Photocontrolled Cationic Degenerative Chain Transfer Polymerizations Via Thioacetal Initiators

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ARTICLE

Photocontrolled Cationic Degenerate Chain Transfer Polymerizations *Via* Thioacetal Initiators

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Recent developments in photocontrolled polymerizations have facilitated the development of previously inaccessible materials. While photocontrolled radical polymerizations have been extensively studied, related processes involving cationic polymerizations are underexplored and limited to RAFT processes. In this study, we disclose a visible light, temporally controlled cationic polymerization of vinyl ethers utilizing thioacetals and a photoredox catalyst. We demonstrate a broad scope of thioacetal initiators that achieve a well-controlled polymerization by recapping propagating chains *via* photocatalyst turnover in combination with a degenerate chain transfer process through sulfonium intermediates. Furthermore, we show that a photocatalyst with a more reducing ground state reduction potential allows for enhanced control and excellent temporal regulation of polymerization.

Introduction

Controlled polymerizations have enabled the synthesis of complex materials, from sequence defined block copolymers to more structurally complex architectures, such as star and brush polymers.[1] Recently, external stimuli-controlled processes have been employed to exert control over macromolecular structure.[2,3] Among these, photoredox catalysis has emerged as an efficient, low cost, and highly modifiable method to enable control of monomer sequence, surface patterning, and temporal regulation of polymers.[4–8] Reversible activation-deactivation polymerizations (RDPs) have been used extensively in controlled radical polymerizations. More specifically, light-mediated controlled radical polymerizations have flourished in recent years, leading to advances in photocontrolled atom transfer radical polymerizations (ATRP)[9–15], photoinduced reversible addition–fragmentation chain transfer (PET-RAFT) polymerizations[16–19], and photoinduced organotellurium-mediated radical polymerizations (TERP).[20,21] Despite many advances in photocontrolled radical polymerizations and recent developments in photocontrolled ring opening metathesis polymerizations (ROMP),[22–25] cationic RDPs in which control arises from the deactivation of propagating chains, analogous to work done by Hawker and coworkers[9], have not witnessed attention in the field of photocontrolled polymerizations.

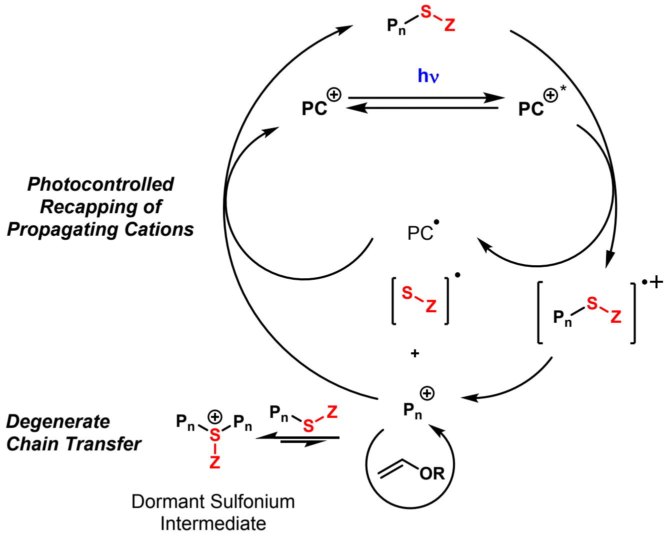

Fig. 1 Proposed mechanism for a photocontrolled cationic degenerate chain transfer polymerization using thioacetal initiators.

To achieve a cationic RDP, cation concentration must be minimized to avoid deleterious side reactions. While acid-initiated cationic RDP is well studied,[26–30] it does not provide spatiotemporal control for advanced macromolecular design. Photoredox catalysis offers a major opportunity to develop a spatially and temporally controlled cationic RDP. Such a process would require photochemical generation of a propagating cation *via* oxidation of an initiator, and then reversible termination of the polymerization by reduction *via* photocatalyst turnover. In 2016, our group reported a cationic RAFT polymerization of vinyl ethers mediated by blue light emitting diodes (LEDs).[31] Upon oxidation of a chain transfer agent, mesolytic cleavage afforded propagating cations, with the polymerization ultimately controlled via the RAFT process. We postulated that we could similarly generate

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photochemically reversible propagating cationic chain ends by oxidizing a thioacetal initiator.[32] Then, we proposed that we could achieve additional control over the polymerization via turnover of the photocatalyst by recapping the propagating cations and minimizing the number of propagating chain ends.

As an extra mechanism of control, we envisaged that a degenerate chain transfer process may also occur via sulfonium intermediates. In 2015, Kamigaito and coworkers demonstrated a controlled cationic degenerate chain transfer polymerization at low temperatures using triflic acid and a thioacetal initiator derived from *n*-butane.[33] This strategy relied on reversibly generating propagating cations through the formation of a stabilized sulfonium intermediate. Although this acid-initiated system demonstrated an advance in living cationic polymerizations, control over the polymerization remained limited to thioacetals with pendant short, linear alkyl groups. Furthermore, control over the polymerization occurred exclusively from the degenerate chain transfer process, and therefore, required non-hindered thioacetals that could sterically and electronically stabilize the sulfonium intermediate.

By utilizing photoredox catalysis, we realized the opportunity to expand the scope of thioacetal initiators that could be used to achieve a controlled polymerization. Mechanistically similar to iniferter polymerizations[34], we hypothesized that both a reversible activation/deactivation through rapid recapping of propagating cations as well as a degenerate chain transfer process, would not only minimize the number of cations during polymerization but would also lead to temporal regulation under mild conditions (Figure 1). Direct oxidation of a thioacetal by a photocatalyst in the excited state would result in a radical cation which would undergo a mesolytic cleavage to form a thiyl radical and an oxocarbenium chain end that could initiate polymerization. Control over polymerization would be achieved by maintaining a low concentration of propagating cations through the formation of a dormant sulfonium intermediates as well as by photocatalyst turnover as it reduces the thiyl radical to the corresponding anion to recap propagating cations. Furthermore, we hypothesized that this rapid recapping of propagating cations could lead to temporal regulation allowing the polymerization to be turned "on" and "off" at will.

Results and Discussion

We began investigating the photocontrolled cationic polymerization of isobutyl vinyl ether (IBVE) using initiator **1**. Successful initiation is dependent on pairing the initiator with a photocatalyst that is sufficiently oxidizing. Upon oxidation, the initiator must subsequently go through a mesolytic cleavage to generate a cation and initiate polymerization. The cyclic voltammogram of **1** shows an irreversible oxidation with a peak potential of +1.47 V vs SCE (Figure 2a), suggesting that **1** undergoes a chemical transformation following its oxidation.[35] Thus, **PMP** and **Ir-1**, which have adequately oxidizing excited state potentials of +1.89 V and +1.68 V vs SCE, respectively, were identified as potential photocatalysts for the oxidation of thioacetal initiators (Figure 2b).

Exposure of IBVE, initiator **1**, and 0.01 mol% of **PMP** to blue LEDs led to 44% conversion of monomer after 1 hour (Table 1, entry 1). The experimental M_n of the resulting polymer was in good agreement with the theoretical M_n and had a $Đ$ of 1.55. A two-fold increase in catalyst loading (0.02 mol%) led to full conversion of monomer within 1 hour and yielded a polymer with a narrower $Đ$ of 1.31 (Table 1, entry 2). Further increasing the loading of **PMP** results in broadened $Đ$s, which we attribute to higher cation concentration during the polymerization, as well as degradation of **PMP** (Table 1, entries 3-4, See supporting information Figure S5).[36–38] Increasing the monomer concentration led to even greater control of the polymerization, yielding a polymer with a $Đ$ of 1.19 (Table 1, entry 5). Good control was also achieved when using photocatalyst Ir-1 in place of **PMP** (Table 1, entry 6).

The ability to target different molecular weights by changing the ratio of initiator to monomer (Table 1, entries 7-9) provides further evidence of a controlled polymerization process. In the absence of initiator, an uncontrolled polymerization is obtained due to direct oxidation of the monomer by the photocatalyst (Table 1, entry 10). In the absence of light, no polymerization is observed, indicating the necessity of light in initiating polymerization (Table 1, entry 11). No polymerization occurs in the absence of photocatalyst, indicating that an electron transfer process between the excited state of the photocatalyst and the thioacetal initiator is required for polymerization to occur (Table 1, entry 12).

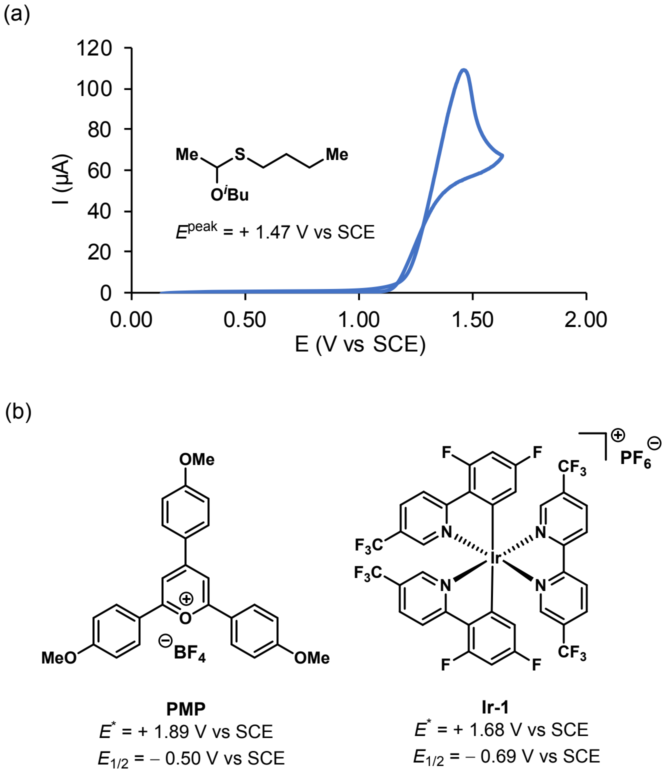
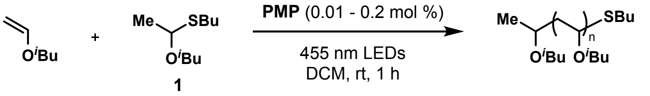


Fig. 2. (a) CV of 5 mM initiator 1 in 0.1 M tetrabutylammonium perchlorate in dichloromethane at 20 mV/s. (b) Oxidizing photocatalysts used in this study.

Table 1. Polymerization of IBVE with **PMP** and initiator **1**.

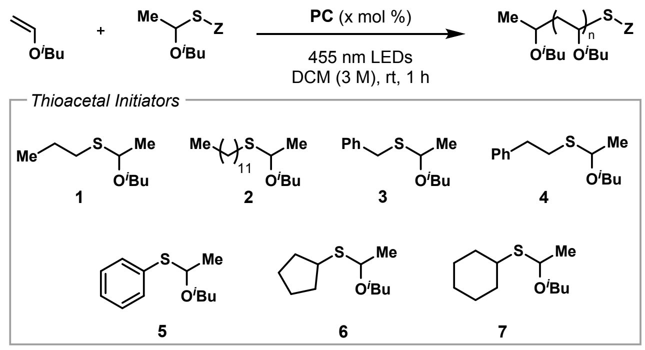


Entry[a]	[IBVE] (M)	**PMP** (mol %)	M_n (theo) (kg/mol)	M_n (exp) (kg/mol)	$Đ$
1	1.0	0.01	4.4	5.5	1.55
2	1.0	0.02	10.0	11.2	1.31
3	1.0	0.05	10.0	13.6	1.35
4	1.0	0.20	10.0	12.7	1.46
5	3.0	0.02	10.0	12.6	1.19
6[b]	3.0	0.02	10.0	8.5	1.35
7	3.0	0.02	5.0	5.4	1.41
8[c]	3.0	0.02	20.0	18.6	1.21
9[c]	3.0	0.02	40.0	34.8	1.49
10[d]	1.0	0.02	–	43	3.84
11[e]	1.0	0.02	10	–	–
12	1.0	0.00	10.0	–	–

[a] Reaction conditions: IBVE (1 equiv), **PMP** (0.01-0.2 mol%), and **1** (0.0025-0.01 equiv). [b] Ir-1 instead of **PMP.** [c] Polymerization time of 1.5 h. [d] Carried out in the absence of **1**. [e] Carried out in the absence of light.

Next, we envisioned that our standard conditions could be applied to other thioacetal initiators which have previously yielded poor control in acid-initiated cationic degenerate chain transfer polymerizations.[33] We suspected that introducing a photocontrolled polymerization would create an additional means to achieving control by recapping propagating cations *via* photocatalyst turnover. We first sought to expand the scope of alkyl thioacetals for this process. Using the initiator derived from dodecane thiol (**2**), we observe a controlled polymerization with a $Đ$ of 1.38 (Table 2, entry 2). Similarly, benzyl and homobenzyl substituents on initiators **3** and **4**, respectively, showed excellent control under the reaction conditions (Table 2, entries 3-4). With bulkier alkyl substituents, $Đ$ increases and control is lost, likely due to increased steric hinderance which destabilizes the sulfonium intermediate (Table S5) and decreases the rate of degenerate chain transfer. Interestingly, when we used the initiator derived from thiophenol (**5**), we observed a controlled polymerization with a $Đ$ of 1.42 and an M_n of 12.6 kg/mol (Table 2, entry 5). In previous reports, no control was achieved with **5** ($Đ$ = 1.93).[33] Unlike the acid initiated degenerate chain transfer process, we propose that reduction of the phenyl thiyl radical *via* turnover of **PMP**$^\bullet$ allows for efficient chain recapping, which improves control of the polymerization.

Table 2. Polymerization of IBVE with thioacetal initiators.



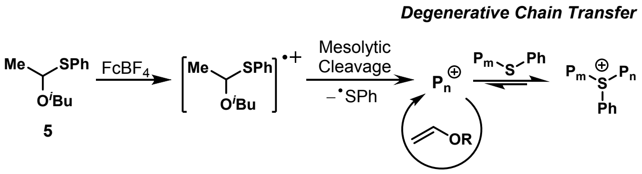
Entry[a]	Initiator	PC	M_n (theo) (kg/mol)	M_n (exp) (kg/mol)	$Đ$
1	**1**	**PMP**	10.0	12.6	1.19
2	**2**	**PMP**	10.0	10.4	1.38
3	**3**	**PMP**	10.0	8.7	1.35
4	**4**	**PMP**	10.0	8.4	1.40
5	**5**	**PMP**	10.0	12.6	1.42
6[b]	**5**	Ir-1	10.0	11.1	1.34
7	**6**	**PMP**	10.0	7.9	1.54
8	**7**	**PMP**	10.0	8.2	1.69
9[c]	**6**	Ir-1	9.0	7.9	1.37
10[c]	**7**	Ir-1	8.6	11.2	1.38

[a] Reaction conditions: IBVE (1 equiv), **PMP** (0.02 mol %), and initiator (0.01 equiv) [b] 0.03 mol% Ir-1 [c] 0.01 mol% Ir-1.

We hypothesized that photocatalyst **Ir-1** would promote more efficient recapping of our polymer chains to produce polymers with narrower $Đ$s. The reduction potential of **Ir-1** is 200 mV more reducing than **PMP** and therefore more efficient recapping will occur, minimizing the number of propagating cations in solution. Gratifyingly, we observed improved control in the polymerization with initiator **5**, achieving a $Đ$ of 1.34 (Table 2, entry 6). Additionally, secondary cyclic alkyl thiols (**6** and **7**) also lead to controlled polymerizations (Table 2, entries 7 and 8); and by replacing **PMP** with **Ir-1**, greater control can be achieved (Table 2, entries 9-10). These data suggest that, in addition to degenerate chain transfer, enhanced control of the polymerization is achieved *via* efficient recapping of propagating cations through photocatalyst turnover, analogous to the photocontrolled polymerizations developed by Hawker and co-workers where control over polymerization is achieved through deactivation of propagating chains.

To further test our hypothesis that enhanced control occurs *via* recapping, catalytic ferrocenium tetrafluoroborate ($FcBF_4$) was added to a solution of monomer and initiator **5**. A direct chemical oxidation of **5** using $FcBF_4$ would still lead to a mesolytic cleavage but control over the polymerization would only occur through a degenerate chain transfer mechanism, without the added control gained from chain recapping *via* photocatalyst turnover (Scheme 1). As hypothesized, chemical oxidation of the initiator afforded a broader $Đ$ of 1.57, suggesting that the recapping of cationic chains *via* turnover of the photocatalyst assists in the improved control of the polymerization (Table S6).

Scheme 1: Cationic polymerization *via* chemical oxidation of **5** using $FcBF_4$.



This contrasts our previous work on controlled cationic RAFT polymerizations in which chemical oxidation of a thiocarbonylthio chain end with $FcBF_4$ still provides narrow *Đ* polyvinyl ethers since control is achieved primarily through the RAFT mechanism.[3] Thus, taking advantage of recapping through photocatalyst reduction assembles a large collection of thioacetal initiators for a controlled cationic degenerate chain transfer polymerization.

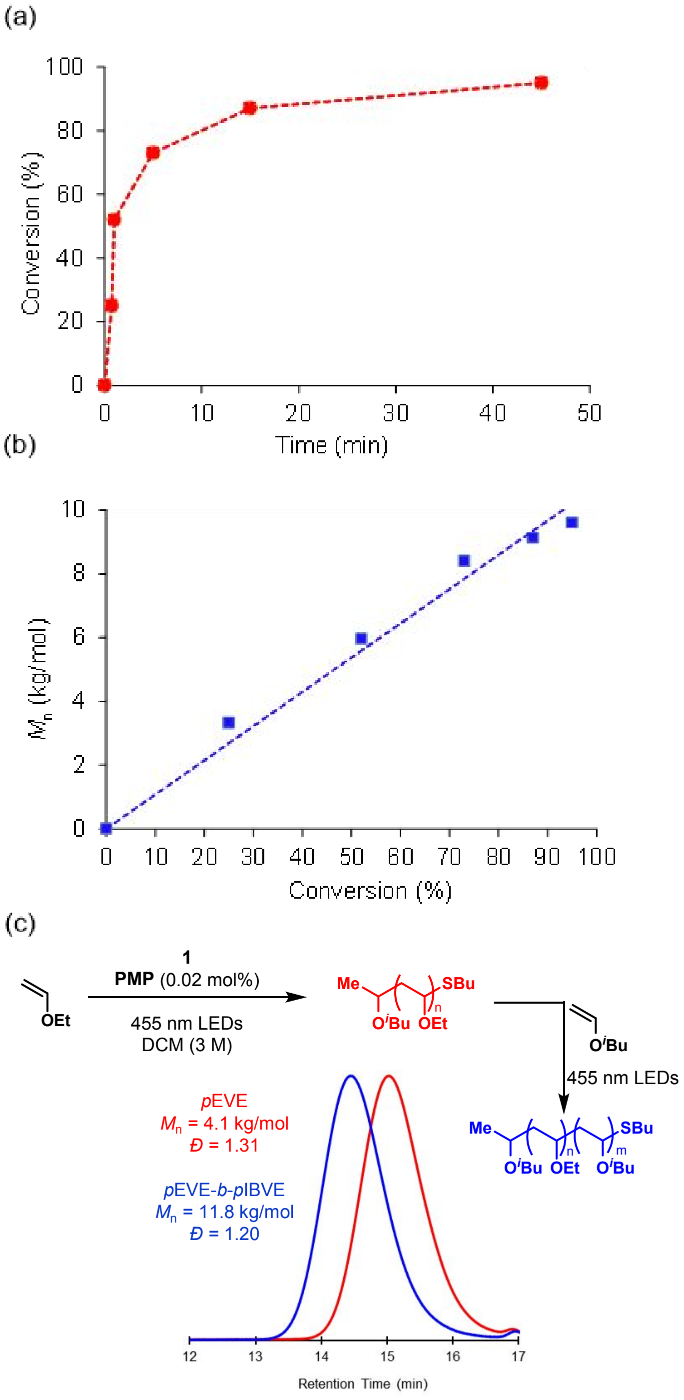


Fig. 3. Polymerization of IBVE with **1** and **PMP** (0.02 mol%). (a) Conversion vs time (b) Conversion vs M_n. (c) Polymerization of *p*EVE-*b*-*p*IBVE with initiator **1** and **PMP**.

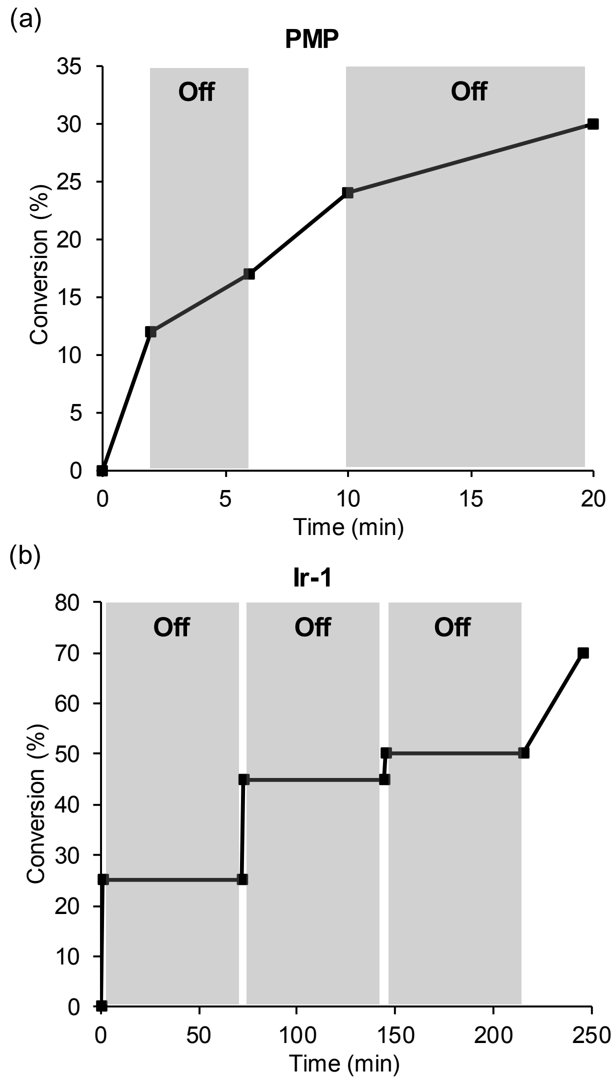


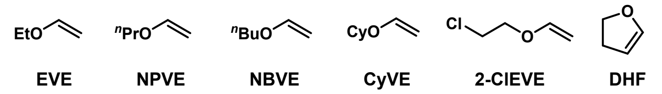
Fig. 4 (a) Conversion vs. time with intermittent light exposure using **PMP** as the photocatalyst. Shaded regions represent the absence of light. (b) Conversion vs. time with intermittent light exposure using Ir-1 as the photocatalyst. Shaded regions represent the absence of light.

Next, to confirm that our polymerization was living, we monitored the reaction over time with initiator **1** and our standard conditions (Table 1, entry 5). We observed 95% conversion of monomer after 45 minutes. (Figure 3a and Figure S6) and a linear relationship between M_n and monomer conversion, providing evidence of a living polymerization (Figure 3b). The chain-end fidelity of our polymerization was also explored through the synthesis of block copolymers. After generating a 4.1 kg/mol poly(ethyl vinyl ether) (pEVE) using our standard conditions with initiator 1, we added IBVE to the reaction vial and continued to expose the reaction to blue LEDs. Analysis by gel permeation chromatography (GPC) and ^1H NMR revealed efficient chain extension to produce a narrow *Đ* block copolymer of pEVE-*b*-pIBVE with a match between the theoretical and experimental M_n (Figure 3c and Figures S2-S6).

In order to achieve true photoregulation, the activation of carbocations must be reversible and dictated by light. We tested the photo-reversibility of our polymerization by exposing a reaction containing monomer, photocatalyst, and initiator **1** to light for 2 min, followed by stirring in the dark for 5 min. The reaction was again exposed to light followed by another off period (in the dark) and aliquots were taken after each switching period for analysis by ^{1}H NMR and GPC. When employing **PMP** as the photocatalyst, conversion of monomer continued even after irradiation was halted, although the rate of polymerization decreased in the absence of light (Figure 4a). This contrasts our previous studies on photocontrolled cationic RAFT polymerizations, in which a dithiocarbamate thioradical has a low enough reduction potential to be efficiently reduced by **PMP**$^{\bullet}$ for recapping of propagating chains.[31] We hypothesized that **PMP**$^{\bullet}$ was not sufficiently reducing to efficiently generate the thiolate anion to recap the propagating cation which would stop the polymerization in the absence of light (Figure S16). As expected, when switching to **Ir-1**, which exhibits a 200 mV more reducing ground state potential, excellent temporal control is achieved, with the ability to turn the polymerization off for long periods of time followed by re-initiation when irradiation is resumed (Figure 4b and Figure S8).[39,40]

Finally, we proposed that this method of photocontrolled cationic polymerization may be applied to a vast range of vinyl ether monomers and extend beyond monosubstituted vinyl ethers. As expected, ethyl vinyl ether (EVE), *n*-propyl vinyl ether (NPVE), and *n*-butyl vinyl ether (NBVE) all led to polymers with excellent agreement between experimental and theoretical M_n with narrow *Đ* (Table 3, entries 1-3). Sterically hindered vinyl ethers such as cyclohexyl vinyl ether (CyVE) yielded polymer with very broad *Đ* but good agreement between experimental and theoretical M_n (Table 3, entry 4). More deactivated vinyl ethers such as 2-chloroethyl vinyl ether (2-ClEVE) exhibited good agreement between experimental and theoretical M_n but polymerized at a slower rate and afforded a slightly broader *Đ* due to a destabilization of the sulfonium intermediate from the electron withdrawing chloride on the polymer backbone (Table 3, entry 5). Furthermore, employment of disubstituted cyclic 2,3-dihydrofuran (DHF) led to a well-controlled polymerization with a narrow *Đ* to give poly(DHF) (Table3, entry 6). [41]

Table 3. Monomer scope of photochemical cationic degenerate chain transfer polymerization.



Entry[a]	Monomer	Conversion (%)	M_n (theo) (kg/mol)	M_n (exp) (kg/mol)	*Đ*
1	EVE	70	5.0	4.4	1.22
2	NPVE	90	8.0	7.7	1.39
3	NBVE	100	10.0	8.8	1.35
4	CyVE	100	10.0	11.8	2.21
5	2-ClEVE	50	5.0	6.9	1.73
6	DHF	100	10.0	14.1	1.19

[a] Reaction conditions: monomer (1 equiv, 3 M), **PMP** (0.02 mol %), and **1** (0.01 equiv).

Conclusions

In conclusion, our results indicate that a photocontrolled cationic degenerate chain transfer polymerization can be achieved with a broad range of thioacetal initiators. By leveraging an oxidizing photocatalyst with a large ground state reduction potential, we can achieve efficient recapping of polymer chains that assist in the controlled polymerization and afford excellent temporal control. The application of photoredox catalysis to a cationic degenerate chain transfer polymerization leads to this exquisite control over the polymerization by taking advantage of photocatalyst turnover. This method expands the scope of initiators that can be used for temporal control over polymerization which may allow for unprecedented post-polymerization functionalization and block copolymer synthesis which cannot be achieved using thiocarbonylthio agents in a RAFT process.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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35 Upon oxidation of initiator **1**, a mesolytic cleavage occurs to form the thiyl radical and the oxocarbenium species. The oxidation is irreversible due to formation of the disulfide when two thiyl radicals couple together (see SI, Figure S16)

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40 Following our work on **PMP** for photocontrolled cationic RAFT, our group has shown that iridium based oxidizing photocatalysts enhance the temporal control of our cationic RAFT polymerization due to their superior reducing ability. Refer to reference 39.

41 Attempts to polymerize styrenic monomers were unsuccessful. No conversion was observed with styrene and slight background polymerization was observed with more electron rich styrenic derivatives, likely due to background radical polymerization. For more information, see SI, Table S8.