,[37] dimethylacrylamide[38]), we focused our attention on its ability to significantly enhance the rate of polymerization of acrylates.

Parameters Affecting Rate of Polymerization. Before discussing the ability of the Cu(I)/Me$_6$-TREN ligand to enhance rates, it will be helpful to first discuss how one is able to obtain faster ATRP reactions in general terms and how adjusting various parameters of the polymerization will affect the overall behavior of the system. Since the rate of a radical polymerization for a given monomer is directly proportional to the concentration of radicals in the system (eq 1),

$$R_p = -\frac{d[M]}{dt} = k_p[M][R^\bullet] \qquad (1)$$

we shall use eq 2

$$\frac{d[R^\bullet]}{dt} = k_a[RX][M_t^{\,n}/L] - k_d[R^\bullet][X - M_t^{\,n+1}/L] - k_t[R^\bullet]^2 \qquad (2)$$

to analyze how changing the components in ATRP will affect rate. Increasing either the catalyst concentration ($[M_t^{\,n}/L]$) or the initiator concentration ([RX]) should lead to faster polymerizations. However, higher radical concentrations leads to more pronounced termination and the formation of increased levels of persistent radicals ($XM_t^{\,n+1}/L$),[23] which reduces the radical concentration and self-regulates the system. Our goal is the development of new catalysts that can be used at lower concentrations rather than increasing the concentration of less efficient catalyst. Additionally, increasing [RX] will lead to the formation of low molecular weight species; if moderate to high molecular weight polymer is desired, this is not necessarily a solution either. Increasing the monomer concentration will enhance the overall rate of polymerization, but the maximum is reached in a bulk polymerization. Monomers with higher k_p values can also lead to faster polymerizations (eq 1) but also higher polydispersities, as more monomer units can be added to the active radical before deactiva-

Table 1. K_{eq} Values for a Variety of Monomers and Catalyst Systems[a]

monomer	2,2′-bipyridyl	PMDETA	Me$_6$-TREN	catalyst X
MMA	*7×10^{-7}*	10^{-5}	$\mathbf{10^{-3}}$	$\mathbf{\sim 10^{-1}}$
styrene	*2×10^{-8}*	10^{-7}	10^{-5}	$\mathbf{\sim 10^{-3}}$
methyl acrylate	*1.2×10^{-9}*	10^{-8}	10^{-6}	$\sim 10^{-4}$
monomer Y	$\sim 10^{-13}$	$\sim 10^{-12}$	$\sim 10^{-10}$	$\sim 10^{-8}$

[a] Values in italics are measured values at 100 °C. Values in boldface represent systems where the polymerization becomes uncontrolled. Values for monomer Y and catalyst X are hypothetical values for a catalyst 100 times more reducing than Me$_6$TREN and a monomer providing alkyl halides 10 000 times less reactive than those derived from acrylates.

tion by the catalyst, i.e., depending on the deactivation rate constant and concentration of XCu(II)/L (cf. eq 3).

$$M_w/M_n = 1 + \frac{k_p[\mathrm{RX}]_0}{k_d[\mathrm{X{-}M_t}^{n+1}/\mathrm{L}]}\left(\frac{2}{p} - 1\right) \qquad (3)$$

Last, one can increase the equilibrium constant ($K_{eq} = k_a/k_d$) between active and dormant species (Scheme 1), either by increasing k_a, decreasing k_d, or through some combination of the two. Increasing k_a will lead to higher rates of formation of radicals ($k_a[\mathrm{RX}][\mathrm{M_t}^n/\mathrm{L}]$) and thus faster rates of polymerization. This is a beneficial observation as small changes in the ligand, redox potential, etc., can have a significant impact on the rate of polymerization; an increase in k_a should lead to a reduction in the polymerization time. However, with increasing K_{eq}, it is advisable to maintain k_d at a high value, e.g., near diffusion-controlled rates ($\sim 10^8$ M^{-1} s^{-1}). This will provide for sufficient deactivation of the growing polymer chains and yield polymers with narrower molecular weight distributions as M_w/M_n is proportional to k_p/k_d, as shown in eq 3.[1]

Simulation of Systems with Various K_{eq}. To analyze how variations in K_{eq} (specifically k_a) affect polymerizations rates, we used Predici, a polymerization kinetics simulation program.[39] In the simulations, the ratios of monomer to initiator to catalyst were held constant (200:1:1). These simulations were simplified; i.e., they did not account for chain length-dependent termination (additionally, the values of activation, deactivation and monomer addition were assumed to be the same for macromolecular and initiating species),[40] assuming all species were completely soluble (except where noted) and were designed to give a qualitative understanding of the effect of K_{eq}. The range of values for K_{eq} was estimated on the basis of kinetic results obtained with Me$_6$-TREN, PMDETA, and bpy as ligands (cf. also Table 1). The values of k_t, k_p, and other rate constants were estimated for 90 °C. In the simulations, we assumed that deactivation was fast ($k_d \sim 10^8$ M^{-1} s^{-1}) for all systems. This should be a valid assumption since low-polydispersity polymers, $M_w/M_n < 1.3$, were obtained for all catalyst systems.

The results show that for BA (Figure 17) and Sty (Figure 18) the overall rates of polymerization did increase with increasing K_{eq}. For the polymerization of MMA (Figure 19), there was an increase in the rate of polymerization when the catalyst with the middle value of K_{eq} was used, but when the catalyst with the highest value of K_{eq} was used, the simulation showed that the rate was significantly reduced at later stages of the reaction and reached lower overall conversions than for other catalysts.

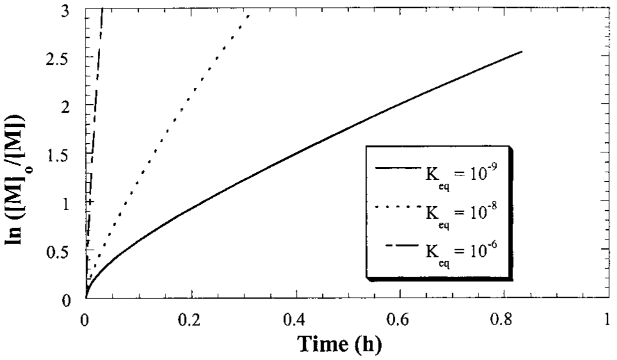

Figure 17. Kinetic data for the simulated polymerization of butyl acrylate using catalysts with various K_{eq}. $k_p = 54\,000$ M^{-1} s^{-1}; $k_d = 10^8$ M^{-1} s^{-1}, $k_t = 3 \times 10^7$ M^{-1} s^{-1}; [M]$_0$ = 6.98 M; [I]$_0$ = 0.035 M; [M]$_0$:[I]$_0$:[M$_t^n$/L]$_0$ = 200:1:1.

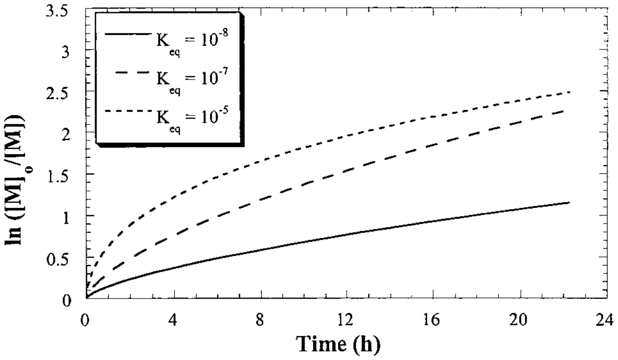

Figure 18. Kinetic data for the simulated polymerization of styrene using catalysts with various K_{eq}. k_p = 900 M^{-1} s^{-1}; k_d = 10^8 M^{-1} s^{-1}; $k_t = 3 \times 10^7$ M^{-1} s^{-1}; [M]$_0$ = 8.74 M; [I]$_0$ = 0.044 M; [M]$_0$:[I]$_0$:[M$_t^n$/L]$_0$ = 200:1:1.

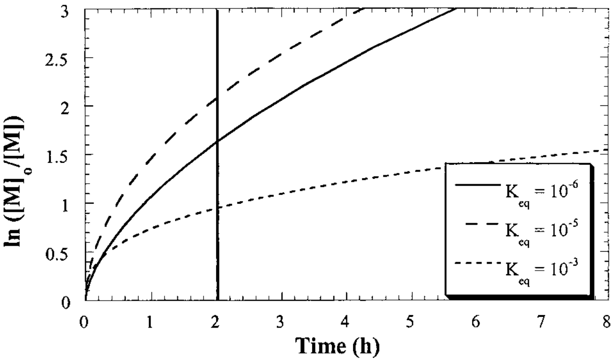

Figure 19. Simulated kinetic data for the polymerization of methyl methacrylate using catalyst with various K_{eq}. k_p = 1600 M^{-1} s^{-1}; k_d = 10^8 M^{-1} s^{-1}; $k_t = 3 \times 10^7$ M^{-1} s^{-1}; [M]$_0$ = 9.35 M; [I]$_0$ = 0.047 M; [M]$_0$:[I]$_0$:[M$_t^n$/L]$_0$ = 200:1:1.

The slower polymerization of MMA when using the catalyst with the highest equilibrium constant was the result of too high a radical concentration during the early stages of the reaction. In any controlled radical polymerization, the ability to regulate the radical levels to low concentrations and thus suppress radical−radical termination is based on the premise that $k_d[\mathrm{R}^\bullet][\mathrm{XM_t}^{n+1}/\mathrm{L}] \gg k_t[\mathrm{R}^\bullet]^2$. This is possible because at the beginning of the polymerization the concentration of deactivator is built up until the rate of deactivation of the radical by XM$_t^{n+1}$/L is faster than the rate of radical consumption by coupling or disproportionation. Thus, if [R$^\bullet$] is too high (or if k_d or [XM$_t^{n+1}$/L] are too low), $k_t[\mathrm{R}^\bullet]^2$ cannot be neglected, and irreversible termination will be significant until XM$_t^{n+1}$/L reaches levels sufficient to

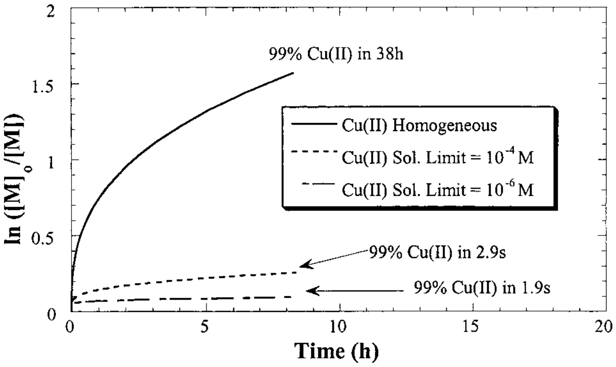

Figure 20. Simulated kinetics for the polymerization of MMA with a high-K_{eq} catalyst (Cu(I)/Me$_6$-TREN, $K_{eq} = 10^{-3}$) and with various limits of the solubility of deactivator (XCu(II)). The percentages quoted above relate to the amount of Cu(I) converted to Cu(II) at the specified times of the polymerization. See Figure 18 for simulation parameters.

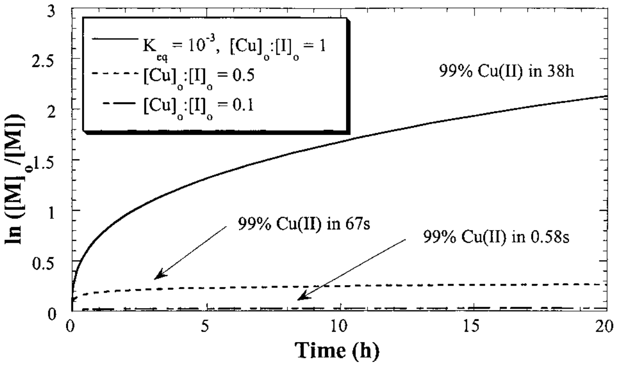

Figure 21. Simulated kinetics for the polymerization of MMA with a high-K_{eq} catalyst (Cu(I)/Me$_6$-TREN) and for varied amounts of catalyst relative to initiator. The percentages quoted above relate to the amount of Cu(I) converted to Cu(II) at the specified times of the polymerization. See Figure 18 for simulation parameters.

suppress termination. As one depletes the amount of initiator and activator while increasing the amount of deactivator in the system (activator is converted to deactivator), the net effect is a slower polymerization.

In successfully controlled radical polymerizations, this process of equilibration occurs rapidly, and the contribution of termination reactions can often be neglected. In some polymerizations where significant amounts of initiator are consumed during the formation of XM_t^{n+1}/L, molecular weights increase linearly with conversion but are higher than predicted by $DP_n = \Delta[M]/[I]_0$, i.e., the initiator efficiencies are less than unity; such behavior was observed in the reverse ATRP of butyl methacrylate in water-borne systems.[32] The worst case scenario is where all of the catalyst[41] is consumed or all of the initiator converted to the termination products (R−R or R^H/R^{2-}) before high monomer conversions can be attained.

Effect of Limited Solubility of Deactivator. The polymerization of MMA using the Cu(I)/Me$_6$-TREN catalyst is an example of the complete transformation of the Cu(I)/Me$_6$-TREN to XCu(II)/Me$_6$-TREN before complete monomer conversion. Initially, the polymerization was conducted in bulk with a [Cu]:[RX] = 0.1:1, but the originally soluble catalyst turned green and precipitated, indicating that the XCu(II)/Me$_6$-TREN complex was poorly soluble in MMA; mixtures of Cu(II)Cl$_2$ and Me$_6$-TREN in MMA were insoluble as well. Thus, precipitation of the XCu(II)/Me$_6$-TREN prevented the efficient deactivation of the growing radical and the establishment of the persistent radical effect (PRE). This resulted in irreversible termination of all radicals before high conversion could be reached.

By using the Predici program, the solubility limit of the catalyst species was attenuated to simulate the effect of poor solubility of the deactivator. Using the catalyst system with $K_{eq} = 10^{-3}$, from Figure 19, the maximum amount of deactivator (XCu(II)) was varied from completely homogeneous to a maximum of 10^{-6} M. The system with the least soluble deactivator resulted in polymerizations with limited conversions (Figure 20). As the concentration of deactivator remained low, the relative rate of deactivation of the radicals by the catalyst ($k_d[R^\bullet][XM_t^{n+1}/L]$) could not compete with bimolecular radical termination ($k_t[R^\bullet]^2$). The result was that the deactivator precipitated out of solution, continuously lowering the overall catalyst concentration, and simultaneously, the alkyl halide (RX) was consumed; both have the effect of reducing the rate of polymerization. The consumption of RX and/or catalyst can be very rapid. For example, with the catalyst solubility limit of 10^{-6} M, 99% of the catalyst (Cu(I)) was converted to deactivator in less than 2 s; for a solubility limit of 10^{-4} M, 99% of the catalyst was consumed in less than 3 s. It should be noted that even for a completely homogeneous system, nearly all of the catalyst (and end groups as well, $[RX]_0 = [M_t^n/L]_0$) was consumed when the polymerization reached high conversions as a consequence of the high K_{eq} of the system.

To enhance the solubility of the XCu(II)/Me$_6$-TREN, the polymerizations were conducted in ethylene carbonate, a highly polar solvent. Although the catalyst (10% relative to initiator) did not precipitate, the solution turned green, and only low conversions were observed. Such behavior indicated that the catalyst was quantitatively converted to XCu(II)/Me$_6$-TREN. To prevent complete conversion of Cu(I)/Me$_6$-TREN to XCu(II)/Me$_6$-TREN, the catalyst concentration was increased to 50% relative to initiator, and XCu(II)/Me$_6$-TREN was added to the reaction at the beginning. Still, only low conversions were observed. High conversions were obtained only with a 1:1 ratio of catalyst to initiator and when 20% of XCu(II)/Me$_6$-TREN relative to Cu(I)/Me$_6$-TREN were added at the beginning of the polymerization (Figure 14). However, significant termination was observed in the SEC chromatograms of the resulting polymers (Figure 16).

Effect of Catalyst Concentration for High-K_{eq} Systems. a. Simulated Experiments. Simulations show that polymerizations using a catalyst with such a high K_{eq} may require the use of higher catalyst concentrations (Figure 21). When less than a 1:1 ratio of catalyst to initiator was used in the simulated polymerization of MMA with a soluble catalyst with $K_{eq} = 10^{-3}$, only limited monomer conversions were obtained as nearly all of the catalyst was consumed at very early stages of the polymerization.

It is instructive to point out that the results obtained in the polymerization of MMA with a high-K_{eq} catalyst, either by simulation or in actual experiment, also highlight the hazards of evaluating single point reaction data in evaluating catalyst efficiency. The vertical line in Figure 19 is shown to indicate what conversions one would obtain if the reactions were analyzed at a single point in time for all three: the $K_{eq} = 10^{-5}$ catalyst would have the highest monomer conversion and be judged to

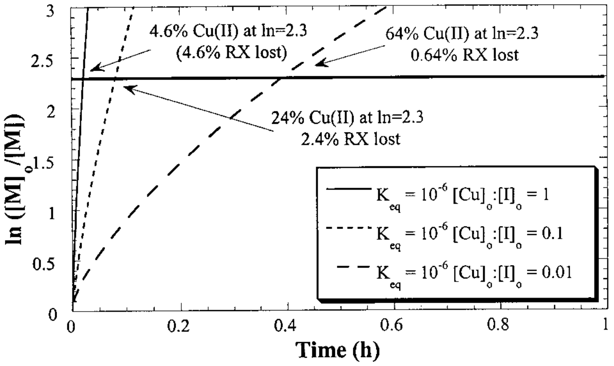

Figure 22. Simulated kinetics for the polymerization of BA with a high-K_{eq} catalyst (Cu(I)/Me$_6$-TREN) and for varied amounts of catalyst relative to initiator. The percentages quoted above relate to the amount of Cu(I) converted to Cu(II) at 90% conversion of monomer. See Figure 17 for simulation parameters.

be the "fastest" followed by $K_{eq} = 10^{-6}$ and $K_{eq} = 10^{-3}$, when in fact, the last one has the highest equilibrium constant. For a complete understanding of individual catalyst systems, it is important to know at least the K_{eq} and preferably k_a and k_d as well.

Further analysis of the simulated data shows that simply increasing the rate of activation by an order of magnitude does not necessarily translate directly into a 10-fold increase in the rate of polymerization (Figures 17−19). Again, this can be explained by the persistent radical effect;[23] the increase in radical concentration must be compensated for by an increase in the deactivator concentration. For the Cu(I)/dNbpy catalyst system, the amount of Cu(I) converted to Cu(II) has been reported to be less than 10%.[24,25] When evaluating catalysts with relatively small differences in K_{eq}, the resulting differences in the amount of deactivator formed may not drastically change the overall polymerization rates of the systems.

However, using similar ratios of $[M_t^n/L]$:[RX] to compare catalysts with large differences in K_{eq} can lead to significant conversion of the M_t^n/L to $X-M_t^{n+1}/L$; this has three effects. First, the deactivator concentrations may be too high. Second, the activator (M_t^n/L) concentrations may be depleted. Third, significant amounts of the initiator may be consumed by termination. Reduction in the initiator and activator concentrations as well as an increase in the deactivator concentration will all result in slower polymerizations (cf. eq 2); collectively the effect can be significant. This can be seen in the simulation of the polymerization of MMA when comparing $K_{eq} = 10^{-6}$ with $K_{eq} = 10^{-3}$.

The simulated polymerization of BA using Cu(I)/Me$_6$-TREN with various levels of catalyst shows how using less catalyst can also result in polymers with higher degrees of functionalization. When using a 1:1 ratio of catalyst to initiator, only 4.6% of the Cu(I) was converted to Cu(II), resulting in a loss of 4.6% end groups to termination reactions at 90% conversion of monomer. However, when 0.1 equiv of catalyst was used, only 2.4% of end groups were lost, although 24% of catalyst was transformed to Cu(II). For the use of 1% catalyst relative to initiator, a significant amount of catalyst was consumed (64%), but only 0.64% of end groups were lost to irreversible termination (Figure 22).

b. Experimental Results. The effects of comparing catalysts with significant differences in K_{eq} can also be seen in actual polymerizations. When we first reported the use of Cu(I)/Me$_6$-TREN as a catalyst for ATRP,[21] the rate of polymerization was compared for Cu(I) catalysts using Me$_6$-TREN (0.2 equiv relative to initiator) and dNbpy (1.0 equiv) and PMDETA (1.0 equiv) as ligands. The results show that the catalyst using PMDETA was slower than the one using dNbpy (Figure 23). However, when the catalyst concentrations were reduced to 0.2 equiv for both the PMDETA and dNbpy catalysts, one can see that Cu(I)/PMDETA was nearly 8 times faster than Cu(I)/2dNbpy. Thus, when evaluating catalysts, it is beneficial to know not just rates of polymerization for a given catalyst but its K_{eq} as well. As a practical matter, this clearly demonstrates the ability to use catalysts with higher K_{eq} at lower concentrations.

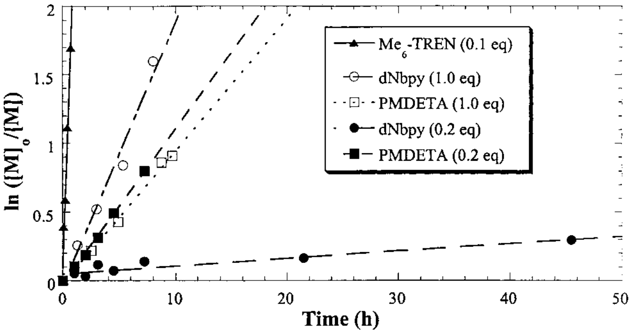

Figure 23. Comparison of rates of polymerization for various catalysts and their concentrations in the polymerization of methyl acrylate. $[MA]_0 = 11.1$ M; $[MA]_0:[MBP]_0 = 232:1$; 50 °C; values in parentheses are $[Cu(I)/ligand]_0:[MBP]_0$.

Minimum Amounts of Deactivator. Although one can decrease the catalyst concentration, there is a limit below which one loses control of molecular weight; this is readily observed in molecular weight distributions. In controlled radical polymerizations that operate by an activation/deactivation cycle, the molecular weight distributions are described by eq 3, where p is conversion of monomer. This equation holds assuming that there are not significant side reactions which would cause the polydispersity to increase and is sufficient for the discussion here.

From eq 3, we can roughly estimate the minimum amount of XCu(II) that must be in solution. Using $k_p \sim 10^4$ M^{-1} s^{-1} (acrylates at 20 °C), $k_d \sim 10^8$ M^{-1} s^{-1} (reaction of radicals with XCu(II)), and $[RX] = 5 \times 10^{-2}$ M ($DP_n = 200$, in bulk monomer) and assuming that the maximum allowable $M_w/M_n = 1.3$, at complete conversion, the minimum $[XCu(II)] = 1.6 \times 10^{-5}$ M. If one assumes that the XCu(II) that is formed is 30% of the original Cu(I), then the total copper concentration, at minimum, is 5×10^{-5} M, i.e., 5 ppm with respect to bulk monomer. It should be noted that these values are highly dependent on the components of the polymerization. If the monomer has a lower k_p (styrene, $k_p \sim 100$ M^{-1} s^{-1}) and higher molecular weight polymer is targeted (lower [RX]), then concentration of copper species may be even much lower.

Using the above simulations and experimental results to evaluate the catalysts, we attempted to establish at what limit can k_a (or overall K_{eq}) be increased and still maintain control of the polymerization. If one looks at K_{eq} as a function of both the catalyst and the monomer being polymerized, a trend appears to be emerging. Table 1 lists values of K_{eq} (measured and estimated) for Cu(I) catalysts with dNbpy, PMDETA, or Me$_6$-TREN ligands versus the monomers MMA, methyl acrylate, and styrene. The K_{eq} values for the dNbpy system have been measured and reported previously.[14,29,42] The values for the PMDETA and Me$_6$-TREN systems are estimates based on our extensive use of these ligands in a variety of polymerizations; we are currently working on determining more accurate values, but these estimates are used to emphasize the effect of K_{eq} on obtaining fast, yet controlled, polymerizations by ATRP.

For the systems using the Cu(I)/dNbpy catalysts, the equilibrium constants are within values that provide for successful ATRP reactions as demonstrated by their effectiveness in the polymerization of a variety of monomers. Indeed, for MMA the K_{eq} is sufficiently high that the polymerizations can be run successfully, and quickly, with less than 1 equiv of catalyst relative to initiator.[43] As one progresses to the more active catalyst, Cu(I)/PMDETA, the rates of polymerization are faster, and for acrylates, significant reductions in the amount of catalyst can be obtained (when compared to the dNbpy systems).[44,45] For the polymerizations of methacrylates, higher molecular weights and a reduction in rate were observed,[18] suggesting that radical−radical termination reactions are beginning to become more significant. With the use of Cu(I)/Me$_6$-TREN, control of the polymerization of MMA is, for all intents and purposes, lost. The polymerization of styrene, although fast, cannot be well-controlled with low amounts of catalyst, but the polymerization of acrylates is fast yet provides a well-defined polymer, even with significantly reduced levels of catalyst.

With this, one may conclude that the “best” catalysts have been found for methacrylates, styrenics, and possibly acrylates, with respect to rate and control. Of course, many other catalysts/ligands and their mixtures (i.e. “hybrid” systems) may be developed to provide for similar performance but also add additional benefits such as lower cost, ease of removal, recyclability, use in suspensions/emulsions, etc. This does not mean, however, that future catalyst development is futile. Future catalysts (catalyst X, Table 1) may provide sufficient reactivity for other monomers that cannot be polymerized using current ATRP catalysts. For example, a monomer that would generate a more stable halogen end group, such as vinyl acetate (chloroacetoxy ethane), vinyl chloride (dichloroalkane), or ethylene (bromoalkane), does not polymerize using the current catalysts due to its low K_{eq} (monomer Y, Table 1). By developing more powerful catalysts, these monomers may be successfully polymerized at rates similar to those of the polymerization of styrene, acrylates, etc., with Cu(I)/bpy or PMDETA. However, if one is to use this catalyst X and screen its usefulness using MMA, styrene, or an acrylate, one may obtain poor results and conclude that the catalyst is “bad” when simply too many radicals are being formed, resulting in significant termination reactions as a consequence of the higher K_{eq} of the catalyst/monomer pair. Indeed, such behavior was seen in the original use of a 1:1 ratio of Cu(I)/Me$_6$-TREN to initiator for the polymerization of methyl acrylate.[21]

Conclusion

Me$_6$-TREN is an efficient ligand for the copper-based ATRP of acrylates and forms a powerful catalyst allowing for the use of very low catalyst amounts. Successful polymerizations of *n*-butyl acrylate were conducted with catalyst concentrations as low as 50−500 ppm. In these systems, the rate of polymerization was quite fast, yet control of the polymerization was maintained. The use of this ligand was less effective for the polymerization of styrene, although a reduction in the catalyst concentration did yield a polymerization with a reasonably fast polymerization rate and good control of the molecular weight and distribution of the final polymer. The Cu(I)/Me$_6$-TREN catalyst was found to be a relatively poor catalyst for MMA, considering that much simpler, and less expensive, ligands, i.e., bpy, PMDETA, provide for systems that can use less catalyst and be conducted in conventional solvents (or bulk).

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