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Origin of Initial Uncontrolled Polymerization and Its Suppression in the Copper(0)-Mediated Living Radical Polymerization of Methyl Acrylate in a Nonpolar Solvent

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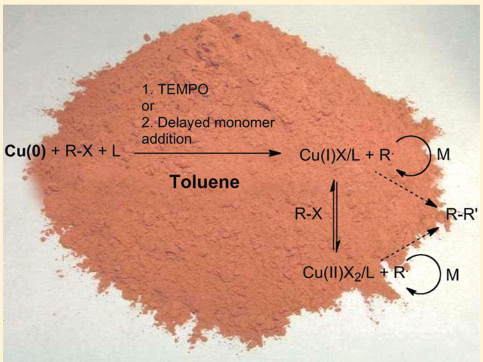
Supporting Information

ABSTRACT: We report the controlled polymerization of methyl acrylate in the presence of elemental copper at room temperature in a nonpolar solvent. As in single electron transfer (SET) living radical polymerization with nonactivated Cu(0), uncontrolled polymerization is observed early in the reaction. In the absence of marked disproportionation of copper(I) in our system, we propose that copper(0) is oxidized to copper(I) while activating the initiator, which triggers uncontrolled polymerization. Copper(I) then reacts with the alkyl halide initiator to generate active species and copper(II), leading to the establishment of the equilibrium between copper(I) and (II). Delaying the addition of monomer until the initial equilibrium between copper(I) and (II) is established, or addition of a small amount of TEMPO, as radical scavenger for the initial uncontrolled propagating radical species, prevent the early loss of control in polymerization. The system provides high chain end fidelity, and the polymers generated can be chain extended with high efficiency. This system displays many similarities to ICAR, with the reaction between RBr and Cu playing the role of the radical initiator. Use of copper(0) also has the advantage that only a very small amount of catalyst is utilized to mediate polymerization, and the copper catalyst is easily removed by filtration.



INTRODUCTION

The independent development of atom transfer radical polymerization (ATRP) in 1994−1995 by Sawamoto and co-workers[1] and Matyjaszewski and co-workers[2] introduced a new method of controlled/living radical polymerization based on the principles of atom transfer radical addition (ATRA).[3] ATRP is characterized by the reversible deactivation of polymer radicals via their reaction with metal (usually Cu^{II}) halides (Scheme 1) in the presence of an appropriate ligand.[4,5] The technique is effective for the polymerization of a wide range of monomers, including styrene,[6] acrylates,[2,7,8] methacrylates,[9,10] and acrylonitrile.[11] Many different ligands may be used, with nitrogen-based species found to be preferential to sulfur, oxygen, and phosphorus compounds due to more favorable binding constants.[12]

Termination reactions are unavoidable in free radical processes and limit the ability of controlled radical polymerizations to provide final products with well-controlled structures. In ATRP, bimolecular termination of two propagating radical species results in the buildup of copper(II). This increase in copper(II) concentration alters the position of the equilibrium between active and dormant polymer chains, resulting in fewer active species. This effect is analogous to the persistent radical effect, with copper(II) playing the role of the persistent radical.[13]

When the total copper concentration is low, the buildup of these persistent radical deactivators may retard the kinetics to such an extent that no polymerization is observed.[14] Several techniques have been developed that alleviate this effect: initiators for continuous activator regeneration (ICAR),[15] activators generated for electron transfer (AGET),[16] and activators regenerated for electron transfer (ARGET).[15] All three systems work by reducing deactivating copper(II) species to copper(I). In ARGET, excess copper(II) is reduced as it forms by a reducing agent such as ascorbic acid or tin ethylhexanoate. This allows the amount of copper catalyst to remain at ppm levels. In ICAR, the addition of a radical initiator provides a continuous supply of new radicals to replace those lost to termination reactions. This maintains the copper(I)/copper(II) equilibrium but results in the formation of unwanted byproducts as new polymer chains are initiated throughout the reaction.

At a similar time to the development of ICAR and ARGET, a process using common ATRP ligands and initiators in which elemental copper was employed as the catalyst was proposed by Percec et al.[17] This process, named SET-LRP,[17,18] has been

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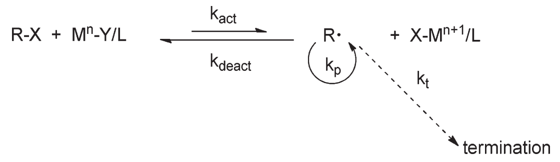
Scheme 1. Generally Accepted ATRP Mechanism



shown to polymerize a wide range of monomers, including acrylates,[17,19−21] methacrylates,[22,23] and acrylamides,[24] and is currently the only method able to polymerize vinyl chloride to a predictable molecular weight,[17,25] all at near-ambient temperatures. In SET-LRP, elemental copper is used to abstract a halogen from a halogenated initiator in the presence of an appropriate ligand to form copper(I) halide and a radical species.[26−28] Under appropriate solvent conditions (e.g., DMSO,[17] ionic liquids,[29] alcohols,[30] and binary mixtures of other polar solvents[31]), copper(I) disproportionates[32] into copper(0) and -(II), while the radical species propagates by addition to monomer. The propagating radical may then abstract a halogen from the copper(II) species, forming a dormant polymer chain, and copper(I), which may again disproportionate into copper(0) and -(II). It should be noted that in the early stages of the reaction each atom of copper(0) generates two propagating radicals, but only one deactivating copper(II) species. The resulting imbalance between radical and deactivator concentrations would be expected to lead to poor control over polymerization until a sufficient concentration of copper(II) species is established. Polymers produced by SET-LRP in the absence of additional copper(II) typically exhibit broad molecular weight distributions at low conversion (PDI > 2),[17−21] although chain-end fidelity remains high.[33] The use of activated copper(0)[34,35] reduces the initial production of high molecular weight polymer but leads to lower initiator efficiency (84−90%)[34] and chain end fidelity at high conversion (90−95%).[34]

Rapid rates of polymerization are characteristic of SET-LRP. The polymerization of methyl acrylate in DMSO using copper wire, Me_6-TREN ligand, and methyl 2-bromopropionate initiator proceeds to complete conversion in 1 h at 25 °C. Haddleton et al. have shown that use of polar solvents such as DMSO[36] and water[37] in ATRP increases the rate of polymerization. In particular, high rates of polymerization were obtained in DMSO at elevated temperatures due to ligation of copper(II) leading to displacement of the equilibrium toward the active species.[36] The polymerization rate may be varied by altering the amount of solvent, ligand, catalyst surface area, initiator structure, addition of copper(II), or temperature.[18] For example, almost complete conversion of methyl acrylate may be obtained within 15 min by increasing the surface area of the copper catalyst,[38,39] while using nanosized copper powder prepared by disproportionation of Cu(I)Br resulted in ~80% conversion in 5 min.[21]

Polymers produced by SET-LRP using copper wire or micrometer-sized copper powder are reported to have >98% chain end functionality,[17,33] which is required to produce very high molecular weight polymers with low polydispersity, as well as for the production of block copolymers by sequential monomer addition. Use of activated copper wire[34,35] or nanosized (≤100 nm) copper powder[21] results in faster polymerization rates, but lower chain end fidelity at high conversion, with results of ~90% reported by Percec's group[21,34,35] and only 51% reported by the Matyjaszewski group (using nanosized Cu powder),[40] with polymers analyzed by multipeak analysis and peak deconvolution of SEC traces. In the latter report, higher chain end functionality was maintained by slowing down the rate of polymerization through reducing the radical concentration.

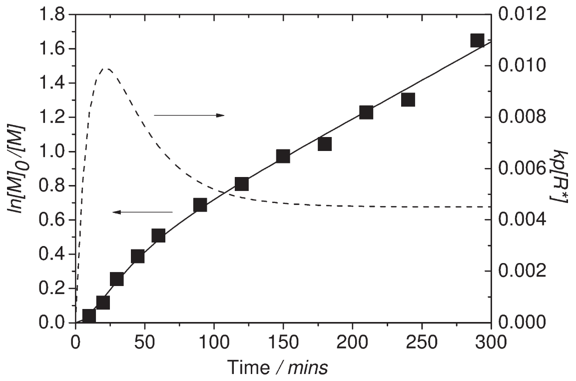


Figure 1. Pseudo-first-order kinetics and associated radical concentration for the polymerization of methyl acrylate carried out at 30 °C using Cu(0)-LRP, showing entry 1. Pseudo-first-order kinetics are fitted using a double-exponential equation.

Copper(0)-mediated living radical polymerization in toluene, a nonpolar solvent, has been investigated by our group[41,42] and others.[19,33,43] Under these conditions, and in other solvents that do not favor disproportionation of Cu(I) such as dichloromethane, acetonitrile, and acetone,[38,44] highly polydisperse polymer is produced in the early part of the reaction. These reactions frequently show a complex kinetic profile, consisting of two approximately linear first-order domains: an initial period of rapid polymerization followed by a slower second stage. It has been suggested[44] that these features are due to the increased contribution of Cu(I) species in the activation process, the difference in reactivity between Cu(0) and Cu(I), and higher levels of bimolecular termination relative to polymerizations in solvents which favor disproportionation of Cu(I).

Simulations under varying conditions,[19] assuming no disproportionation, have predicted a rapid initial increase in conversion, broad initial polydispersities, and high initial molecular weights which approach a controlled evolution of molecular weight with conversion as the reaction proceeds. This is accompanied by an increase in the concentration of Cu(I), which becomes the dominant copper species in solution, in contrast to the simulated behavior in disproportionating solvents such as DMSO, in which the dominant dissolved copper species is predicted to be Cu(0). These simulations, however, assumed high concentrations of dissolved "nascent" Cu(0) (ranging from 0.03 to 30 mM). In reality, "nascent" Cu(0) must be a transient species and will either react with initiator or precipitate from solution shortly after it is formed. Thus, while these simulations have successfully predicted many of the features of SET polymerization, their predictions regarding the nature and concentration of dissolved copper must be treated with caution.

The results above suggest that living radical polymerizations in the presence of Cu(0) under conditions which do not favor disproportionation of Cu(I) combine attributes of SET and ATRP polymerizations,[18,19,33,44] with initiation by both Cu(0) and Cu(I) species taking place. The details remain unclear, however, and there is currently no explanation for the two-stage kinetics observed or what prompts the transition from one stage to another. Additionally, the production of highly polydisperse, poorly controlled polymer in the early stages of the reaction is undesirable. We attempt to address these issues in this report of our investigation of the living radical polymerization of methyl acrylate (MA) in toluene at room temperature in presence of Cu(0) (Cu(0)-LRP).

■ RESULTS AND DISCUSSION

When Cu-mediated polymerization of methyl acrylate is carried out in toluene, a nonpolar solvent, high molecular weight polymer is produced at low conversion (Figures 1 and 2), in line with previous simulated[19] and experimental[33] results. The molecular weight decreases as conversion increases. At ~20% conversion, M_n matches the theoretical values, after which point it increases with conversion in accordance with expectation.

A graph of $-\ln(1 - \text{conversion})$ vs time has gradient equal to $1/[M]\ d[M]/dt$. As the rate of conversion of monomer, $d[M]/dt = k_p[M][R^*]$, where $[R^*]$ is the radical concentration, this graph gives insight into the radical concentration as the reaction progresses. This plot (Figure 1) shows a short induction period in which the radical concentration increases, peaking at ~20 min. During this time high molecular weight poly(methyl acrylate) is produced (Figure 2). After this, the radical concentration decreases, reaching a constant rate as the radical concentration reaches equilibrium in the later stages of the polymerization ($t > 100$ min).

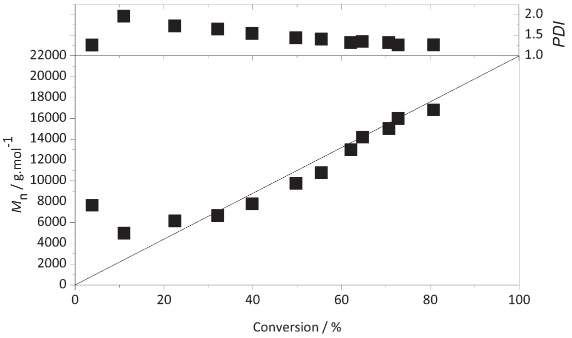


Figure 2. Evolution of molecular weight and polydispersity vs conversion for the polymerization of methyl acrylate carried out at 30 °C using Cu(0)-LRP, showing entry 1.

Similar changes in polymerization rate have been observed in copper(0)-mediated polymerizations of methyl acrylate in acetonitrile,[37,45] methyl ethyl ketone,[44] acetone,[44] dichloromethane,[44] and even in DMSO, in experiments using nanosized copper(0) nanoparticles which had been produced by the disproportionation of copper(I) in a polar solvent.[21] In the last case, however, the unusual kinetics were attributed to consumption of the smallest and most active copper nanoparticles at the beginning of the reaction.

On completion of the polymerization, a small amount of copper powder is visible in the polymerization media. As a stoichiometric amount of ligand and initiator is present, this confirms that less than one equivalent of copper powder is consumed during the polymerization.

The reaction can be divided into four parts as follows:

initiation :

$$\text{Cu} + \text{RBr} \rightarrow \text{CuBr} + \text{R}^* \ (R_i = k_i[\text{RBr}] \sim \text{constant}) \tag{1a}$$

activation :

$$\text{CuBr} + \text{RBr} \rightarrow \text{CuBr}_2 + \text{R}^* \ (R_a = k_a[\text{CuBr}][\text{RBr}] \sim k_a'[\text{CuBr}]) \tag{1b}$$

deactivation :

$$\text{CuBr}_2 + \text{R}^* \rightarrow \text{CuBr} + \text{RBr} \ (R_d = k_d[\text{CuBr}_2][\text{R}^*]) \tag{1c}$$

termination :

$$2\text{R}^* \rightarrow \text{P}_x \ (R_t = k_t[\text{R}^*]^2) \tag{1d}$$

In the presence of copper(0) and an appropriate ligand, it has been shown that an alkyl halide initiator will irreversibly form a copper(I)/ligand complex and generate a radical species (eq 1a).[26−28] CuBr-mediated activation and deactivation of dormant polymer chains are well understood (eqs 1b and 1c).[4,11] Finally, bimolecular combination and disproportionation reactions lead to dead polymer (eq 1d).

In the early stages of the reaction, only initiation, activation, and termination are significant. CuBr and R* are formed at a near-constant rate equal to k_i[RBr]. Because of bimolecular termination,

Table 1. Final Products for the Polymerization of Methyl Acrylate Using Copper(0) in the Presence of Me_6-TREN Undertaken in Toluene[a]

entry	$[M]_0/[I]_0/[L]_0/[Cu]_0/[TEMPO]_0$[b]	time (min)	conv (%)	delay (min)	$M_{n,theo}$[c]	$M_{n,exp}$[d]	PDI[d]	initiator efficiency[e]
1	240/1/1/1/0	150	81		15 800	16 800	1.26	0.94
2	62/1/1/1/0	1080	99		5 250	7 500	1.29	0.70
3	165/1/1/1/0	1080	99		14 100	20 000	1.28	0.71
4	565/1/1/1/0	1080	80		38 850	44 700	1.25	0.87
5	240/1/1/1/0	210	54	10[f]	11 200	16 000	1.21	0.70
6	240/1/1/1/0	240	65	15[f]	13 400	20 860	1.20	0.64
7	240/1/1/1/0	270	67	45[f]	13 800	19 300	1.38	0.72
8	240/1/1/1/0.02	240	65		13 400	13 700	1.28	0.98
9	240/1/1/1/0.05	240	70		14 450	14 370	1.22	1.00
10	240/1/1/1/0.1	300	56		11 700	15 400	1.27	0.76

[a] Polymerizations undertaken at 30 °C, ratio monomer:solvent = 2:1 by volume. [b] All polymerizations were a midgreen color, noticeably lighter in color than an equivalent ATRP polymerization and similar to an analogous polymerization undertaken using SET-LRP. [c] $([MA]_0/[EBP]_0) \times$ conversion. [d] Calculated by SEC. [e] $M_{n,theo}/M_{n,exp}$ [f] Polymerizations undertaken using "monomer last" method with varying delays before monomer addition. In other reactions, the "initiator last" method was used.

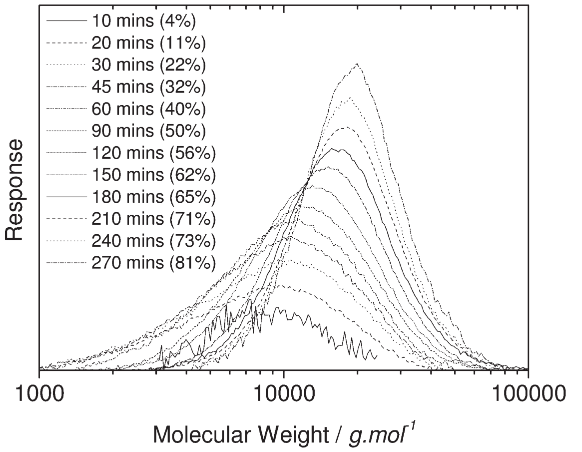


Figure 3. Evolution of molecular weight vs SEC response for the polymerization of methyl acrylate carried out at 30 °C using Cu(0)-LRP, showing entry 1, Table 1.

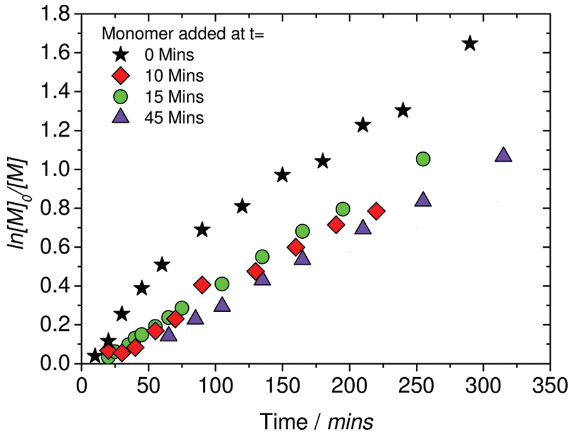


Figure 4. Pseudo-first-order kinetics for the polymerization of methyl acrylate carried out at 30 °C using Cu(0)-LRP. Ratio monomer:solvent = 2:1 by volume. Ratio monomer:initiator:ligand:copper = 240:1:1:1. Monomer added at t = 0, 10, 15, 30, and 45 min.

however, the majority of radicals form dead polymer chains (see SEC traces of low conversion polymer, Figure 3). Thus, [CuBr] quickly becomes large relative to [R*]. Given the nonpolar nature of the solvent, the disproportionation of Cu^I is negligible and $CuBr_2$ is mainly formed by reaction of CuBr with RBr—this reaction is initially much slower than the formation of CuBr, as it is proportional to [CuBr] which is 0 at $t = 0$. As the reaction proceeds, however, the rate of formation of $CuBr_2$ increases, becoming proportional to d[CuBr]/dt. The ratio of [CuBr]:[$CuBr_2$] also falls as [$CuBr_2$] increases, approaching a limiting ratio as R_a approaches R_d:

$$[\mathrm{CuBr}]/[\mathrm{CuBr_2}] \rightarrow k_d[\mathrm{R^*}]_{eq}/k_a[\mathrm{RBr}] \tag{2}$$

where $[\mathrm{R^*}]_{eq}$ is the steady-state radical concentration.

As [$CuBr_2$] increases, deactivation becomes more important. This causes the rate of growth of the radical concentration to slow and eventually reverse. The radical concentration is limited by the CuBr/$CuBr_2$ equilibrium:

$$[\mathrm{R^*}] < k_a[\mathrm{CuBr}][\mathrm{RBr}]/k_d[\mathrm{CuBr_2}] \propto [\mathrm{CuBr}]/[\mathrm{CuBr_2}] \tag{3}$$

Finally, at ~100 min, steady-state conditions are reached, in which d[R*]/dt = 0, and $R_i + R_a = R_d + R_t$.

The conversion data in Figure 1 were fitted to a biexponential model (details in Supporting Information), in which the radical concentration was assumed to vary according to eq 4a, while the conversion followed eq 4b.

$$k_p[\mathrm{R^*}] = Ae^{-k_1 t} - Be^{-k_2 t} + (B - A),$$
$$\text{where } B > A > 0 \text{ and } k_2 > k_1 > 0 \tag{4a}$$

$$\int_0^t k_p[\mathrm{R^*}]\mathrm{d}t = -\ln\left(1-p\right) = A/k_1\left(1-\mathrm{e}^{-k_1 t}\right)$$
$$- B/k_2\left(1-\mathrm{e}^{-k_2 t}\right) + (B-A)t \tag{4b}$$

Using a value of 7.3×10^5 L mol^{-1} min^{-1} for k_p of methyl acrylate at 25 °C,[46] the conversion data indicate a peak radical concentration of 1.4×10^{-8} M, which declines to an equilibrium concentration of 6.2×10^{-9} M ($\approx 10^{-8.2}$ M). The k_t of methyl acrylate has been measured at 40 °C to be $10^{8.4}$ L mol^{-1} s^{-1} and is relatively insensitive to temperature.[47] Hence, at $t > 100$ min, $R_t \approx 10^{8.4-(2\times 8.2)} = 10^{-8}$ mol L^{-1} s^{-1}. If we assume that at this stage of the reaction a steady-state ratio of CuBr:$CuBr_2$ has been reached, such that $R_a = R_d$, then R_i must be equal to $R_t = 10^{-8}$ mol L^{-1} s^{-1}. Assuming negligible change in initiator concentration throughout the reaction (and neglecting chain length effects on all rates), R_i is constant throughout the reaction. The rate of increase of radical concentration at the beginning of the reaction (obtained from differentiation of the first order fit at $t = 0$) is 2×10^{-9} mol L^{-1} s^{-1}, in approximate agreement with the calculated value of R_i (with allowances for the large uncertainties in the values of the rate constants). This rate of termination is consistent with the assumption of negligible change in [RBr]: for a typical initial [RBr] of 10^{-2} M, it would take 10^5 s (30 h) of reaction to produce a 10% reduction in initiator concentration, greatly in excess of the time required for the polymerization (5 h).

Interestingly, the ongoing initiation reaction (1a) results in continuous formation of soluble copper species throughout the reaction. This means that the concentrations of CuBr and $CuBr_2$ never reach an equilibrium value. However, the concentrations of the two species approach a constant ratio, given by eq 2. At this ratio, the rates of activation and deactivation are equal, even though the concentrations of copper salts are steadily increasing. This system is similar to an ICAR polymerization,[15] in which the balance between copper(I) and copper(II) species is maintained by *in situ* generation of carbon-centered radicals. In this case, however, radical generation occurs through reaction of dormant polymer chains with copper metal. The result is a constant radical concentration, as observed in ICAR, while maintaining high α-chain end fidelity due to the use of a single initiating species.

Order of Reagent Addition. SET polymerizations are typically carried out by simultaneous addition of all reagents,[17] or by addition of initiator after degassing the polymerization solution. We hoped that by delaying the addition of monomer until after an equilibrium between copper(I) and -(II) had been achieved, it would be possible to avoid the formation of uncontrolled polymer in the early stages of the reaction. In the absence of monomer, reaction of copper(0) with the alkyl halide initiator forms copper(I), and further reaction of copper(I) with a second alkyl halide species generates copper(II). The radical species formed in this process will terminate bimolecularly by either combination or disproportionation, forming small molecules that can be easily removed on recovery of the final polymer.

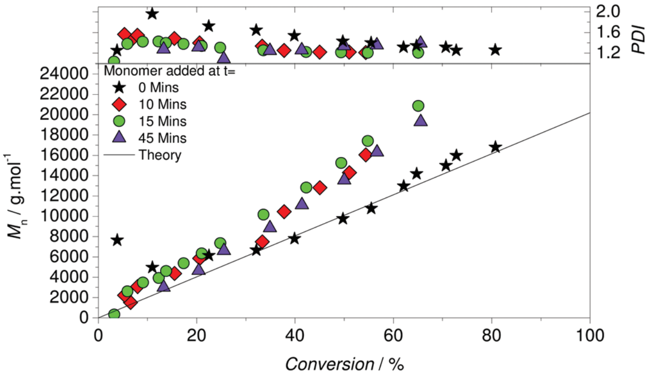
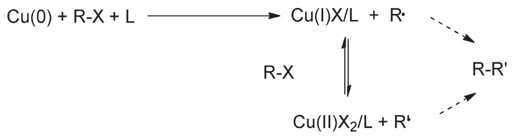


Figure 5. Evolution of molecular weight and polydispersity vs conversion for the polymerization of methyl acrylate carried out at 30 °C using Cu(0)-LRP. Ratio monomer:solvent = 2:1 by volume. Ratio monomer:initiator:ligand:copper = 240:1:1:1. Monomer added at *t* = 0, 10, 15, and 45 min.

Scheme 2. Proposed System Prior to Monomer Addition, Allowing the Formation of Copper(I) and -(II) Prior to Monomer Addition



Therefore, on addition of monomer, control would be obtained immediately as the copper(I) and copper(II) concentrations have reached an ATRP-type equilibrium. By altering the delay before monomer addition, it may also be possible to determine when an equilibrium between copper(I) and -(II) is achieved.

Linear pseudo-first-order kinetics were observed in all "monomer last" reactions (Figure 4), and the rates of polymerization were similar to that of linear stage of the control reaction (monomer added at *t* = 0), suggesting that the Cu(I)/Cu(II) equilibrium is reached from the start of polymerization. Molecular weight evolves linearly with conversion (Figure 5), without producing the uncontrolled, high molecular weight polymer generated in the early stages of previous reactions. Because of reaction of the initiator prior to monomer addition, a small amount of initiator is sacrificed to generate copper(I) and -(II) in solution, leading to a polymer product of molecular weight higher than expected.

This data suggests that an equilibrium is formed between copper(I) and -(II) prior to the addition of monomer, leading to a controlled polymerization (Scheme 2). It is also shown that altering the delay after which the monomer is added has little effect on the rate of polymerization (Figure 4), suggesting an equilibrium between copper(I) and -(II) is formed early in the reaction.

While delaying addition of monomer allows generation of an equilibrium between copper(I) and -(II) for synthesizing polymers of controlled molecular weight and low polydispersity, the approach is not without flaws. Indeed, due to the decreased initiator efficiency—a byproduct of the irreversible bimolecular termination of the alkyl halide in establishing the controlling equilibrium between copper(I) and copper(II)—it is difficult to predict the final molecular weight as the amount of initiator terminated prior to monomer addition is difficult to ascertain.

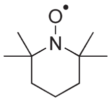


Figure 6. Stable 2,2,6,6-tetramethylpiperidine-1-oxyl nitroxide radical, TEMPO.

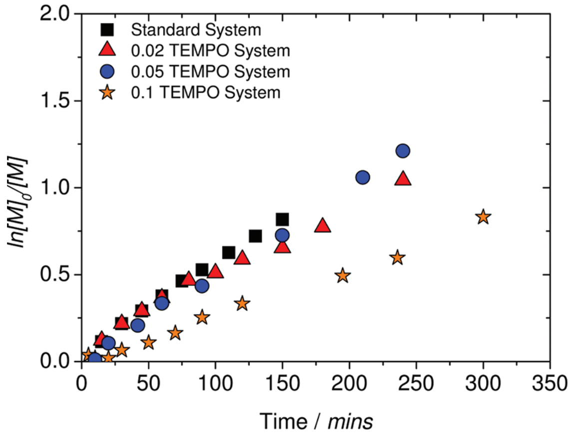


Figure 7. Pseudo-first order kinetics for the polymerization of methyl acrylate carried out at 30 °C using Cu(0)-LRP. Ratio monomer:solvent = 2:1 by volume. Ratio monomer:initiator:ligand:copper:TEMPO = 240:1:1:1:0 and 240:1:1:1:0.02/0.05/0.1. Initiator added last.

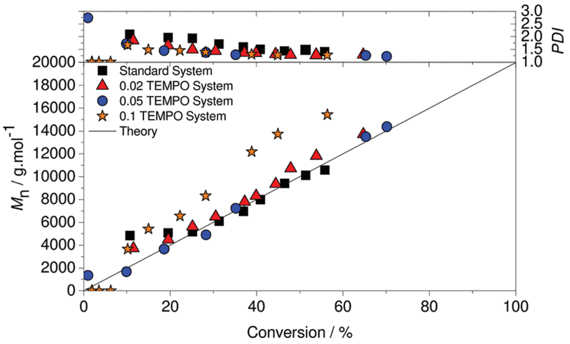


Figure 8. Evolution of molecular weight and polydispersity vs conversion for the polymerization of methyl acrylate carried out at 30 °C using Cu(0)-LRP. Ratio monomer:solvent = 2:1 by volume. Ratio monomer:initiator:ligand:copper:TEMPO = 240:1:1:1:0 and 240:1:1:1:0.02/0.05/0.1. Initiator added last.

Use of a Radical Trap. As it is difficult to reproduce polymerizations by delaying the addition of the monomer, we investigated an alternative method of retarding polymerization until the equilibrium Cu(I)/Cu(II) is reached.

A potential method is the use of a radical trap, such as the persistent radical species 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, Figure 6) to trap radicals produced at the start of the reaction. Previously, addition of a radical trap such as TEMPO has been used to study the early stages of polymerization[40,48,49] or, in the absence of monomer, to prepare alkoxyamine initiators for nitroxide-mediated polymerization.[50−52] While TEMPO is used as a reversible capping agent at elevated temperatures, at the low temperatures used in this study TEMPO binds irreversibly to carbon-centered propagating radicals.[53,54] The oxidation of copper(0) in the presence of an alkyl halide and an appropriate ligand leads to a propagating

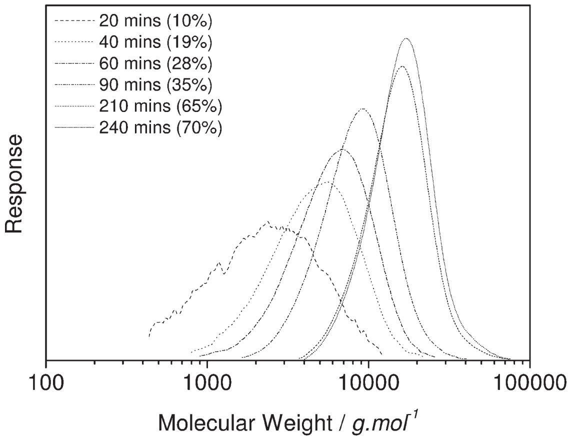


Figure 9. Molecular weight evolution of polymerization of methyl acrylate carried out at 30 °C using Cu(0)-LRP (with TEMPO). Ratio monomer:solvent = 2:1 by volume. Ratio monomer:initiator:ligand:copper:TEMPO = 240:1:1:1:0.05. Initiator added last.

radical and a copper(I) species. By irreversibly capturing radical species formed early in the reaction through addition to TEMPO, propagation is inhibited, while the copper(I)/copper(II) equilibrium is established. The amount of TEMPO can be tuned to capture all early radicals formed, until enough copper(II) is present in the system to act as radical deactivator and control the polymerization. The presence of a radical trap in the system has little effect on the polymerization, apart from consuming initiator, thus leading to the generation of polymeric chains of higher than expected degree of polymerization.

Even a small amount of TEMPO (2% with respect to $[EBP]_0$) reduces the formation of high molecular weight species at the beginning of the reaction (Figure 8) and causes a slight decrease in rate of polymerization compared to the parent system in which TEMPO is absent (Figure 7). This may be attributed to TEMPO trapping radicals formed in the early stages of polymerization from the oxidation of copper(0) to copper(I). By eliminating the uncontrolled polymerization generated by such radicals, TEMPO slows down the overall rate of polymerization. However, the evolution of molecular weight with conversion is only slightly above theory, indicating that this new target molecular weight ($= (1/0.98) \times [\text{monomer}]_0 \times \text{FW(MA)}$, where $[\text{monomer}]_0$ is the concentration in monomer at $t = 0$ and FW(MA) is the molecular weight of MA) is only marginally higher than that of the parent system as the TEMPO only captures a maximum of 2% of initiator species.

On addition of an intermediate amount of TEMPO (5% with respect to $[EBP]_0$), a slight decrease in rate is observed when compared to the parent system in which TEMPO is absent. With this amount of TEMPO present, polymerization is controlled over the entire molecular weight range, and the initial high molecular weight polymer is effectively eliminated (see molecular weight evolution with conversion in Figure 8 and molecular weight distributions during reaction in Figure 9). This intermediate amount of TEMPO appears to optimize the amount of radicals captured by the nitroxide and the amount of unreacted initiator species remaining in order to generate a stable equilibrium between copper(I) and -(II) early in the polymerization. A comparison of molecular weight distributions generated by the parent system (Figure 3) and the system containing 5% TEMPO with respect to [initiator] (Figure 8) shows that in the presence of TEMPO controlled molecular species are generated even at low conversions (10 min, 1% conversion).

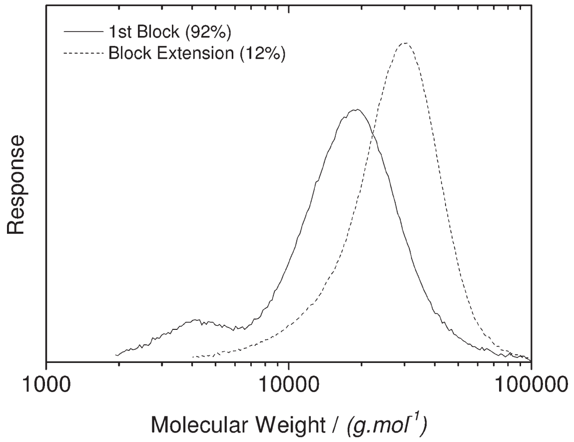


Figure 10. Chain extension of poly(methyl acrylate) by ATRP in the absence of TEMPO. First block synthesized using Cu(0)-LRP (without TEMPO). Ratio monomer:solvent = 2:1 by volume. Ratio monomer:initiator:ligand:copper:TEMPO = 240:1:1:1:0. Initiator added last. Chain extension carried out by ATRP. Ratio monomer:solvent = 2:1 by volume. Ratio monomer:PMA-Br:PMDETA:CuBr = 1000:1:1:1.

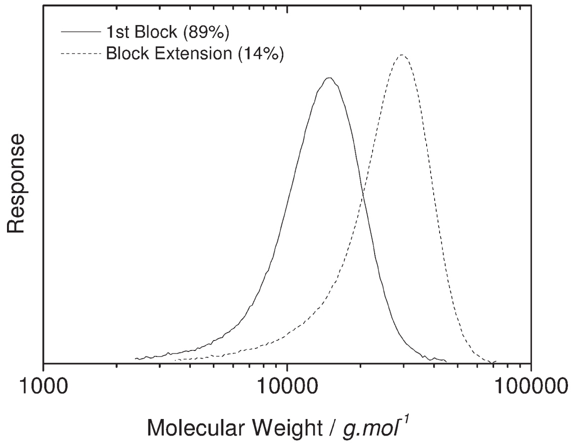
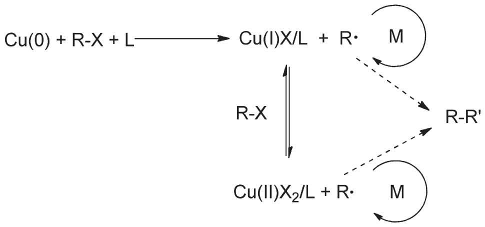


Figure 11. Chain extension of poly(methyl acrylate) by ATRP in the absence of TEMPO. First block synthesized using Cu-LRP (with TEMPO). Ratio monomer:solvent = 2:1 by volume. Ratio monomer:initiator:ligand:copper:TEMPO = 240:1:1:1:0.05. Initiator added last. Chain extension carried out by ATRP. Ratio monomer:solvent = 2:1 by volume. Ratio monomer:PMA-Br:PMDETA:CuBr = 1000:1:1:1.

Further increasing the amount of TEMPO (10% with respect to $[EBP]_0$) retards the rate of polymerization after a short inhibition period (Figure 7). Polymers of higher molecular weight than expected are generated (Figure 8), indicating the consumption of an appreciable fraction of the initiator-generated radicals. Similar rates of polymerization and evolution of molecular weight with conversion (ca. 15 000 g mol^{-1} at 60% conversion in ca. 5 h) were observed in the polymerizations in which monomer was added last (Figures 4 and 5). The polymerization kinetics exhibit a linear pseudo-first-order relationship after a short induction period, whereas molecular weight vs conversion data show the molecular weight to be higher than theory. This suggests that the TEMPO scavenges enough radicals generated from the reaction of alkyl halides with copper to allow the formation of copper(I) and -(II) so that control is gained as soon as polymerization starts.

Scheme 3. Proposed Mechanism of Cu(0)-LRP



Determination of Livingness of the System. In simulated SET-LRP polymerizations of methyl acrylate in nonpolar solvents performed by Monteiro et al., approximately half of the chains produced were "dead" at conversions above 50%.[19] In order to determine the livingness of our system, block extensions of poly(methyl acrylate) produced using the system containing both 0 and 5% TEMPO with respect to $[EBP]_0$, respectively, were carried out in the presence of a large excess of methyl acrylate using conventional ATRP mediated by Cu(I)Br and PMDETA. The clear shift in molecular weight in both cases demonstrates that it is possible to chain extend both systems with high efficiency (Figures 10 and 11). In the absence of TEMPO, it was determined by peak deconvolution that ∼94% of chains were living, whereas in the presence of 5% TEMPO with respect to $[EBP]_0$, 99% of chains were shown to be living. It is worth noting that, prior to purification, the polymerization undertaken in the absence of TEMPO exhibits a low-MW shoulder due to initial uncontrolled polymerization generating dead chains, as seen in Figure 3 and even more clearly in Figure 10.

Proposed Mechanism. From these experiments, we propose the following mechanism (Scheme 3). Initially, copper(0) is oxidized in the presence of a ligand and a brominated initiator to form a copper(I)/ligand complex and a carbon-centered radical. The lack of deactivating copper(II) at this point causes the polymerization to occur both rapidly and in an uncontrolled manner. This copper(I) species may then be further oxidized to a copper(II)/ligand complex by further reaction with a bromine-capped species (either initiator or polymer chain), producing another carbon-centered radical. As copper(II) is generated and the uncontrolled propagating chains terminate, control over polymerization is established, following an ATRP-type equilibrium between the dormant chain/copper(I) species and active chain/copper(II) species. The rate of comproportionation of copper(0) in toluene is expected to be negligible since it has been shown that comproportionation is a relatively slow process even in polar solvents such as acetonitrile, DMF, and DMSO.[40] As in all radical polymerization systems, termination reactions still occur, although in small amount. This means a high proportion of chains are end-capped by a bromine atom, and thus it is possible to chain extend the polymers with high efficiency.

CONCLUSIONS

We have demonstrated that it is possible to control the polymerization of methyl acrylate, using elemental copper in the presence of a conventional ATRP ligand and initiator, at room temperature, in a nonpolar solvent. While uncontrolled polymerization occurs early in the reaction, this may be prevented by delaying the addition of monomer until after the initial equilibrium between copper(I) and -(II) has been established. Alternatively, the same effect may be obtained by addition of a small amount of TEMPO, a radical scavenger, to the system. TEMPO irreversibly captures the radicals formed initially, and prior to their propagation, while allowing the generation of copper(I). Copper(I) reacts with the alkyl halide initiator to generate active species and copper(II), leading to the establishment of the equilibrium between copper(I) and -(II).

The system provides high chain end fidelity, as the polymers generated can be chain extended with 99% efficiency. This system displays many similarities to ICAR, with the reaction between RBr and Cu playing the role of the radical initiator. Use of copper(0) also has the advantage that only a very small amount of catalyst is utilized to mediate polymerization. The copper catalyst is easily removed by filtration.

EXPERIMENTAL SECTION

Materials. Methyl acrylate (99%) was purchased from Sigma-Aldrich and was passed over HQ/MeHQ removal packing before use to remove extant inhibitor. Tris(2-dimethylaminoethyl)amine (Me_6-TREN) was synthesized using the method outlined by Britovsek et al.[55] Ethyl 2-bromopropionate (EBP, Fluka) was used as purchased. All other chemicals were purchased from Sigma-Aldrich and used without further purification, unless otherwise stated. Molecular weight distributions were obtained using gel permeation chromatography (GPC) at 40 °C with a system equipped with a guard column and two PLGel Mixed-B columns (Polymer Laboratories) with a Shimadzu RID-10A differential refractive-index detector. Tetrahydrofuran (THF) was used as the eluent with a flow rate of 1 mL min^{-1}, with toluene used as a flow rate marker. The system was calibrated with polystyrene standards ranging from 162 to 1 670 000 g mol^{-1} using Mark—Houwink—Sakurada parameters or $k = 19.7$ and $\alpha = 0.66$. ^1H NMR spectra were recorded on a Bruker Avance 300 MHz instrument for solutions in $CDCl_3$ containing 0.03% tetramethylsilane (TMS).

Polymerizations. Polymerizations were undertaken in a Schlenk tube into which various reactants were weighed into using one of two methods as described below. In each case, a green solution was produced, although these were noticeably lighter in color than an equivalent ATRP reaction and similar to an equivalent SET-LRP polymerization.

Typical Reaction Conditions, Polymerization by Adding Initiator Last. Methyl acrylate (3.00 g, 35 mmol), toluene (1.36 g, 17.5 mmol), Me_6-TREN (0.036 g, 0.1 mmol), and copper powder (0.09 g, 0.1 mmol) were weighed into a Schlenk flask and sealed before being subjected to five cycles of freeze—pump—thaw degassing. For polymerizations undertaken using TEMPO, a volumetric solution of TEMPO in toluene was prepared before weighing into the Schlenk tube. Once backfilled with nitrogen, the reaction vessel was placed in a thermostated water bath at 30 °C for 30 min in order to equilibrate before addition of ethyl 2-bromopropionate (0.026 g, 0.1 mmol). Samples were taken at various intervals for analysis by ^1H NMR and GPC to determine conversions and molecular weights, respectively.

Polymerization by Adding Monomer Last. Initiator, copper, ligand, and solvent (amounts as for Typical Reaction Conditions above) (see above) were weighed into one Schlenk tube and sealed before being subjected to five cycles of freeze—pump—thaw degassing each. The Schlenk tube containing the initiator, copper, ligand, and solvent was then placed in a thermostated water bath at 30 °C for various intervals before addition of the degassed monomer by cannulation. Samples were taken at various intervals under nitrogen and analyzed using ^1H NMR and gel permeation chromatography to determine conversions and molecular weights, respectively.

Chain Extension. The first block was synthesized following the procedure described above. The obtained poly(methyl acrylate) macroinitiator was analyzed prior to isolation by precipitation into cold hexane and subjected to centrifugation before drying under vacuum.

The macromonomer was then dissolved in the required amount of monomer. Copper(I) bromide was subjected to an inert atmosphere before addition of previously degassed solvent/ligand solution and cannulated into the macroinitiator/monomer solution before being subjected to five cycles of freeze−pump−thaw degassing. The Schlenk tube was then placed into a thermostated water bath at 75 °C for 19 h. The obtained polymer was subjected to analysis using gravimetry and gel permeation chromatography to determine conversion and molecular weight, respectively. To calculate the percentage of living chains present, the logarithm of the molecular weight was fitted to a Gaussian. The values obtained for this fit were used to fit the residual macroinitiator. The block was then fitted and integration of the areas of the deconvoluted peaks were compared.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Fit of conversion data in Figure 1 to a biexponential model. This material is available free of charge via the Internet at http://pubs.acs.org.

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