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ARGET ATRP of Methyl Acrylate with Inexpensive Ligands and ppm Concentrations of Catalyst

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ABSTRACT: A simple and versatile polymerization technique via activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP) of methyl acrylate (MA) with inexpensive commercially available ligands, including diethylenetriamine (DETA), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), and tris(2-aminoethyl)amine (TREN), is reported. Catalytic amounts of catalyst were utilized achieving ppm levels of $Cu^{II}Br_2/L$ in the presence of a zerovalent copper metal (i.e., copper powder or wire) at 25 °C. High molecular weight poly(methyl acrylate) (PMA) could also be obtained with $M_n > 1.5$ million and $M_w/M_n \sim 1.25$. A "map" was generated, illustrating minimal catalyst concentrations (i.e., copper and ligand) required over a range of targeted degrees of polymerization with various ligands. Several conclusions were made: (1) lower catalyst concentrations require higher targeted degrees of polymerization to produce equally controlled polymerizations, (2) higher catalyst concentrations are necessary for lower targeted degrees of polymerization, to ensure every activation−deactivation cycle adds fewer monomer units, (3) catalyst performance decreased from Me_6TREN > TREN > PMDETA > DETA, and (4) degrees of polymerization ≥1000 exhibited a catalyst concentration boundary, which required higher $Cu^{II}Br_2/L$ catalyst concentrations to produce similarly controlled polymerizations. Successful chain extension of a PMA macroinitiator demonstrated excellent chain-end functionality and living character.

Introduction

Atom transfer radical polymerization (ATRP)[1] has become a preferred controlled radical polymerization (CRP)[2] technique enabling synthetic control of functional polymeric materials with well-defined compositions, architectures, and functionalities to include block copolymers,[3] stars,[4] combs,[5] hybrids,[6] and polymeric bioconjugates.[7] Control in ATRP is achieved by maintaining a dynamic equilibrium between dormant and active species (i.e., propagating radical) via a reversible redox process by the aid of transition metal catalysts,[8] such as Cu,[1a,b] Ru,[1h] Fe,[9] Os,[10] and Mo.[11] Scheme 1a illustrates the general mechanism of ATRP[2c,12] which involves homolytic cleavage of a carbon−(pseudo)halogen bond (R−X)[13] by a lower oxidation state copper ligand complex (Cu^IX/L), generating a propagating radical ($R^\bullet$) capable of reversible deactivation by a higher oxidation state copper ligand complex ($Cu^{II}X_2/L$). Each of these processes is governed by their respective rate constants of activation, propagation, and deactivation defined as k_a, k_p, and k_{da}, respectively. Repetitive transfer of the (pseudo)halogen between the transition metal complex and propagating chain end essentially mediates the polymerization process, resulting in well-defined polymers with predetermined molecular weights and narrow molecular weight distributions. The ratio of k_a/k_{da} provides the overall ATRP equilibrium constant (K_{ATRP}) which determines the concentration of radicals and, consequently, the rate of polymerization (R_p). Alternatively, the dispersity of molecular weights (M_w/M_n), defined as the ratio of weight- and number-average molecular weights, respectively, is dependent upon k_{da} and conversion (p).[14] The influence of the previously described parameters on R_p and M_w/M_n is given in eqs 1 and 2, where $[P^\bullet]$ and [M] signify the propagating radical and monomer concentrations. The $[R-X]_0$ and $[R-X]_t$ correspond to the concentrations of initiator present initially and at any given time during the polymerization.

$$R_p = k_p[P^\bullet][M] = \frac{k_pk_a[R-X]_0[Cu^I/L]}{k_{da}[Cu^{II}/L]}[M] \qquad (1)$$

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_p([R-X]_0 - [R-X]_t)}{k_{da}[Cu^{II}/L]}\right)\left(\frac{2}{p} - 1\right) \qquad (2)$$

In theory, absolute concentrations of copper catalyst can be significantly decreased under normal ATRP conditions without affecting the R_p, provided that a suitable ratio of $[Cu^I/L]/[Cu^{II}/L]$ is maintained, as inferred through eq 1. However, in reality, due to unavoidable and irreversible radical−radical termination events the $[Cu^{II}/L]$ increases, as described by the persistent radical effect,[15] and effectively depletes the system of $[Cu^I/L]$. Consequently, the polymerization stops once the initial concentration of Cu^I becomes lower than that of the total amount of radical−radical termination events. For this reason, one cannot decrease the concentration of copper catalyst below that of chains involved in radical−radical termination reactions, which is typically ca. 100−1000 ppm versus monomer if the targeted degree of polymerization is 100.

Lowering the amount of catalyst would be beneficial from both commercial and environmental standpoints. Successful attempts to decrease the amount of catalyst used in ATRP

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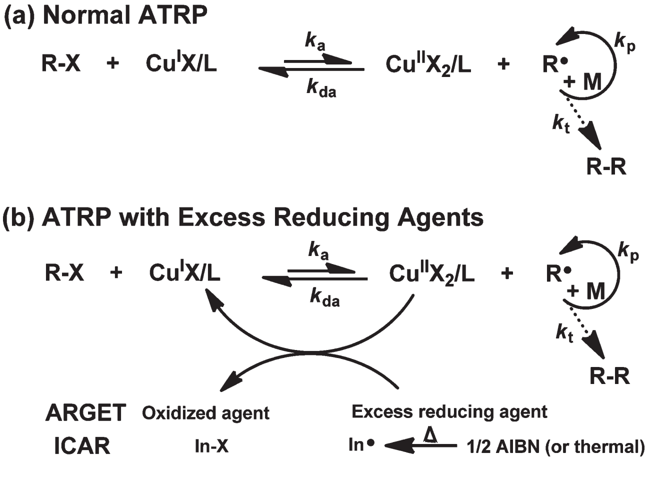
systems are exemplified by activators regenerated by electron transfer (ARGET)[16] and initiators for continuous activator regeneration (ICAR).[16d,17] When copper catalysts are in the presence of a large excess of reducing agent (Scheme 1b), both systems are capable of continuous regeneration of Cu^I activators from Cu^{II} deactivators formed through radical−radical termination. These methods allow ATRP to be conducted with significantly lower concentrations of catalyst (i.e., $[Cu^{II}Br_2] \leq 10$ ppm). In an effort to make environmentally friendly, efficient, and cost-effective ARGET (ICAR) procedures, rigorous studies have been devoted to find suitable reducing agents, which proceed in a manner devoid of side products, facilitate facile removal, and efficiently perform at catalytic concentrations. A variety of reducing agents have been identified, including tin(II) 2-ethylhexanoate ($Sn(EH)_2$), ascorbic acid, glucose, hydrazine, phenols, and also nitrogen-containing ligands (e.g., PMDETA) and monomers, for ARGET ATRP which are able to successfully provide a wide range of polymers in a well-controlled fashion.[16a−k,17] Tris[2-(dimethylamino)ethyl]amine (Me_6TREN, Scheme 2) and tris[(2-pyridyl)methyl]amine (TPMA) are frequently used ligands for ARGET or ICAR systems due to their high complex stabilities with Cu^{II},[18] allowing production of low M_w/M_n polymers with ppm concentrations of a catalyst. Moreover, ARGET ATRP conducted with low copper catalyst concentrations are capable of providing polymers with high molecular weight (HMW), narrow molecular weight distributions, and preserved chain-end functionalities which are an outcome of reduced side reactions between the propagating radicals and copper catalysts.[16e,i,j] Shen and co-workers reported ATRP with a $Cu^{II}Br_2$/*N*,*N*,*N*′,*N*′-tetra[(2-pyrydal)methyl]ethylenediamine catalyst complex with 10−100-fold excess tertiary amine as a reducing agent.[19] Hutchinson and co-workers investigated ARGET ATRP of (meth)acrylates with stoichiometric ratios of ligand in a range of 6−60 ppm with respect to monomer in the presence of a large excess of $Sn^{II}(EH)_2$ (500−700 ppm versus monomer) and later applied this technique to polymerizations in tubular reactors.[20]

Scheme 1. Mechanism of (a) Normal ATRP and (b) ATRP with Excess Reducing Agent: ARGET (Activators Regenerated by Electron Transfer) and ICAR (Initiators for Continuous Activator Regeneration) ATRP



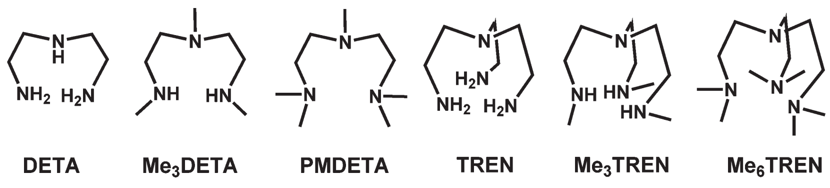
Zerovalent metal, particularly copper, has been extensively employed for many organic and polymeric synthetic procedures.[21] Reduction of Cu^{II} to Cu^I utilizing zerovalent copper (Cu^0) was first demonstrated in 1997 and shown to increase the rate of polymerization (R_p) under various ATRP conditions,[21a−c] proceed in the presence of oxygen,[21d] and at ambient temperatures with Me_6TREN.[21e] In other areas, ARGET ATRP conducted with copper wire was combined with reversible addition−fragmentation chain transfer polymerization[22] producing polymethacrylates with unprecedented HMW (e.g., $M_n = 1.25 \times 10^6$) and narrow molecular weight distributions with less than ppm concentrations of catalyst.[13b] Atom transfer radical coupling with Cu^0 has also been shown to be an efficient method to prepare alkoxyamines in high yields and purities,[21g] chain transfer agents,[21h−j] and block and hyperbranched polymers through polymer−polymer coupling reactions.[21k−o] Mechanistic studies on the role of Cu^0 in ATRP suggest it functions primarily as a reducing agent; hence, polymerizations of this nature belong to a class of ARGET ATRP.[21f] ATRP without any externally added Cu^I or Cu^{II} in the presence of Cu^0 and ligand also proceeds as reported in 1997.[21a−c] Nevertheless, this process was recently proposed to proceed through a different pathway named single-electron transfer living radical polymerization (SET-LRP).[21p−r] Mechanistic details of this process are outside the scope of this paper, and a comprehensive mechanistic study will be published in a separate report.

Herein, we report the CRP of methyl acrylate (MA) under mild conditions via ARGET ATRP with stoichiometric amounts of Cu^{II} and ligand to concentrations as low as 3 ppm in the presence of Cu^0. ARGET ATRP conducted in this work was accomplished by initially adding oxidatively stable Cu^{II} and Cu^0 without any air-sensitive Cu^I. Cu^0 functions as a mild reducing agent to produce Cu^I but may also act as a supplemental activator for alkyl halides. The use of a copper metal, specifically wire, serving as a solid heterogeneous reducing agent facilitates simplified reaction setup, handling, and facile removal from resulting polymer. This work, in part, has the specific aim of utilizing commercially available and relatively inexpensive ligands[23] at ppm concentrations, including diethylenetriamine (DETA), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), and tris-(2-aminoethyl)amine (TREN), and providing a phenomenological comparison between six nitrogen-based ligands (Scheme 2). This work also provides a cost-effective protocol capable of scale-up, while at the same time preserving polymerization control. A systematic study on $[Cu^{II}Br_2/L]$ versus targeted degree of polymerization with a variety of ligands generated a guideline regarding the minimum required catalyst concentration to achieve a well-controlled polymerization.

Experimental Section

Chemicals. MA (99%, Aldrich) was passed through a column filled with basic alumina prior to use. Copper(II) bromide ($Cu^{II}Br_2$, 99.999%, Aldrich), copper powder (<75 μm, 99%, Aldrich), copper wire (diameter = 0.5 mm, 99.9%, Alfa Aesar), ethyl 2-bromoisobutyrate (EBiB, 98%, Aldrich), diethylenetriamine (DETA, 99%, Aldrich), 1,4,7-trimethyldiethylenetriamine (Me_3DETA, Aldrich), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), tris(2-aminoethyl)amine

Scheme 2. Ligand Structures Used for ARGET ATRP of MA



(TREN, 99%, Pressure Chemical), tris[2-(methylamino)ethyl]-amine (Me_3TREN, 97%, Aldrich), and tris[2-(dimethylamino)-ethyl]amine (Me_6TREN, 99%, ATRP Solutions) were used as received. All the other reagents and solvents were used as received.

Analysis. Number-average molecular weight (M_n) and M_w/M_n values were determined by gel permeation chromatography (GPC). The GPC was conducted with a Waters 515 HPLC pump and a Waters 2414 refractive index detector using PSS columns (Styrogel 10^2, 10^3, 10^5 Å) in tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL/min at 35 °C. The column system was calibrated with 12 linear polystyrene (PSt, M_n = 376−2 570 000) standards. Conversion of monomer was determined with known concentrations of polymers in THF. Experimental and theoretical molecular weight values compared in this work are qualitative. Absolute values of PMA may be calculated utilizing universal calibration as reported in the literature.[24] ^1H NMR spectra were recorded in DMSO-d_6 as a solvent using a Bruker 300 MHz spectrometer with a delay time of 1 s.

Polymerization Procedure of PMA by ARGET ATRP. An example ARGET ATRP procedure formulated with 250 ppm of $Cu^{II}Br_2$ catalyst and targeted degree of polymerization equal to 1000 is given as follows (*throughout this report the [$Cu^{II}Br_2$] catalyst is described in ppm units calculated as a molar ratio versus monomer*). In a typical polymerization, Cu^0 powder (2.6 mg, 4.1×10^{-2} mmol) was added to a dried Schlenk flask equipped with a stir bar. < 75 μm sized copper powder and a stoichiometric ratio of $Cu^{II}Br_2$ and ligand were used for all experiments, unless otherwise mentioned. After sealing with a rubber septum, the flask was degassed and backfilled with nitrogen (N_2) five times and then left under N_2. Subsequently, a mixture of solvent (5.0 mL), MA (7.0 g, 81.3 mmol), and EBiB (15.9 mg, 8.2×10^{-2} mmol) was added to a glass vial and degassed by three freeze−pump−thaw cycles. The solution was then transferred to the Schlenk flask, which was placed in a thermostated water bath at 25 °C, followed by the addition of a solution of $Cu^{II}Br_2$ (4.5 mg, 2.0×10^{-2} mmol) and Me_6TREN (4.7 mg, 2.0×10^{-2} mmol) in purged deoxygenated solvent (2.32 mL). Samples were taken periodically under N_2 using an N_2-purged syringe, diluted by THF to a known concentration, passed through a column filled with neutral alumina to remove the copper complex, and analyzed by GPC.

Macroinitiator Synthesis. Poly(methyl acrylate)−Br (PMA-Br) macroinitiator was prepared by following similar procedures to that described above for ARGET ATRP with a ratio of MA/EBiB/Cu^0/$Cu^{II}Br_2$/Me_6TREN = 1000/1/0.5/0.25/0.25 in 50% (v/v) DMSO at 25 °C. The polymerization was stopped after 25 min by opening the flask and exposing the catalyst to air. The mixture was then passed through a column filled with neutral alumina to remove the copper complex. The polymer was precipitated by addition to a large amount of cold methanol. Dissolution and precipitation were repeated until a colorless viscous PMA was obtained. The precipitated polymer was dried in a vacuum oven at 40 °C until a constant weight was reached and analyzed by GPC (M_n = 19 800, M_w/M_n = 1.06 at 18.7% conversion).

Chain Extension of PMA-Br Macroinitiator with MA. Cu^0 (1.5 mg, 2.0×10^{-2} mmol) was added to a dried Schlenk flask equipped with a stir bar. After sealing with a rubber septum, the flask was degassed and backfilled with nitrogen (N_2) five times and then left under N_2. Subsequently, a mixture of solvent (3.0 mL), MA (2.0 g, 23.2 mmol), and PMA-Br (M_n = 19 800, M_w/M_n = 1.06, 92 mg, 4.6×10^{-3} mmol) was added to a glass vial and degassed by three freeze−pump−thaw cycles. The solution was then transferred to the Schlenk flask, which was placed in a thermostated water bath at 25 °C, followed by the addition of a solution of $Cu^{II}Br_2$ (1.0 mg, 4.6×10^{-3} mmol) and Me_6TREN (1.1 mg, 4.6×10^{-3} mmol) in deoxygenated solvent (1.18 mL). The polymerization was stopped after a 30 min by opening the flask and exposing the catalyst to air. The sample was diluted by THF to a known concentration, passed through a column filled with neutral alumina to remove the copper complex, and analyzed by GPC (M_n = 112 300, M_w/M_n = 1.09 at 22.6% conversion).

Model Reaction of Primary Amine with MA (Michael Addition Reaction). A deoxygenated solution of TREN (30 mM) and MA (300 mM) in DMSO-d_6 (1.0 mL) was added to a NMR tube under a N_2 atmosphere, which was end-sealed with a rubber septum and was placed in a thermostated water bath at 25 °C. ^1H NMR was measured periodically at 25 °C. Another reaction involving a Cu^IBr/TREN complex was carried out by a procedure similar to that described above.

Results and Discussion

ATRP of MA with Cu^0 and Ligand without $Cu^{II}Br_2$. ATRP of MA with stoichiometric ratios of Cu^0 and an assortment of ligands, designated as "L" and shown in Scheme 2, without $Cu^{II}Br_2$ were performed with molar ratios of MA/EBiB/Cu^0/L = 1000/1/0.25/0.25 in 50% (v/v) DMSO at 25 °C. The polymerization medium with Me_6TREN was initially clear but gradually became light green after 10 min without any further color change. Transition from an initial clear to green color during the reaction indicates an accumulation of $Cu^{II}Br_2$/Me_6TREN, a probable result of radical−radical termination events. In the current system, copper powder functions to activate (macro)initiators in the early stages of polymerization generating Cu^I/L complexes which are also capable of activation. Activation of (macro)initiators by Cu^I/L complexes is known to be faster than that by Cu^0.[21f,25] Quantification of Cu^0 and Cu^I effects on activation and those of Cu^0 on comproportionation (i.e., reduction) and disproportionation are outside the scope of this paper and will be reported in a future paper.

Polymerization of MA with Me_6TREN without $Cu^{II}Br_2$ resulted in a well-controlled polymerization. First-order kinetic behavior was observed in the semilogarithmic plot indicating a constant concentration of propagating radicals (Figure 1a). In addition, M_n values increased linearly with conversion while, at the same time, correlating strongly with their theoretically predetermined values ($M_{n,th}$) (Figure 1b). The values of M_w/M_n were greater than 1.5 below 20% conversion and then progressively decreased to less than 1.1 above 50% conversion (Figure 1b). This is due to an insufficient concentration of deactivator (i.e., $Cu^{II}Br_2$/L) at the beginning of the polymerization, which indicates that control is established by the persistent radical effect.[15] These observations are in agreement with previous literature reports.[21f,q]

Another control experiment was carried out with PMDETA, formulated with molar ratios of MA/EBiB/Cu^0/PMDETA = 1000/1/0.25/0.25 in 50% (v/v) DMSO at 25 °C. Contrary to the Me_6TREN system, polymerization with PMDETA was poorly controlled. Although the concentration of propagating radical was constant as illustrated in the first-order kinetic plot (Figure 2a), M_n values decrease exponentially with conversion (Figure 2b) instead of increasing linearly with conversion. The highest molecular weight was observed at the lowest conversion value. Moreover, M_w/M_n values were consistently larger than 2 and increased with conversion (Figure 2b). These results demonstrate that ATRP of MA with only Cu^0/PMDETA is not suitable to produce well-defined polymers. MA polymerizations with similar conditions except with different ligands, DETA, Me_3DETA, TREN, and Me_3TREN, were also examined. All the polymerizations had similar rates, although Me_6TREN was ca. 1.5−2 times faster, as shown in Figure 3.

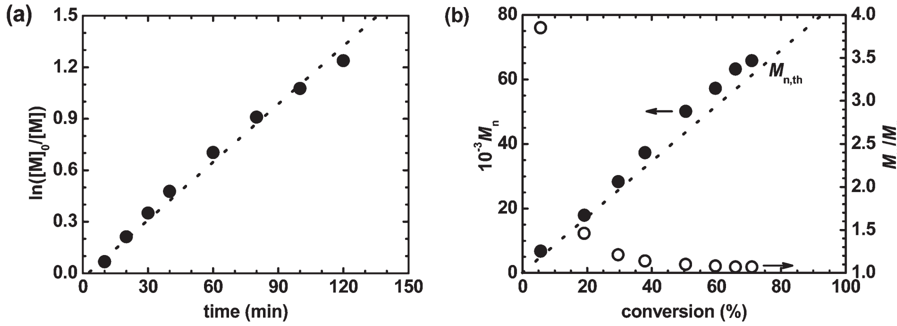


Figure 1. (a) Kinetic plot of monomer conversion and (b) dependence of M_n (filled symbols) and M_w/M_n (open symbols) vs conversion for MA polymerization with 250 ppm of Me$_6$TREN and Cu^0 at 25 °C: MA/EBiB/Cu^0/Me$_6$TREN = 1000/1/0.25/0.25 in 50% (v/v) DMSO.

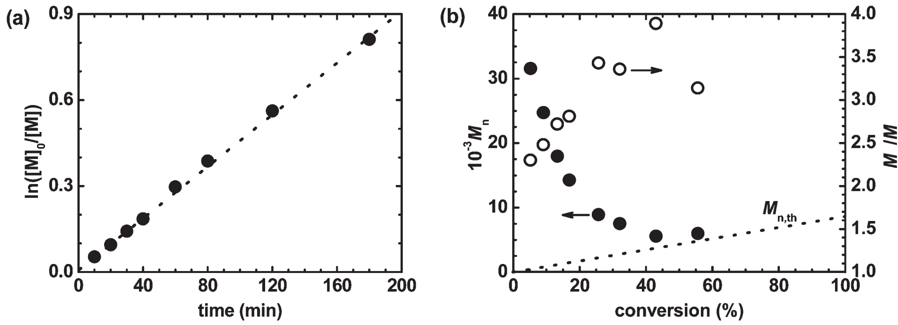


Figure 2. (a) Kinetic plot of monomer conversion and (b) dependence of M_n (filled symbols) and M_w/M_n (open symbols) vs conversion for MA polymerization with 250 ppm of PMDETA and Cu^0 at 25 °C: MA/EBiB/Cu^0/PMDETA = 1000/1/0.25/0.25 in 50% (v/v) DMSO.

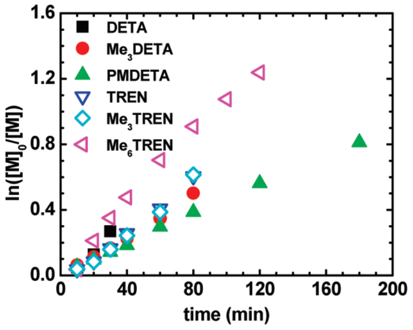


Figure 3. Kinetic plot of monomer conversion for MA polymerizations with 250 ppm of Cu^0 and various ligands at 25 °C: MA/EBiB/Cu^0/L = 1000/1/0.25/0.25 in 50% (v/v) DMSO.

Similar to the PMDETA system, MA polymerizations with Me$_3$TREN, TREN, Me$_3$DETA, and DETA were poorly controlled (see Supporting Information Figures 1−4).

ARGET ATRP of MA with in Situ Generation of Cu^I by the Reduction of Cu^{II} with Cu^0. As described above, MA polymerizations starting with stoichiometric ratios of Cu^0 and ligands resulted in poorly controlled polymerizations due to an insufficient concentration of deactivator, except with Me$_6$TREN. On the basis of these observations, ARGET ATRP of MA starting initially from Cu^{II}Br$_2$/L, with Cu^0 acting as a reducing agent, was conducted. Increased deactivation from the onset of polymerization should theoretically produce well-controlled polymerizations with narrow molecular weight distributions even in the early stages of polymerization (refer to eq 2). MA polymerizations were performed with molar ratios of MA/EBiB/Cu^0/CuBr$_2$/L = 1000/1/0.5/0.25/0.25 in 50% (v/v) DMSO at 25 °C. As shown in Figure 4a,b, all polymerizations with DETA, Me$_3$DETA, and PMDETA were well controlled, contrary to the results with only Cu^0 in the absence of Cu^{II}Br$_2$. The first-order kinetic plots were linear with respect to time for all ligands, with the largest R_p observed with PMDETA, followed closely by Me$_3$DETA, and the smallest with DETA. Linear first-order behavior indicates a constant concentration of propagating radicals and ratio of [Cu^I/L]/[Cu^{II}/L] were maintained throughout the polymerization. Contrary to the systems without Cu^{II}Br$_2$, M_n values increased in a linear fashion with conversion and matched closely to their $M_{n,th}$ in all cases. Values of M_w/M_n were improved (1.3−1.6) at lower conversions and continued to decrease with conversion. Polymers prepared with PMDETA (Figure 4b, open triangle) had smaller M_w/M_n values than those prepared with DETA or Me$_3$DETA.

ARGET ATRP of MA was also carried out with TREN-based ligands (TREN, Me$_3$TREN, and Me$_6$TREN) under similar conditions as described above. All the polymerizations were well controlled (Figure 5a,b). The R_p gradually decreased, and may in part be, due to an increase of Cu^{II}Br$_2$ from radical−radical termination reactions and because TREN-based ligands preferentially bind with Cu^{II} over Cu^I complexes, or from a reduction of propagating centers due to irreversible termination.[18] This complexation favors disproportionation of Cu^{I}Br with TREN-based ligands to a larger degree than DETA-based ligands. Regarding the R_p, ATRP with Me$_6$TREN was fastest, followed by that with Me$_3$TREN, and last TREN. The relative activity of each catalyst system may be rationalized by a balance between K_{ATRP} established by each copper−ligand complex and relative stability of these complexes toward disproportionation. The curvature observed in the semilogarithmic plots can be partially attributed to a decreasing [Cu^{I}Br/L]/[Cu^{II}Br$_2$/L] ratio due to radical termination and an insufficient concentration of ligand which preferentially complexes with Cu^{II}Br$_2$ species. This behavior is exemplified with Me$_6$TREN, Me$_3$TREN, and TREN, requiring ca. 2, 7.5, and

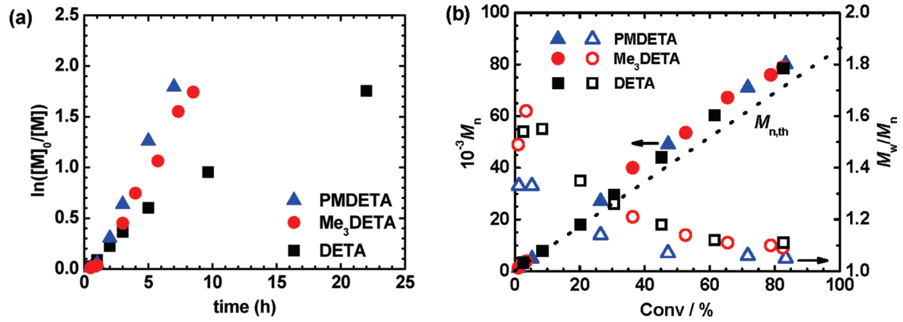


Figure 4. (a) Kinetic plot of monomer conversion and (b) dependence of M_n (filled symbols) and M_w/M_n (open symbols) vs percent conversion for MA polymerization with 250 ppm of $Cu^{II}Br_2/L$ (DETA, Me_3DETA, and PMDETA) and 500 ppm of Cu^0 at 25 °C: $MA/EBiB/Cu^0/Cu^{II}Br_2/L$ = 1000/1/0.5/0.25/0.25 in 50% (v/v) DMSO.

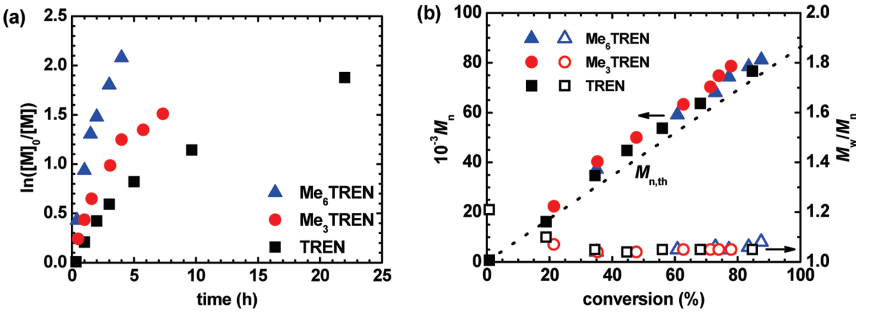


Figure 5. (a) Kinetic plot of monomer conversion and (b) dependence of M_n (filled symbols) and M_w/M_n (open symbols) vs percent conversion for MA polymerization with 250 ppm of $Cu^{II}Br_2/L$ (TREN, Me_3TREN, and Me_6TREN) and 500 ppm of Cu^0 at 25 °C: $MA/EBiB/Cu^0/Cu^{II}Br_2/L$ = 1000/1/0.5/0.25/0.25 in 50% (v/v) DMSO.

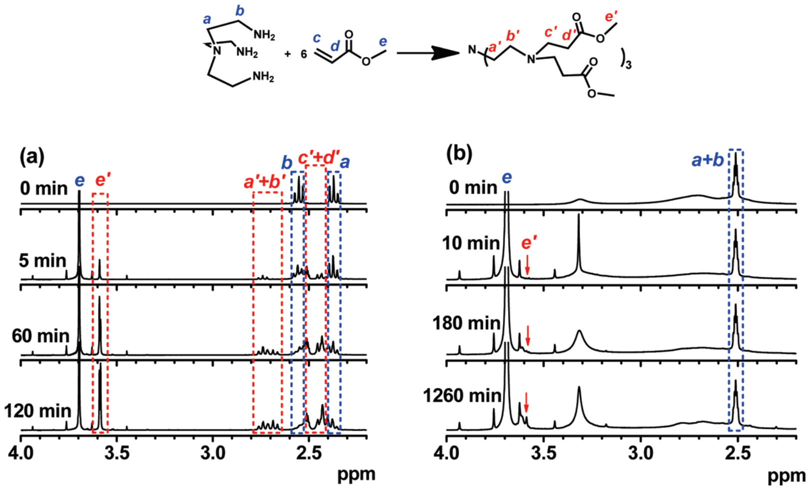


Figure 6. ^1H NMR spectra in DMSO-d_6 of a mixture containing (a) TREN/MA (= 30/300 mM) and (b) Cu^IBr/TREN/MA (= 30/30/300 mM) at 25 °C: spectra of 0 min for (a) and (b) were measured with TREN (30 mM) and Cu^IBr/TREN (30 mM), respectively, without MA. A preformed Cu^IBr/TREN (30 mM) complex was used for the experiment (b).

15.5 h to reach ~80% conversion, respectively. With each ligand, M_n values increased linearly with conversion and were almost identical to $M_{n,th}$ values. M_w/M_n values in all polymerizations were low (~1.1) throughout the polymerization due to high absolute concentrations of $Cu^{II}Br_2/L$, as TREN-based ligands have higher stability constants with $Cu^{II}Br_2/L$ compared to DETA-based ligands. It is noteworthy to mention that primary amine ligands, TREN or DETA, resulted in well-controlled polymerizations, even though they are known to participate in Michael additions (MA).[26] The basicity (or activity) of amines is decreased by forming stable complexes with $Cu^{II}Br_2$, which will be discussed in further detail below.

Reaction between Primary Amine and MA (Michael Addition). Addition of primary and secondary amines to acrylates occurs efficiently and has been applied as a practical means to synthesize various acrylate-modified TREN-based ligands.[26] The Michael addition between TREN and MA was carried out with a [TREN] and [MA] of 30 and 300 mM, respectively, in DMSO-d_6 at 25 °C. As shown in Figure 6a, addition of the amines contained in TREN to MA rapidly progressed, reaching 90% conversion within 1 h. Resonances corresponding to the methyl group of MA (*e*, 3.7 ppm) gradually decreased and shifted upfield for the MA modified adduct (*e*′, 3.58 ppm). Simultaneously, new adduct resonances appeared and gradually increased, at approximately

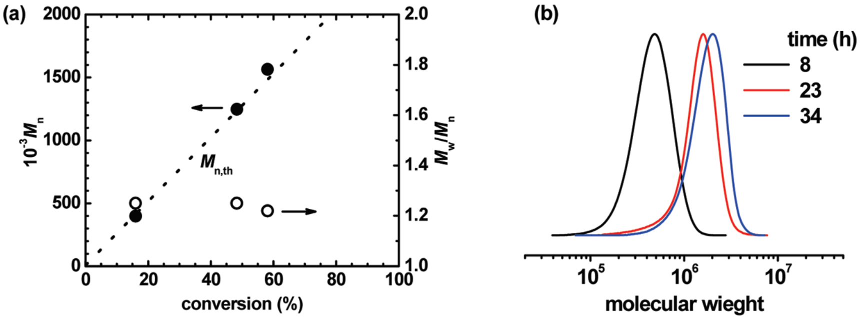


Figure 7. (a) Dependence of M_n (filled symbols) and M_w/M_n (open symbols) vs conversion for MA polymerization with 50 ppm of $Cu^{II}Br_2$/PMDETA and 500 ppm of Cu^0 at 25 °C: MA/EBiB/Cu^0/$Cu^{II}Br_2$/PMDETA = 30 000/1/15/1.5/1.5 in 75% (v/v) DMSO at 25 °C. (b) Evolution of molecular weight with polymerization time.

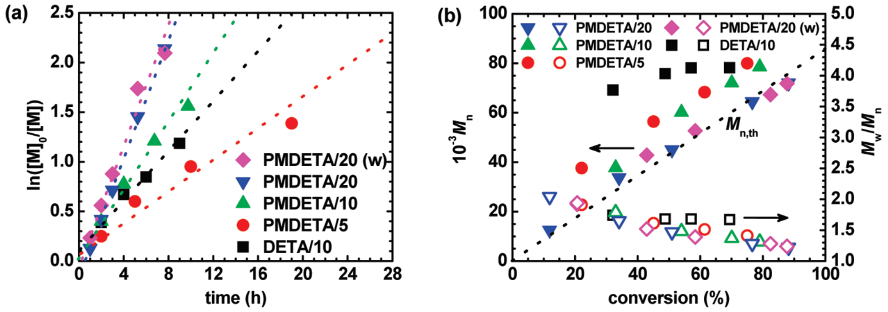


Figure 8. (a) Kinetic plot of monomer conversion and (b) dependence of M_n (filled symbols) and M_w/M_n (open symbols) vs conversion for MA polymerization with 5−20 ppm of $Cu^{II}Br_2$/L (DETA and PMDETA) and Cu^0 at 25 °C: MA/EBiB/Cu^0 = 1000/1/0.5 in 50% (v/v) DMSO; $Cu^{II}Br_2$/L = 0.005 (5 ppm), 0.01 (10 ppm), and 0.02 equiv (20 ppm); (+w) indicates Cu^0 wire (diameter = 0.5 mm, length = 30 cm) instead of Cu^0 powder.

2.7 ppm ($a' + b'$) and 2.5−2.4 ppm ($c' + d'$), whereas reagent TREN peaks (a and b) disappeared as the reaction proceeded. Acceleration of this reaction would occur under typical polymerization conditions, from the increased [MA]; however, complexation between TREN and Cu^IBr resulted in greatly diminished reaction rates. An identical reaction as described above, except with a preformed Cu^IBr/TREN complex, reached ca. 5% conversion in 21 h (Figure 6b). Broader signals in Figure 6b are likely due to the presence of paramagnetic Cu^{II} species and some exchange reactions, whereas the resonance at 3.3 ppm is that of HDO caused from slow exchange with d-DMSO. Inhibition of Michael addition reaction through copper−ligand complexes, in part, explains how polymerizations conducted with primary and secondary amine ligands behave in a controlled fashion. Polymerizations with free ligands and Cu^0, without a preformed $Cu^{II}Br_2$/L catalyst complex, readily undergo Michael additions changing the activity of the original ligand, resulting in a loss of polymerization control.[25]

Preparation of High Molecular Weight PMA. Versatility of ARGET ATRP was tested by attempting to synthesize high molecular weight PMA with 50 ppm of $Cu^{II}Br_2$ and PMDETA. The polymerization was formulated with a molar ratio of MA/EBiB/Cu^0/$Cu^{II}Br_2$/PMDETA = 30 000/1/15/1.5/1.5 in 75% (v/v) DMSO and conducted at 25 °C. M_n values increased linearly with conversion and correlated well to the $M_{n,th}$, reaching ~1.5 million, while maintaining low M_w/M_n values (~1.22) after 34 h (Figure 7a,b). This polymerization was stopped at ca. 60% conversion due its very high viscosity. GPC traces revealed a monomodal distribution which shifted to higher molecular weight with time, devoid of any significant low molecular weight tailing. In a separate polymerization, conducted with 25 ppm of $Cu^{II}Br_2$/L, PMA with a M_n = 1.3 million and M_w/M_n = 1.25 (51% conversion) was obtained after 8 h by using a molar ratio of MA/EBiB/Cu^0/$Cu^{II}Br_2$/PMDETA = 30 000/1/15/0.75/0.75 in 75% (v/v) DMSO at 25 °C.

ARGET ATRP of MA with ppm Amount of Catalyst. ARGET ATRP of MA was conducted with a 1:1 molar ratio of $Cu^{II}Br_2$ and ligand (i.e., either PMDETA or DETA) at 5−20 ppm concentrations. Polymerizations discussed below were conducted with a molar ratio of MA/EBiB/Cu^0/($Cu^{II}Br_2$/L) (L = DETA or PMDETA) = 1000/1/0.5/0.005−0.02 in 50% (v/v) DMSO at 25 °C. All reaction media were transparent, although the initial color was light blue at 20 ppm and colorless at 5−10 ppm of catalyst. The first-order kinetic plot shows linear behavior with [$Cu^{II}Br_2$/PMDETA] ≥ 10 ppm, whereas a decreasing slope was realized at 5 ppm of $Cu^{II}Br_2$/PMDETA (Figure 8a). Monomer conversions reached ca. 80% after 5.5, 8.5, and 19 h with 20, 10, and 5 ppm of $Cu^{II}Br_2$/PMDETA, respectively, indicating faster rates of polymerization with higher concentrations of catalyst. All PMDETA polymerizations resulted in a linear increase of the M_n with conversion (Figure 8b); however, the deviation of M_n from $M_{n,th}$ was dependent on the catalyst concentration. Initiation efficiency values calculated from $M_{n,th}/M_n$ were closest to unity at the highest catalyst concentration (i.e., 20 ppm with copper powder and wire) and progressively decreased with diminishing catalyst concentrations. For all $Cu^{II}Br_2$/PMDETA catalyst concentrations, M_w/M_n values were similar and decreased gradually with monomer conversion. MA polymerization with 20 ppm of $Cu^{II}Br_2$/PMDETA in the presence of Cu^0 wire (diameter = 0.5 mm, length = 30 cm) resulted in well-controlled polymerization, as shown in Figure 8a,b, and produced almost identical results as the Cu^0 powder system. The initial and final reaction media involving Cu^0 wire were almost completely colorless, as shown in Figure 9a,b. After the polymerization, the Cu^0 wire reducing agent was easily removed from the crude reaction product. Substitution of PMDETA

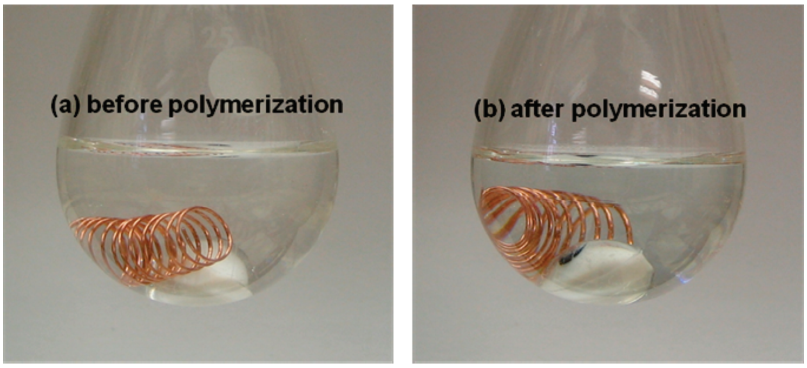


Figure 9. Images of the reaction flask (a) before and (b) after ARGET ATRP of MA with 20 ppm of $Cu^{II}Br_2$/PMDETA and Cu^0 wire as a reducing agent: MA/EBiB/Cu^0 wire/$Cu^{II}Br_2$/PMDETA = 1000/1/−/0.02/0.02 in 50% (v/v) DMSO; Cu^0 wire = 0.5 mm (diameter) × 30 cm (length).

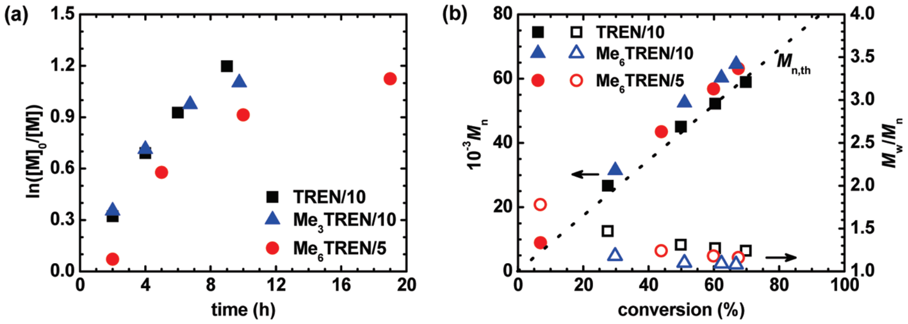


Figure 10. (a) Kinetic plot of monomer conversion and (b) dependence of M_n (filled symbols) and M_w/M_n (open symbols) vs conversion for MA polymerization with 5−10 ppm of $CuBr_2$/L (TREN and Me_6TREN) and Cu^0 at 25 °C: MA/EBiB/Cu^0 = 1000/1/0.5 in 50% (v/v) DMSO; $Cu^{II}Br_2$/L = 0.005 (5 ppm) and 0.01 (10 ppm).

with DETA at 10 ppm of $Cu^{II}Br_2$/TREN resulted in linear first-order kinetic behavior, although, significantly higher M_n values as compared to $M_{n,th}$ values were observed along with a small increase in M_n with conversion. Values of M_w/M_n remained close to 1.7 during the whole duration of the polymerization.

ARGET ATRP of MA was conducted with a 1:1 molar ratio of TREN or Me_6TREN with $Cu^{II}Br_2$ (5−10 ppm) and Cu^0 under similar conditions as described above. Within this catalyst concentration range, reaction mixtures were nearly colorless. As shown in Figure 10a, all the polymerizations preceded relatively fast at the beginning but became slower at longer polymerization times. A 2 h induction period was observed with 5 ppm of $Cu^{II}Br_2$/Me_6TREN. In all polymerizations involving TREN-based ligands, a linear increase of the M_n and good correlations with $M_{n,th}$ were observed, as shown in Figure 10b. M_w/M_n values decreased with conversion for all ligands but were the highest with 10 ppm of $Cu^{II}Br_2$/TREN, followed by 5 ppm of $Cu^{II}Br_2$/Me_6TREN, and lowest with 10 ppm of $Cu^{II}Br_2$/Me_6TREN. All polymerizations with TREN and Me_6TREN gave substantially smaller M_w/M_n values compared to those with DETA or PMDETA at similar catalyst concentrations. The above results demonstrate that low concentrations of $Cu^{II}Br_2$ with TREN or Me_6TREN (5−10 ppm) are effective at catalyzing ARGET ATRP with sufficient polymerization control.

Correlation of Minimal [$Cu^{II}Br_2$/L] vs Targeted DP for Controlled ARGET ATRP. Four ligands (i.e., Me_6TREN, TREN, PMDETA, and DETA) were selected and probed to determine the minimum catalyst concentrations required at numerous targeted degrees of polymerization (DP) to achieve well-controlled polymerizations. In these experiments, polymerizations that resulted in polymers with an $M_w/M_n \sim 1.3$ at ~80% conversion were defined as the criteria for a well-controlled polymerization. Comparable conversion values were required, as the extent of monomer consumption is an important polymerization variable factor effecting M_w/M_n, according to eq 2. Table 1 of the Supporting Information summarizes the results of each polymerization. General observations are as follows: (1) lower [$Cu^{II}Br_2$/L] require higher targeted degrees of polymerization to produce equally controlled polymerizations, (2) higher [$Cu^{II}Br_2$/L] are necessary for lower targeted degrees of polymerization, which require increased deactivator concentrations (i.e., $Cu^{II}Br_2$) such that every activation−deactivation cycle adds fewer monomer units, (3) the performance of the copper ligand complexes follows the order of Me_6TREN > TREN > PMDETA > DETA, and (4) [$Cu^{II}Br_2$/L] should be increased, when a targeted DP is large (i.e., DP = 5000), to produce polymers with low M_w/M_n values. This could be due to limited copper complex stability, which becomes an issue below a certain concentration of Cu^{II}/L (ca. 3 and 8 ppm for Me_6TREN and PMDETA, respectively). Initiation efficiencies greater than 100%, in the case of a DP = 5000 (see Supporting Information Table 1, entry 5), correspond to smaller apparent values of M_n compared to $M_{n,th}$ and can be attributed to transfer.

The above experimental results were plotted as targeted degree of polymerization versus minimum [$Cu^{II}Br_2$/L] using logarithmic scales, as shown in Figure 11. This graph displays the lowest required [$Cu^{II}Br_2$/L] to produce controlled polymerizations at any specified degree of polymerization. The plots of targeted DP versus [$Cu^{II}Br_2$/L] for each ligand were linearly proportional when the targeted degrees of polymerization were smaller than 10^3 (i.e., targeted DP < 1000). The value of M_w/M_n is defined by the ratio of the

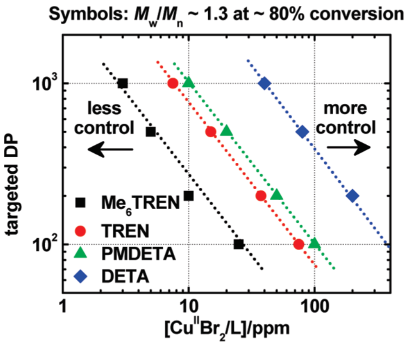


Figure 11. Plot of targeted degree of polymerization vs [Cu^{II}Br$_2$/L] for MA polymerizations with four different ligands (DETA, PMDETA, TREN, and Me$_6$TREN) and Cu^0 as a reducing agent in 50% (v/v) DMSO at 25 °C: targeted DP = $[MA]_0/[EBiB]_0$; 0.5 equiv of Cu^0 vs Cu^{II}Br$_2$ was used.

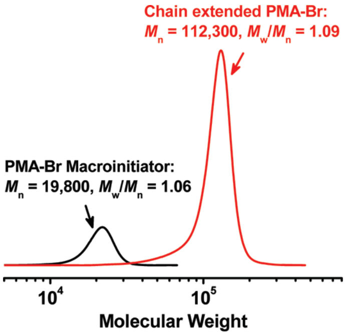


Figure 12. GPC traces of PMA-Br macroinitiator before (black line, left) and after (red line, right) chain extension with MA. Experimental condition: MA/PMA-Br macroinitiator/Cu^0/Cu^{II}Br$_2$/Me$_6$TREN = 5000/1/5/1/1 in 66% (v/v) DMSO at 25 °C.

number of units added in one activation−deactivation cycle to the targeted DP.[14] Therefore, one can add 10 more units in one activation−deactivation cycle when DP is increased by a factor of 10, leading to the same value of M_w/M_n.[27] Figure 11 illustrates that the catalyst performance is highest with Me$_6$TREN, followed by TREN and PMDETA, and last DETA. The minimum [Cu^{II}Br$_2$/L] for a constant DP, resulting in a similarly controlled polymerization, decreases in the order of DETA > Me$_3$DETA > TREN > Me$_6$TREN. For example, 3 ppm of Cu^{II}Br$_2$/Me$_6$TREN was enough to produce a controlled polymerization when the DP = 1000, while 7.5, 10, and 40 ppm of a catalyst are required for TREN, PMDETA, and DETA, respectively. These concentrations are the lowest [Cu^{II}Br$_2$/L] to produce polymers that have a $M_w/M_n \sim 1.3$ at ~80% conversion and well-preserved chain-end functionality. However, if one decreases catalyst concentration further, such as to 1 ppm of [Cu^{II}Br$_2$/Me$_6$TREN] for DP = 1000, polymers with M_w/M_n values higher than 1.3 at ~80% conversion will be obtained. Conversely, if one increases the concentration to 5 ppm for the same DP, polymers with M_w/M_n lower than 1.3 at ~80% conversion. Figure 11 provides an estimation of the minimum amount of copper catalyst for each ligand at different targeted DPs for well-controlled polymerizations.

Chain Extension of MA from PMA-Br. To confirm the retention of the bromine chain ends and demonstrate living character, chain extension with MA from a PMA-Br macroinitiator was evaluated. PMA-Br macroinitiator was prepared, in a similar fashion as described above, with a ratio of MA/EBiB/Cu^0/CuBr$_2$/Me$_6$TREN = 1000/1/0.5/0.25/0.25 in 50% (v/v) DMSO at 25 °C. After 25 min, a macroinitiator with a M_n = 19 800 and M_w/M_n = 1.06 was obtained. A chain extension with MA from the macroinitiator was carried out with a molar ratio of MA/macroinitiator/Cu^0/Cu^{II}Br$_2$/Me$_6$TREN = 5000/1/5/1/1 in 66% (v/v) at 25 °C. After 30 min, a nearly quantitative chain extension (M_n = 112 300, M_w/M_n = 1.09) was observed without detectable macroinitiator remaining ($f_{dead} \leq 5\%$, Figure 12). This result demonstrates successful preservation of bromine chain ends, evident from an efficient chain extension with MA while retaining a low M_w/M_n.

Conclusions

ARGET ATRP of MA with inexpensive ligands, such as DETA, PMDETA, and TREN, and ppm concentrations of a Cu^{II}Br$_2$/L in the presence of copper powder or wire was successfully performed and well controlled at room temperature (25 °C). This technique operated by the reduction of an oxidatively stable compound (Cu^{II}Br$_2$/L) by a Cu^0 reducing agent. ARGET ATRP of MA with only Cu^0 and ligand in the absence of Cu^{II}Br$_2$ resulted in poorly controlled polymers due to insufficient amount of deactivator throughout the polymerization, except in the case of Me$_6$TREN. Polymers prepared with Cu^{II}Br$_2$/L maintained excellent chain end functionalities, which was confirmed through chain extension of a PMA-Br macroiniator. High molecular weight polymers with M_n > 1.5 million and low M_w/M_n values (~1.25) were prepared. A “map” of the minimum [Cu^{II}Br$_2$/L] versus targeted DP with various ligands was completed, and it led to several conclusions: (1) catalyst performance was the highest with Me$_6$TREN, followed by TREN and PMDETA, and last with DETA, (2) lower [Cu^{II}Br$_2$/L] require higher targeted DPs to produce similarly controlled polymers as lower targeted DPs, and (3) a catalyst concentration boundary exists (DP ~ 1000) that requires higher concentration of a catalyst to produce similarly controlled polymerizations compared to DP < 1000.

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Supporting Information Available: Results of polymerization kinetics, characterization, and summary tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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