Copper(II)/Tertiary Amine Synergy in Photoinduced Living Radical Polymerization: Accelerated Synthesis of ω-Functional and α,ω-Heterofunctional Poly(acrylates)

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S *Supporting Information*

ABSTRACT: Photoinduced living radical polymerization of acrylates, in the *absence* of conventional photoinitiators or dye sensitizers, has been realized in "daylight'"and is enhanced upon irradiation with UV radiation ($\lambda_{max} \approx 360$ nm). In the presence of low concentrations of copper(II) bromide and an aliphatic tertiary amine ligand (Me_6-Tren; Tren = tris(2-aminoethyl)amine), near-quantitative monomer conversion (>95%) is obtained within 80 min, yielding poly(acrylates) with dispersities as low as 1.05 and excellent end group fidelity (>99%). The versatility of the technique is demonstrated by polymerization of methyl acrylate to a range of chain lengths (DP_n = 25−800) and a number of (meth)acrylate monomers, including macromonomer poly(ethylene glycol) methyl ether acrylate ($PEGA_{480}$), *tert*-butyl acrylate, and methyl methacrylate, as well as styrene. Moreover, hydroxyl- and *vic*-diol-functional initiators are

compatible with the polymerization conditions, forming α,ω-heterofunctional poly(acrylates) with unparalleled efficiency and control. The control retained during polymerization is confirmed by MALDI-ToF-MS and exemplified by in situ chain extension upon sequential monomer addition, furnishing higher molecular weight polymers with an observed reduction in dispersity (Đ = 1.03). Similarly, efficient one-pot diblock copolymerization by sequential addition of ethylene glycol methyl ether acrylate and $PEGA_{480}$ to a poly(methyl acrylate) macroinitiator without prior workup or purification is also reported. Minimal polymerization in the absence of light confers temporal control and alludes to potential application at one of the frontiers of materials chemistry whereby precise spatiotemporal "on/off" control and resolution is desirable.
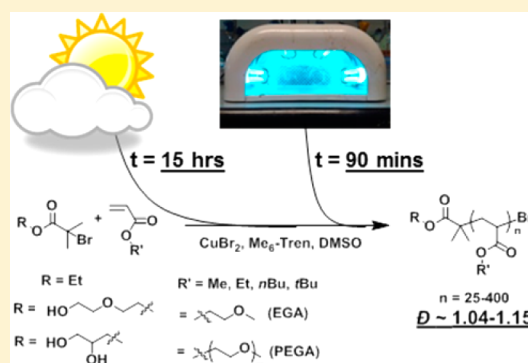
■ INTRODUCTION

Controlled/living radical polymerization (CLRP)[1−7] has made a significant impact in polymer science due to the ability to regulate molecular weight, dispersity, polymer architecture, and end group functionality. Among the numerous techniques, transition-metal-mediated approaches such as atom transfer radical polymerization (ATRP)[3,4,8] and single-electron transfer living radical polymerization (SET-LRP)[6,7,9] have made significant contributions. The current state-of-the-art exploits methodology focused on the manipulation of the activation−deactivation equilibrium between active (P_n·) and dormant (P_n-X) species to maximize control during polymerization. Simply, this relies on selection of an appropriate Cu−ligand complex to optimize the overall rate of polymerization and manage the concentration of deactivating species which can accumulate through either the persistent radical effect (PRE)[10,11] or disproportionation[12−17] mechanisms. Currently, this allows rapid access to quantitative monomer conversions, yielding extremely low dispersities (Đ < 1.10), relatively high molecular

weights, retention of end group fidelity, and a wide variety of polymer compositions and architectures (blocks, stars, grafts, etc. and combinations thereof).[18−23] Moreover, the scope of monomer and solvent choice is ever-expanding, promising novel polymer synthesis in increasingly relevant and complex media for a wider variety of applications.[24−26]

Recently, considerable interest has been directed toward controlling the activation−deactivation equilibrium using various stimuli,[27] including photochemical,[28,29] pressure,[30,31] and electrochemical.[32] In an ideal synthesis such stimuli should result in lower activation energies for crucial steps such as initiation and repeated activations, allowing in situ generation of more active catalysts and thus faster CLRP under milder conditions. Many of these requirements are imparted by photomediated polymerization with potential additional advantages over traditional thermal processes, including faster

rates of polymerization and spatial control over polymerization. However, traditional photochemical processes lack the control desired to convey compositional and architectural design,[33,34] a limitation that has been challenged in recent literature.

Hawker and co-workers recently showed that CLRP of methacrylates can be efficiently controlled using visible light.[35] Mechanistically, an activation–deactivation equilibrium was identified between an excited Ir[III] photoredox catalytic complex (Ir[III]*) and an Ir[IV] complex which act as the activator and deactivator, respectively. This was achieved by use of highly absorbing ligands in the photoactive complex *fac*-[Ir(ppy)$_3$] (ppy = 2-pyridylphenyl) (Figure 1). Under irradiation, polymer-
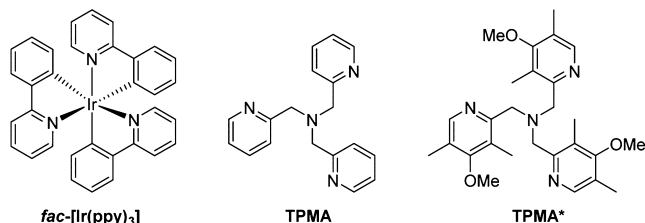

Figure 1. Ir complex[35] and pyridine-based ligands[41] reported to promote photomediated CLRP.

ization of methyl methacrylate (MMA) was shown to proceed in a well-controlled manner up to 60% conversion ($Đ \approx 1.19$–1.25), while reversible chain termination occurred upon removal of light, demonstrating a high degree of temporal control. The reversible termination was exemplified by block copolymerization of the poly(methyl methacrylate) (PMMA) macroinitiator with benzyl methacrylate (BnMA), while spatiotemporal control has recently been elaborated using surface-initiated CLRP in the presence of photomasks and density filters.[36]

Traditional Cu-mediated polymerization has also been shown to benefit from photoirradiation. Yagci and co-workers have developed Cu-mediated, photoinduced controlled radical polymerization (PCRP) systems both in the presence and in the absence of conventional photoinitiators or photosensitizers.[34,37−40] In the absence of photosensitizers it has been suggested that light induces polymerization by *direct* reduction of Cu[II](L)X$_2$ to Cu[I](L)X.[34,37,39] The bulk polymerization of MMA was performed using a Cu[II](L)X$_2$ complex (L = N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA)) as a precatalyst. Upon irradiation, reduction of Cu[II](L)X$_2$ is proposed to proceed via homolysis, furnishing Cu[I](L)X and X[•]. The halide radical can either reoxidize the Cu[I](L)X species or is quenched, allowing the Cu[I](L)X to activate a dormant chain. Interestingly, in the presence of MeOH as a cosolvent, polymerization was aided by improved dissolution of the Cu[II](L)X$_2$ complex. Moreover, the X[•] formed was shown to abstract H[•] from MeOH, forming HX and hydroxymethyl radicals which could act as reducing agents for the reduction of Cu[II](L)X$_2$ to Cu[I](L)X.

Matyjaszewski et al. recently reported visible/sunlight photoinduced ATRP using Cu[II](TPMA)Br$_2$ with subtle differences from the mechanism suggested by Yagci. They propose photoreduction of Cu[II](TPMA)Br$_2$ to Cu[I](TPMA)Br by ligand to metal charge transfer in the photoexcited state.[41] Polymerization was then initiated by either Cu[I](TPMA)Br or a bromine radical, both proposed products of the photoreduction of the Cu[II] complex, which was said to imply a hybrid mechanism somewhere between initiators for continuous

activator regeneration ATRP (ICAR-ATRP)[42] and activators regenerated by electron transfer ATRP (ARGET-ATRP).[43] A variety of wavelengths were investigated, and well-controlled polymerizations were obtained using a modified TPMA ligand (tris((4-methoxy-3,5-dimethylpyridin-2-yl)amine), TPMA*) (Figure 1) in sunlight and at λ_{max} = 392 nm. Reaction times were generally between 12 and 32 h, and optimum results were obtained in sunlight. Similar observations were made during the photomediated polymerization of MMA at λ_{max} > 350 nm. Initiation from 2-bromopropionitrile in the presence of Cu[II](TPMA)Br$_2$ or Cu[II](PMDETA)Br$_2$ resulted in well-controlled polymerization with conversions reaching 80%.[44] Temporal control[37,41,44] by consecutive light and dark reactions has also been reported and readily translates into spatial resolution in light-induced surface-initiated ATRP (SI-ATRP).[45]

Herein we present a polymerization protocol exploiting photoactivation in the presence of a cupric precursor (Cu[II](Me$_6$-Tren)Br$_2$; Tren = tris(2-aminoethyl)amine) and an excess (with respect to Cu[II](Me$_6$-Tren)Br$_2$) of *aliphatic* tertiary amine Me$_6$-Tren. For the first time, under UV irradiation ($\lambda_{max} \approx 360$ nm) we report near-quantitative conversions for a range of targeted molecular weights (DP$_n$ = 25−800). Moreover, the breadth in scope of photoinduced polymerization is also recognized employing a variety of acrylate monomers as well as functional initiators, furnishing α,ω-heterofunctional poly-(acrylates). The resulting polymers are characterized by their narrow dispersities ($Đ$) and end group fidelity as exemplified by chain extension and block copolymerization. Significantly, temporal control is also observed during intermittent light and dark reactions. We also offer insight into the possible mechanism through a series of control experiments, with a view to gaining some clarity over the overall mechanism asserted in this photoactivated polymerization in the presence of traditional Cu complexes.

■ RESULTS AND DISCUSSION

Photoactivated Polymerization of Methyl Acrylate in Visible Light. Photoinduced controlled radical polymerization (PCRP) was fortuitously observed during investigation of Cu-mediated living radical polymerization of methyl acrylate (MA) in a flow system,[46] whereby the mixture in a Pyrex syringe in the absence of copper(0) but in the presence of copper(II) gave slow but effective polymerization. Deoxygenated mixtures containing [MA]:[EBiB]:[Me$_6$-Tren]:[Cu[II]Br$_2$] = 50:1:0.12:0.02 in DMSO (50%, v/v) were found to yield well-defined PMA ($M_n \approx 4500$ g·mol^{-1}, $Đ \approx 1.05$) at quantitative conversion upon standing in a fume hood for a period of 1 day in the absence of any known activators or apparent reducing agents. Kinetic investigations revealed quantitative conversion (~99%) within 15 h following an initial induction period of ~3 h (Figure 2a). Following this induction period, a linear dependence of $\ln([M]_0/[M]_t)$ on time demonstrated the rate of the polymerization to be first order in monomer concentration (Figure 2a), while M_n increased linearly with time and $Đ$ values remained narrow (≤ 1.10) throughout the reaction (Figure 2b). Additionally, both MALDI-ToF-MS and ^{1}H NMR (Figure S2, Supporting Information) spectroscopic analyses confirmed the living characteristics, with both techniques illustrating agreement between $M_{n,th}$ and $M_{n,exptl}$ and excellent end group fidelity (Figure 2c,d).
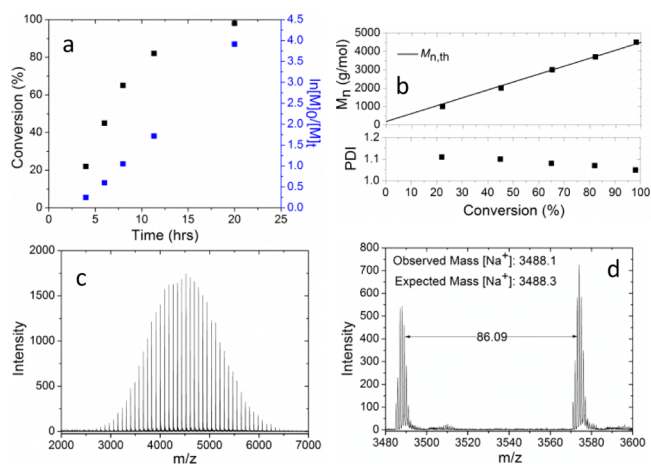
Figure 2. Kinetic (a) and molecular weight/dispersity (b) data of the polymerization of MA in sunlight. MALDI-ToF-MS (c, d) confirms high end group fidelity.

Initially we were perplexed by the degree of control associated with these polymerizations in the absence of established Cu-based activators such as Cu(0) or Cu(I). Previous research has described excess Me_6-Tren adopting the role of a reducing agent for the reduction of $Cu^{II}(L)X_2$ to $Cu^I(L)X$ during Cu(I)-mediated polymerization, as evidenced by a reduction of the intensity of the UV−vis spectrum of $Cu^{II}(Me_6\text{-}Tren)Br_2$.[47−49] However, there is limited evidence to support this claim, and our own experiments showed that this decrease in the UV−vis absorption from the d^9 d−d transition in Cu(II) in DMSO is explained by the Cu(II) complex forming deep blue microcrystals on the side of the cuvette, thus reducing the concentration in solution, and not by a reduction to colorless d^{10} Cu(I). A change of solvent to 2-propanol, which fully solubilizes this complex, proved to show no loss in absorption and thus no reduction of $Cu^{II}(Me_6\text{-}Tren)Br_2$.[50]

We decided to repeat the polymerization in a homemade "black box" to eliminate this potential reduction by excess Me_6-Tren, present under the chosen reaction conditions. No polymerization was observed over a period of 48 h, adding further evidence to the inability of Me_6-Tren to act as a reducing agent of $Cu^{II}(Me_6\text{-}Tren)Br_2$ to $Cu^I(Me_6\text{-}Tren)Br$, which might have acted as a source of activation if this report was reproducible. The lack of polymerization also suggested that the presence of light was essential for polymerization. We envisaged that light could be generating radicals via either C−X bond homolysis or autoinitiation of the alkyl halide initiator (EBiB), with control invoked by the presence of the $Cu^{II}(Me_6\text{-}Tren)Br_2$ to reversibly terminate the propagating chains. This process would generate $Cu^I(Me_6\text{-}Tren)Br$, which could either activate a dormant chain or disproportionate (to Cu(0) and $Cu^{II}(Me_6\text{-}Tren)Br_2$), depending on the reaction conditions. Alternatively, the light could be directly reducing $Cu^{II}(Me_6\text{-}Tren)Br_2$ to $Cu^I(Me_6\text{-}Tren)Br$ as eloquently described by Yagci et al. in related complexes.[34,37,39] A series of control experiments were performed to probe these hypotheses.

Photoactivated Polymerization of MA in UV Light ($\lambda_{max} \approx 360$ nm). The effect of wavelength was investigated by varying the light source to cover the UV−vis spectrum (Table S1, Supporting Information). Optimal results were obtained from polymerization under a UV lamp with $\lambda_{max} \approx 360$ nm. Applying the previous conditions ([MA]:[EBiB]:[Me_6-Tren]: [$Cu^{II}Br_2$] = 50:1:0.12:0.02 in DMSO (50%, v/v)), PMA was

prepared in high conversion (96%) within 80 min including an initial induction period of 15 min (Figure 3a). This represents a
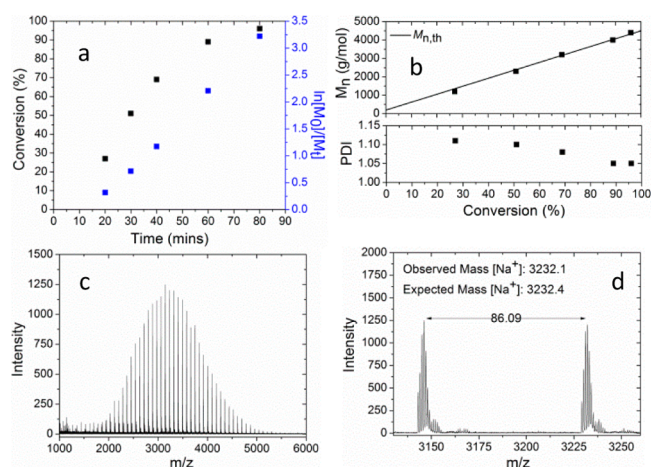

Figure 3. Kinetic (a) and molecular weight/dispersity (b) data of the polymerization of MA under UV ($\lambda_{max} \approx 360$ nm) irradiation. MALDI-ToF-MS (c, d) confirms high end group fidelity.

remarkable acceleration in the rate of polymerization relative to that of the daylight reaction. Polymerization control was retained as indicated by low Đ values, which decreased as the reaction progressed (from 1.11 to 1.05, Figure 3b). Kinetic analysis revealed a linear increase of $\ln([M]_0/[M]_t)$ vs time as well as linear evolution of M_n with monomer conversion. Correlation between $M_{n,th}$ and $M_{n,exptl}$ values further confirms the controlled/living character of the polymerization.

Initially, prevailing thermal effects from the UV bulbs had to be investigated. The temperature of the reaction under UV irradiation was monitored with a thermocouple and found to fluctuate between 50 and 55 °C. To determine the effect of temperature, we repeated polymerizations both under UV irradiation in a jacketed cell, with a steady flow of cold water to reduce the internal temperature, and under purely thermal conditions at 55 °C (no UV irradiation). After identical reaction times (80 min), the pure thermal reaction yielded no polymer, whereas the jacketed reaction, under UV irradiation, gave results nearly identical to those of the uncooled system ($\lambda_{max} \approx 360$ nm).

Consequently, the remaining control experiments were performed under UV irradiation at $\lambda_{max} \approx 360$ nm without water cooling ($T \approx 50$−55 °C). Polymerizations were systematically repeated in the absence of a single reagent to further elucidate key components in the polymerization (Table 1). The most significant finding from these control experiments was that radicals are likely formed via a number of different mechanisms under UV exposure (Table 1, entries 1−7). Polymerization of MA was possible under a variety of conditions, proceeding in an uncontrolled manner (Đ = 1.76−2.20) with variable conversions (10−61%). Considered in the context of those experiments which yielded no polymer, it is evident that radicals can be produced separately by both uncomplexed Me_6-Tren (free ligand) and EBiB under UV irradiation, even in the absence of copper compounds, and that MA autoinitiation is also possible.

The [$Cu^{II}Br$]:[Me_6-Tren] ratio was subsequently investigated (Table 1, entries 8−11). The initial reaction conditions ([MA]:[EBiB]:[Me_6-Tren]:[$Cu^{II}Br_2$] = 50:1:0.12:0.02) employed [$Cu^{II}Br_2$]:[Me_6-Tren] = 1:6. This could be reduced to

Table 1. Series of Control Experiments Investigating Photomediated Polymerization in the Presence of UV Light ($\lambda_{max} \approx 360$ nm)

entry	$[M]:[I]:[Cu^{II}]:[L]^{a,b}$	conversn[b] at 90 min (%)	$M_n{}^c$ (g·mol^{-1})	Đ
1	50:−:0.02:0.12	12	12600	1.65
2	50:1:−:0.12	61	30000	1.76
3	50:1:0.02:−			
4	50:1:−:−	38	88000	2.2
5	50:−:0.02:−			
6	50:−:−:0.12	45	24100	1.79
7[d]	50:−:−:−			
8	50:1:0.02:0.02			
9	50:1:0.02:0.04	90	4400	1.07
10	50:1:0.02:0.06	95	5000	1.07
11	50:1:0.02:0.12	95	4500	1.05

^{a}L = Me$_6$-Tren. ^{b}DMSO (50%, v/v) used as solvent. ^{b}Determined from ^{1}H NMR. ^{c}Determined from CHCl$_3$ SEC analysis. ^{d}Not reproducible when repeated in triplicate, 0−12% conversion obtained.

Figure 4. SEC analysis of PMA with various DP$_n$ prepared by photomediated polymerization in the presence of UV light ($\lambda_{max} \approx 360$ nm).

1:3 and 1:2, respectively, with retention of both high conversion (90−95%) and narrow dispersities (Đ = 1.07). However, when the relative stoichiometries were balanced ($[Cu^{II}Br_2]:[Me_6\text{-Tren}] = 1:1$), no polymerization was observed. At this stoichiometry all of the ligand should be complexed to Cu^{II}Br$_2$, forming Cu^{II}(Me$_6$-Tren)Br$_2$; thus, the lack of polymerization implicates excess Me$_6$-Tren as being essential for photoactivation.

While maintaining a $[Cu^{II}Br_2]:[Me_6\text{-Tren}]$ ratio of 1:6, the effect of the initial $[Cu^{II}Br_2]$ and $[Me_6\text{-Tren}]$ loadings relative to initiator was investigated. Increasing the ratio ($[EBiB]:[Cu^{II}Br_2]:[Me_6\text{-Tren}] = 1:0.05:0.30$) resulted in a slight decrease in monomer conversion (85%) but preservation of polymerization control over the 90 min irradiation period. It was possible to decrease the $[I]:[Cu^{II}Br_2]:[Me_6\text{-Tren}]$ ratio to 1:0.005:0.03 without significant loss of control (Đ = 1.12) or reaction rate (Table S2, Supporting Information). However, further reduction in $[Cu^{II}Br_2]$ to 0.001 relative to initiator was shown to compromise the polymerization control (87%, Đ = 1.42).

Investigation into the Scope of the Photoactivated Polymerization. To probe the potential of this technique in maintaining control for higher molecular weights, a range of polymerizations were conducted, targeting degrees of polymerization (DP$_n$) from 25 to 800 (Figure 4; also see Table S3, Supporting Information). The ratio $[Cu^{II}Br_2]:[Me_6\text{-Tren}] = 1:6$ was maintained for each polymerization, resulting in high conversions (≥93%) within 90 min, with good correlation observed between $M_{n,exptl}$ and $M_{n,th}$, and dispersities remained very low (Đ ≈ 1.05, Table S3). When the chain length was extended to DP$_n$ = 800, although polymerization control was seemingly retained (Đ = 1.12), $M_{n,exptl}$ (46000 g·mol^{-1}) and $M_{n,th}$ (63500 g·mol^{-1}) were found to deviate considerably (Figure S4, Supporting Information).

The scope of the reaction was extended to a number of acrylate monomers, including ethyl acrylate (EA), n-butyl acrylate (nBA), protected/functional acrylates, tert-butyl acrylate (tBA), ethylene glycol acrylate (EGA), and poly-(ethylene glycol) acrylate ($M_n \approx 480$ g·mol^{-1}, PEGA$_{480}$).

Polymerization of the acrylates reached high conversion (92−97%) and exhibited narrow dispersities (Đ ≈ 1.07−1.16, Table 2). The light-induced polymerization of nBA in DMSO
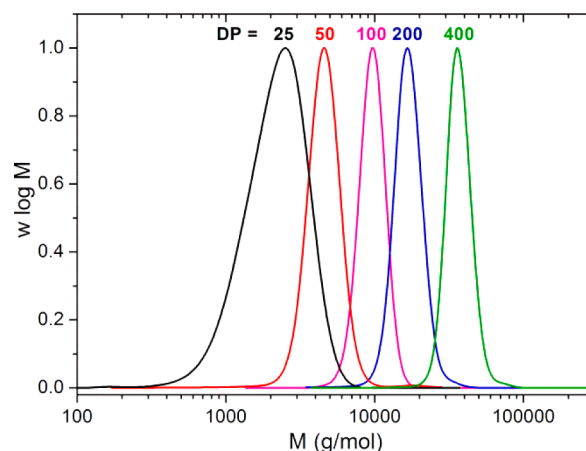
(Table 2, entry 2) was found to proceed with phase separation as previously observed for a thermal process.[51,52] Conversely, the polymerization of tBA in DMSO was problematic, reproducibly furnishing no polymer within the 90 min reaction time. The choice of solvent in conventional Cu-mediated polymerization is crucial when using increasingly hydrophobic monomers. A phase separation phenomenon has been reported during the Cu(0)-mediated polymerization of hydrophobic acrylates.[51,52] In the case of tert-butyl acrylate, an adverse effect on the polymerization control, manifest as a broader dispersity relative to that of related butyl isomers, was reported when DMSO was used as the solvent. In the case of the photoactivated reaction, this was rectified by performing the polymerization in DMF whereby high conversion (96%) and good control (Đ = 1.10) were attained (Table 2, entry 3). On expanding the technique to less activated monomers, MMA and styrene (Sty) conversions were limited (78% and 40%, respectively) with an observable reduction in control (Đ ≈ 1.29−1.40, respectively). The lower conversions are consistent with relative rates of propagation (k_p) with acrylate > methacrylate > styrene. Furthermore, in the few reports of the polymerization of styrene at ambient temperature, DMSO has been highlighted as a poor solvent leading to a loss of control during the polymerization.[53] However, with a careful choice of solvent and catalyst system, relatively well-defined polymers can be obtained via traditional thermal polymerization,[53,54] suggesting that optimization of this photoactivated process could furnish comparable results.

Hydoxy-functional[55] and vic-diol-functional[56] initiators **2** and **3** were also tolerant of the irradiation conditions, resulting in incorporation of α-functionality into well-defined PMA. Polymerization from **2** (Table 2, entry 6) and **3** (Table 2, entry 7) gave high conversions (>90%) with dispersities of 1.11 and 1.15, respectively, indicative of a high degree of ω-chain end functionality to complement the α-functionality.

The degree of control attained in the UV-light-activated polymerization from all three initiators was confirmed using MALDI-ToF-MS (Figure 3; Figure S12 and S13, Supporting Information) and ^{1}H NMR spectroscopy for the lower DP$_n$ polymers (Figures S2, S12, and S13). MALDI-ToF-MS of PMA initiated from EBiB revealed a single distribution in linear mode corresponding to polymer chains initiated by the expected EBiB fragment and bromo-terminated (Figure S14, Supporting

Table 2. Photomediated Polymerization of a Variety of Acrylate Monomers[a]
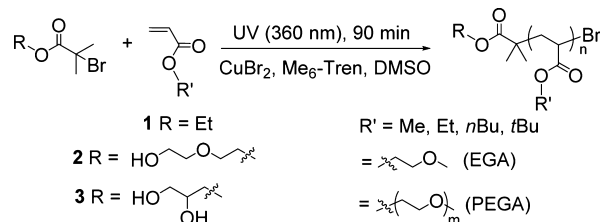
entry	R	R'	conversn[b] (%)	$M_{n,th}$ (g·mol^{-1})	$M_{n,SEC}$[c] (g·mol^{-1})	Đ
1	1	Et	97	5200	5900	1.07
2	1	nBu	97	6600	6800	1.16
3[d]	1	tBu	96	6600	4500	1.10
4	1	EGA	97	6700	6600	1.07
5	1	PEGA	92	5000	6000	1.09
6[e]	2	Me	92	2400	2400	1.11
7[e]	3	Me	93	2400	2300	1.15

[a]$[M]:[I]:[Cu^{II}]:[L]$ = 50:1:0.02:0.12 in DMSO (50%, v/v) solvent. [b]Determined by ^{1}H NMR. [c]Determined by CHCl$_3$ SEC analysis (see the Supporting Information). [d]DMF (50%, v/v) used as solvent. [e]DP$_n$ = 25 targeted for subsequent MALDI-ToF-MS analysis (see the Supporting Information).
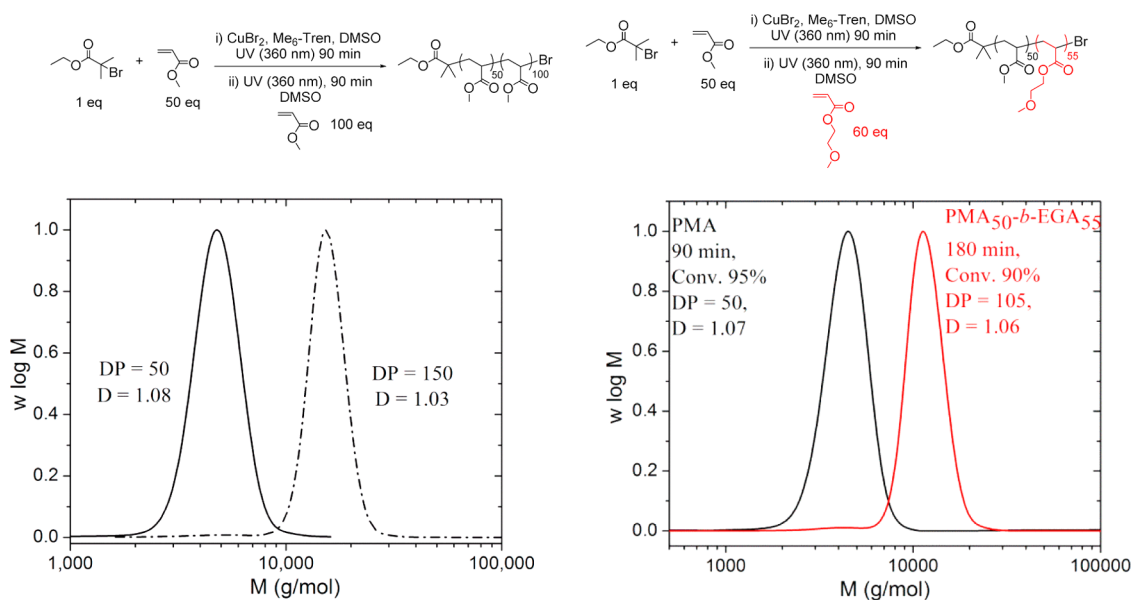

Figure 5. In situ chain extension and block copolymerization from a PMA macroinitiator. Initial conditions: $[MA]:[EBiB]:[Cu^{II}Br_2]:[Me_6\text{-}Tren]$ = 50:1:0.02:0.12, DMSO (50%, v/v). Chain extension (left) achieved upon addition of an aliquot of MA (100 equiv) in DMSO (33%, v/v) and block copolymerization (right) achieved by addition of EGA (60 equiv) in DMSO (33%, v/v).

Information). ^{1}H NMR confirmed a bromo ω-end functionality close to 100% fidelity on comparing signals corresponding to the −CH$_3$ groups of the isobutyrate group of EBiB (α-terminal; two singlets, 6H, 1.0 ppm) with the ω-terminal methine signal (triplet, 1H, 4.3 ppm; Figure S2, Supporting Information). In situ chain extension verified these end group analyses (Figure 5). Excellent control was observed, with the molecular weight distribution shifting to higher molecular weight with an observable decrease in dispersity ($Đ \approx 1.03$) upon addition of a second aliquot of MA (Figure 5; ~95% conversion attained within 90 min for the second MA block). Addition of a second acrylate monomer (EGA) resulted in a one-pot block copolymerization as indicated by SEC (Figure 5) and ^{1}H NMR (Figure S15, Supporting Information), allowing access to a well-defined poly(MA)-b-(EGA) block copolymer without the need for a macroinitiator purification step. Amphiphilic block copolymers were also prepared using PEGA$_{480}$ as the

comonomer with equal efficiency (Figures S16 and S17, Supporting Information).

Synthesis of PMA with Temporal Control. The possibility of "on/off" temporal control during polymerization was investigated using intermittent light and dark exposure for alternating 20 min periods. Approximately 30% monomer conversion was attained in the first period of UV irradiation (Figure 6). Confinement of the polymerization mixture to a black box at this point resulted in nearly complete discontinuation of polymerization. On re-exposing the mixture after 40 min (20 min dark reaction), the original polymerization rate was restored. These cycles were repeated, equating to a total exposure time of 80 min and resulting in PMA (93%, M_n = 4900 g·mol^{-1}, $Đ$ = 1.07; Figure S18, Supporting Information), comparable to the standard polymerization under uninterrupted UV irradiation. The kinetic profile of the polymerization was also directly comparable, highlighting the robust nature of
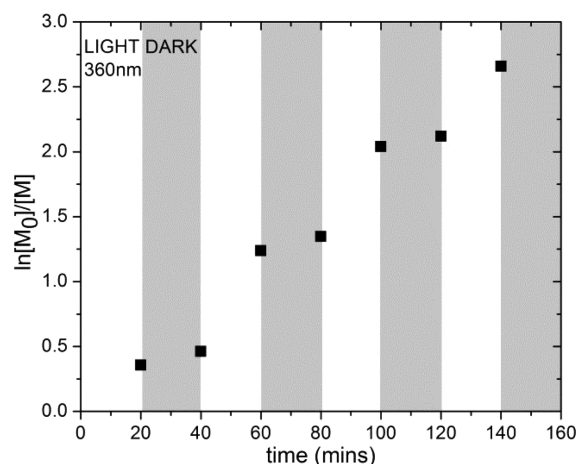
Figure 6. Evidence of temporal control via consecutive light (white area) and dark (shaded area) exposure. [M]:[I]:[Cu^{II}]:[L] = 50:1:0.02:0.12 in DMSO (50%, v/v) solvent.

this polymerization protocol unaffected by repeated on/off exposure.

While temporal control presents positive implications for future applications, it also offers valuable mechanistic insight, underlining how the polymerization requires photoexposure at an appropriate wavelength for initiation and sustained reactivation/propagation in the presence of Me$_6$-Tren. This may imply direct involvement in the activation step or indirect involvement via continuous photoregeneration of an active catalyst which is required throughout the duration of the polymerization.

Effect of the Source and Relative Concentration of Cu on Photoactivated Polymerization of MA. A series of kinetic experiments were performed, initially varying the source of Cu followed by the overall loading of the Cu^{II}Br$_2$ in the system. No appreciable difference, within error, was observed in the rate of reaction when the polymerization was performed in the presence of Cu^{I}Br, Cu^{II}Br$_2$, Cu^{II}Cl$_2$, or Cu(0) (formed from the disproportionation of Cu^I(Me$_6$-Tren)Br in H$_2$O according to a literature procedure)[24] present in a 1:6 ratio with Me$_6$-Tren, in accordance with the standard polymerization conditions (Figure S19, Supporting Information). The final polymers obtained exhibited good agreement between $M_{n,th}$ and $M_{n,exptl}$ and narrow dispersities ($Đ \approx 1.07-1.18$, Figure S20−S23, Supporting Information).

Modification of the standard conditions ([I]:[Cu^{II}Br$_2$]:[Me$_6$-Tren] = 1:0.02:0.12), imposing a gradual increase in [Cu^{II}Br$_2$] (0.02−0.08) resulted in a steady reduction in the rate of polymerization (Figure S24, Supporting Information). There

seemed two possible explanations for the observed decrease in rate. Increasing [Cu^{II}Br$_2$] results in an increase of Cu^{II}(Me$_6$-Tren)Br$_2$ deactivator concentration, shifting the polymerization equilibrium to the dormant chains. This coincides with a reduction in the concentration of free Me$_6$-Tren, which has been identified as an essential reagent in these photoactivated reactions. To investigate these theories, [Me$_6$-Tren] was increased, while maintaining the higher [Cu^{II}Br$_2$], to reinstate [Cu^{II}Br$_2$]:[Me$_6$-Tren] = 1:6 (i.e., [I]:[Cu^{II}Br$_2$]:[Me$_6$-Tren] = 1:0.08:0.48). Under these conditions the rate of polymerization increased, although the rate observed under the standard conditions ([I]:[Cu^{II}Br$_2$]:[Me$_6$-Tren] = 1:0.02:0.12) was not fully restored, inferring that while the free Me$_6$-Tren is vital, a high concentration of deactivator can still retard/deactivate polymerization.[57]

Effect of Ligand and Solvent on Photoactivated Polymerization of MA. The polymerization was screened in a selection of disproportionating and nondisproportionating solvents (Table 3). In solvents that are proposed to promote disproportionation (DMF and MeOH), excellent control was retained ($Đ$ = 1.08 and 1.05, respectively), albeit with conversions lower than those observed in DMSO (69% and 84%, respectively). In nondisproportionating solvents, MeCN and toluene, conversions remained lower than those obtained with DMSO (67% and 62%, respectively), and the dispersities were variable. Comparable control was exhibited by MeCN ($Đ$ = 1.06), whereas a significant drift was observed during polymerization in toluene ($Đ$ = 1.54). This could be attributed to the poor solubility of the Cu^{II}(Me$_6$-Tren)Br$_2$ complex in toluene, culminating in insufficient deactivation and free radical polymerization, mirroring slightly the result of the controlled experiment performed in the absence of Cu^{II}Br$_2$ (Table 1, entry 2).

A range of ligands were also explored in this photoactivated polymerization, including aliphatic amino ligands Tren and PMDETA as well as bipyridine (bpy) (Table 3). The results indicate little difference between Me$_6$-Tren (96%, $Đ$ = 1.05) and Tren (96%, $Đ$ = 1.10), whereas a significantly reduced polymerization rate and a drift in the dispersity were observed when PMDETA was employed as the ligand over an identical irradiation time (90 min, 48%, $Đ$ = 1.27). Interestingly, no polymer was formed in the presence of bpy as the ligand, reinforcing the implication that aliphatic amino-based ligands (CNR$_2$ groups) are required.

Mechanistic Insight: UV−Vis Spectroscopy. To further investigate the mechanism, a series of UV−vis spectroscopy experiments were performed to follow polymerization. A deoxygenated solution of [Cu^{II}Br$_2$]:[Me$_6$-Tren] = 1:6 in DMSO (polymerization ratio and concentration) revealed the

Table 3. Effect of Solvent and Ligand on Photomediated Polymerization of MA[a]

solvent	L	conversn[b] (%)	$M_{n,th}$ (g·mol^{-1})	$M_{n,SEC}$[c] (g·mol^{-1})	$Đ$
DMSO	Me$_6$-Tren	96	4400	4500	1.05
DMSO	Tren	96	4400	4200	1.10
DMSO	PMDETA	48	2200	1900	1.27
DMSO	Bipy				
DMF	Me$_6$-Tren	69	3100	3800	1.08
MeOH	Me$_6$-Tren	84	3800	4500	1.05
MeCN	Me$_6$-Tren	67	3000	3700	1.06
toluene	Me$_6$-Tren	62	2800	7800	1.54

[a][M]:[I]:[CuBr$_2$]:[L] = 50:1:0.02:0.12, 90 min irradition time, solvents used at 50%, v/v. [b]Determined by ^{1}H NMR. [c]Deterrmined by CHCl$_3$ SEC.

characteristic absorbance at λ_{max} = 950 nm with an additional absorbance at λ = 750 nm, attributed to the d–d transitions of the d^9 Cu^{II} complex (Figure 7a). The mixture was subsequently
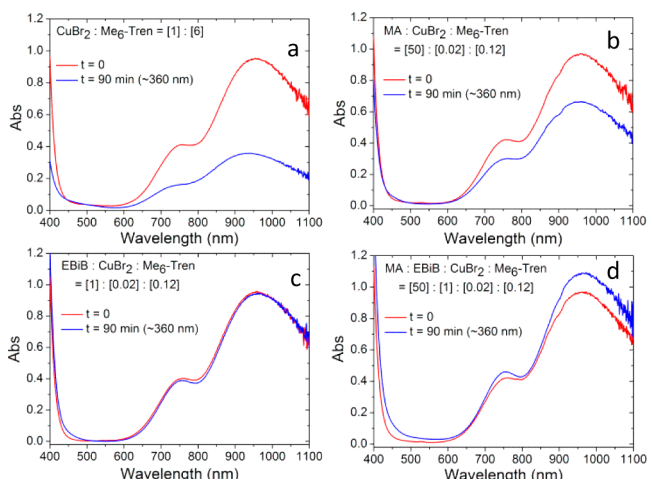

**Figure 7.** Monitoring effect of UV irradiation on $[Cu^{II}(Me_6\text{-}Tren)Br_2]$ as a function of time by UV–vis spectroscopy.

exposed to UV irradiation for 90 min, to mimic the polymerization conditions, before the absorbance spectrum was remeasured. An approximate 75% decrease in the characteristic absorbance was observed, suggesting a significant reduction in $[Cu^{II}(Me_6\text{-}Tren)Br_2]$ (Figure 7a). The absorbance continues to decrease over a period of 9 h; however, it is noted that it never reaches zero. Continued irradiation over 72 h results in no further reduction in the absorbance but does result in a significant deviation in the baseline signal at $\lambda \approx 450$–600 nm (Figure S31, Supporting Information).

In the presence of nonfunctional initiator ([EBiB]:[$Cu^{II}Br_2$]: [$Me_6\text{-}Tren$] = 1:0.02:0.12), no quantifiable change was seen in the absorbance spectrum after 90 min of UV irradiation (Figure 7b). The presence of the initiator (in significant excess relative to Cu^{II}) could reoxidize $Cu^{I}(Me_6\text{-}Tren)Br$ back to $Cu^{II}(Me_6\text{-}Tren)Br_2$ relatively quickly on the polymerization time scale. Alternatively, photoactivated $Me_6\text{-}Tren$ could activate the alkyl halide initiator, in preference to acting as a direct photoreducing agent of $Cu^{II}(Me_6\text{-}Tren)Br_2$. Repeating the experiment in the presence of monomer, thus fully replicating the polymerization conditions, leads to a similar observation, perhaps supporting the latter hypothesis (Figure 7d).

While the reduction of $Cu^{II}(Me_6\text{-}Tren)Br_2$ to $Cu^{I}(Me_6\text{-}Tren)Br$ is not readily observed in the presence of initiator or under polymerization conditions, the fact that rapid controlled polymerization is observed underlines how sufficient active species are generated under these conditions. Indeed, the ability of this polymerization to proceed in the presence of $Cu^{II}(Me_6\text{-}Tren)Br_2$ is likely a crucial factor in the success and overall control of this protocol, with deactivation expected to dominate over side reactions such as bimolecular termination and/or chain transfer etc. Upon generation of $Cu^{I}(Me_6\text{-}Tren)Br$, either from reduction by photoactivated $[Me_6\text{-}Tren]^*$ or via deactivation of propagating chains, its lifetime is probably short on the polymerization time scale. Under the reaction conditions $Cu^{II}(Me_6\text{-}Tren)Br_2$ can be regenerated either by disproportionation or oxidation of $Cu^{I}(Me_6\text{-}Tren)Br$ by an oxidative intermediate (radical cation) of free $Me_6\text{-}Tren$ (see the section "Proposed Mechanism").

Proposed Mechanism. The results of control, kinetic, and UV–vis experiments provide preliminary mechanistic insight and enable the proposal of a potential mechanism for this photomediated process (Scheme 1). In organic chemistry

Scheme 1. Proposed Mechanism for Tertiary-Amine-Mediated, Photoinduced Living Polymerization of Acrylates
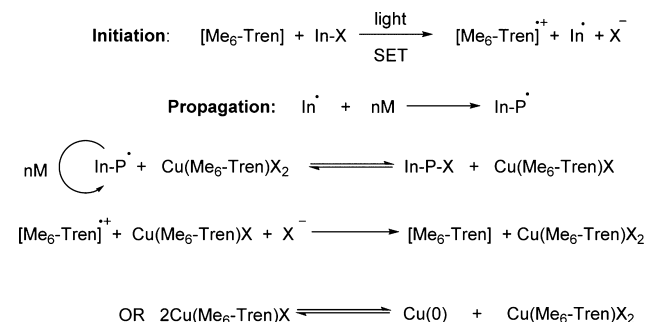
amines have been employed as outer-sphere electron donors and photoelectron donors in a number of synthetic transformations, including reductive dehalogenation[58,59] and cyclization[60–62] reactions of alkyl halides, believed to proceed via a radical mechanism. More importantly, tertiary amines and their salts have been cited as organocatalysts for thermal and photochemical CLRP.[63–65] With this in mind, we propose initial photoactivation occurs into free ligand ($Me_6\text{-}Tren$; Figure S32 and S33, Supporting Information). Outer-sphere single-electron transfer (OSET) then occurs from photoexcited $[Me_6\text{-}Tren]^*$ to the alkyl halide initiator, resulting in homolysis of the C–Br bond. This would furnish the required initiating radical and a $Me_6\text{-}Tren$ radical cation with a Br^- counterion. In the presence of an appropriate acrylate, polymerization can then occur with excellent control imposed by the presence of $Cu^{II}(Me_6\text{-}Tren)Br_2$. Deactivation results in reduction of $Cu^{II}(Me_6\text{-}Tren)Br_2$ to afford a dormant polymer chain (P_n-Br) and $Cu^{I}(Me_6\text{-}Tren)Br$.

Here the mechanism becomes complex due to the variable fate of the $Cu^{I}(Me_6\text{-}Tren)Br$ complex. Relative rates of reaction will be highly dependent upon the conditions employed, including solvent, temperature, and catalyst loading. Nevertheless, what is clear from the data is that, under UV irradiation ($\lambda_{max} \approx 360$ nm), a synergistic relationship exists between free amine ($Me_6\text{-}Tren$) and the cupric complex ($Cu^{II}(Me_6\text{-}Tren)Br_2$), affording poly(acrylates) in excellent conversions, rates, and end group fidelity.

■ CONCLUSIONS

We report an efficacious photoactivated living polymerization of acrylates mediated by $Cu^{II}Br_2$ in the presence of aliphatic tertiary amine ligands. We have proposed that initial photoactivation occurs into free ligand which acts as a photoelectron donor and promotes polymerization via single-electron transfer (SET) into the alkyl halide initiator. The ligands and transition metals used are routinely employed for thermal polymerization, and no added photoactivator is employed. Outstanding degrees of control and end group fidelity, as indicated by narrow dispersities, have been exemplified by chain extension and block copolymerization via sequential monomer addition. The scope of the reaction has been expanded to include a variety of acrylates, including biologically relevant PEG acrylate monomers. Furthermore, α-hydroxy and *vic*-diol functionalities are

tolerated when incorporated into the alkyl halide initiator. Reaction rates are rapid and temporal control is possible during polymerization via intermittent light and dark reactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of experimental and analytical procedures and supplementary figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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