Photoredox Catalysis in Photocontrolled Cationic Polymerizations of Vinyl Ethers

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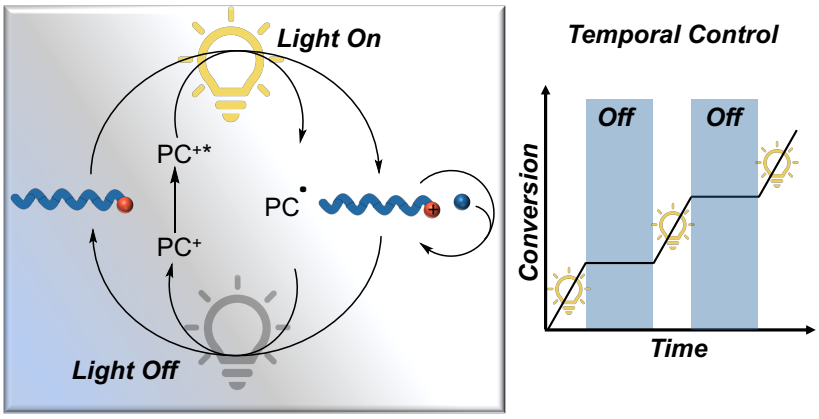
CONSPECTUS: Advances in photocontrolled polymerizations have expanded the scope of polymer architectures and structures that can be synthesized for various applications. The majority of these polymerizations have been developed for radical processes, which limits the diversity of monomers that can be used in macromolecular design. More recent developments of photocontrolled cationic polymerizations have taken a step toward addressing this limitation and have expanded the palette of monomers that can be used in stimuli regulated polymerizations, enabling the synthesis of previously inaccessible polymeric structures. This Account will detail our group's studies on cationic polymerization processes where chain growth is regulated by light and highlight how these methods can be combined with other stimuli-controlled polymerizations to precisely dictate macromolecular structure.

Photoinitiated cationic polymerizations are well-studied and important processes that have control over initiation. However, we wanted to develop systems where we had spatiotemporal control over both polymer initiation and chain growth. This additional command over the reaction provides the ability to manipulate the growing polymer with an external stimulus during a polymerization, which can be used to control structure. To achieve this goal, we set out to develop a method to photoreversibly generate a cation at a growing chain end that could participate in a controlled polymerization process. We took inspiration from previous work on cationic degenerate chain transfer polymerizations of vinyl ethers that used thiocarbonylthio chain transfer agents. These polymerizations were initiated by a strong acid and gave well-defined polyvinyl ethers. We posited that we could remove the acid initiator in these systems and reversibly oxidize the thiocarbonylthio chain ends in these reactions with a photocatalyst to give a photocontrolled cationic polymerization of vinyl ethers. This Account will focus on our journey to discover cationic photocontrolled polymerizations. We will summarize our initial developments and detail our mechanistic understanding of these reactions using both organic and inorganic based photocatalysts and we will outline more recent efforts to expand cationic degenerate chain transfer polymerizations to other thioacetal initiators. Finally, we will detail how these photocontrolled cationic polymerizations can be used to switch monomer selectivity *in situ* using light to control polymer structure. At the end of the article, we will discuss our vision for future potential applications of these photocontrolled cationic polymerizations in the synthesis of novel block copolymers and next generation crosslinked networks.



KEY REFERENCES

- Kottisch, V.; Michaudel, Q.; Fors, B.P. Cationic Polymerization of Vinyl Ethers Controlled by Visible Light. *J. Am. Chem. Soc.*, **2016**, *138*, 15535-15538.[1] This work reports a photocontrolled cationic polymerization of vinyl ethers. Using an organic photocatalyst to reversibly oxidize a chain transfer agent, the polymer growth can be temporally controlled by regulating the external stimulus.

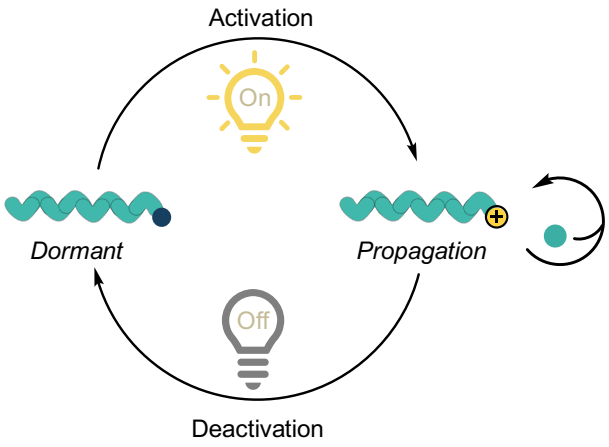
- Michaudel, Q.; Chauvire, T.; Kottisch, V.; Supej, M.J.; Stawiasz, K.J.; Shen, L.; Zipfel, W.R.; Abruña, H.D.; Freed, J.H.; Fors, B.P. Mechanistic Insight into the Photocontrolled Cationic Polymerization of Vinyl Ethers. *J. Am. Chem. Soc.,* **2017**, *139*, 15530-15538.[2] This work investigates the mechanism of our previously reported photocontrolled cationic polymerization of vinyl ethers. Upon one-electron oxidation of the chain transfer agent by photocatalyst, a generated radical cation species undergoes mesolytic cleavage and produces an active cation to initiate the polymerization. The reversible addition-fragmentation chain transfer equilibrium leads to a control over polymer growth.

- Ma, Y.; Kottisch, V.; McLoughlin, E.A.; Rouse, Z.W.; Supej, M.J.; Baker, S.P.; Fors, B.P. Photoswitching Cationic and Radical Polymerizations: Spatiotemporal Control of Thermoset Properties. *J. Am. Chem. Soc.,* **2021**, *143*, 21200-21205.[3] This work extends our previously developed photoswitchable polymerization to

thermoset materials. Vinyl ethers and acrylates can be selectively incoporated at growing chain ends by switching light. Through regulating the wavelenghth and dosage of light, the mechanical properties of crosslinked vinyl ethers can be tuned both spatially and temporally.

- Sifri, R.J.; Kennedy, A.J.; Fors, B.P. Photocontrolled Cationic Degenerate Chain Transfer Polymerizations via Thioacetal Initiators. *Polym. Chem.*, **2020**, *11*, 6499-6504.[4] This work expands photocontrolled cationic polymerization of vinyl ethers using thioacetal initiators and photocatalysts. The highly reducing ground state potential of photocatalyst contributes to an efficient recapping of propagating cations, resulting in enhanced control of the polymerization.

Scheme 1. General mechanistic pathway to achieve photocontrolled cationic polymerizations.



INTRODUCTION

Precise regulation over polymer chain growth has led to unparalleled advances in the fields of polymer chemistry and materials science. Controlled radical polymerizations, such as reversible addition chain transfer polymerizations (RAFT),[5–12] nitroxide mediated polymerizations (NMP),[13–17] and atom transfer mediated polymerizations (ATRP),[18–23] have set the foundation for the design and synthesis of complex polymer architectures and multi-block copolymers. More recently, the integration of photoredox catalysis with polymer synthesis has created even further innovations, providing newfound capabilities in surface patterning, photolithography, and multifaceted 3D printed materials.[24–26]

Light as an external stimulus is an attractive tool to mediate polymerization processes due to its low cost, practicality, and minimal environmental hazard. Furthermore, light provides a means for temporal and spatial control over polymer chain growth. While photoinitiated polymerizations have existed for several decades,[27,28] these processes do not exhibit control over chain growth. Thus, they do not offer the opportunity to systematically turn a polymerization "on" and "off" or control the rate of chain growth with light intensity. In contrast, photocontrolled polymerizations, where light reversibly activates and deactivates a "living" polymerization, have more recently emerged in the field, launching new avenues for control over polymer structure and design. In general, these systems are more challenging than their photoinitiated counterparts because the propagating chain end must be reversibly generated with light.

Extensive studies on photocontrolled polymerizations have been focused on radical processes.[26,29–31] Several up-to-date methods include photo-ATRP,[32,33] photo-induced electron transfer RAFT (PET-RAFT),[34–38] and photoinduced organotellurium-mediated radical polymerizations (TERP);[39–42] by turning light on and off, polymer chain growth can be reversibly activated, while maintaining polymers with narrow $Đ$s and precise M_ns. In some photocontrolled radical polymerizations, imperfect temporal control over polymer growth was often observed. For example, in Cu-mediated ATRP, due to the unwanted activity of Cu(I) catalyst remaining in organic media, polymer growth could not be completely turned off during "dark" periods. Thus, optimizations using reduced catalyst concentrations and aqueous media were conducted to improve the temporal control.[43–47] Compared to the radical processes, the development of photocontrolled cationic polymerizations could provide new opportunities to control polymer growth. Additionally, metal-free ring opening metathesis polymerizations (ROMP) have also been developed by Boydston and coworkers by utilizing photoredox catalysis to achieve temporal control over norbornene polymerizations.[48] Despite these developments, there is still a void in the field of photocontrolled cationic polymerizations.[49]

Early studies on photoinitiated cationic polymerizations took advantages of photoacid generators with metal or organic photocatalysts to generate polymers under light exposure.[50–54] More recently, Spokoyny[55] and Nicewicz[56] used photooxidants to achieve pseudo-living polymerizations of styrene derivatives under visible light. While these

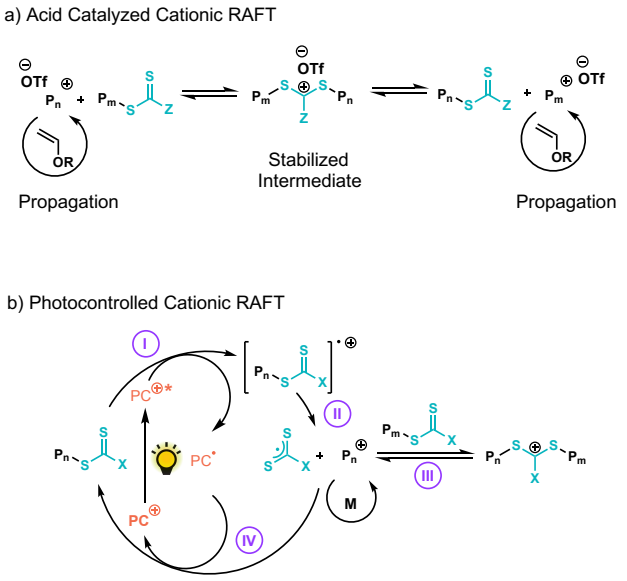


Fig. 1. a) Acid-initiated cationic RAFT polymerization b) Proposed catalytic cycle for photocontrolled cationic RAFT polymerization. Reproduced with permission from ref 60, 1. Copyright 2015 John Wiley and Sons and Copyright 2016 American Chemical Society.

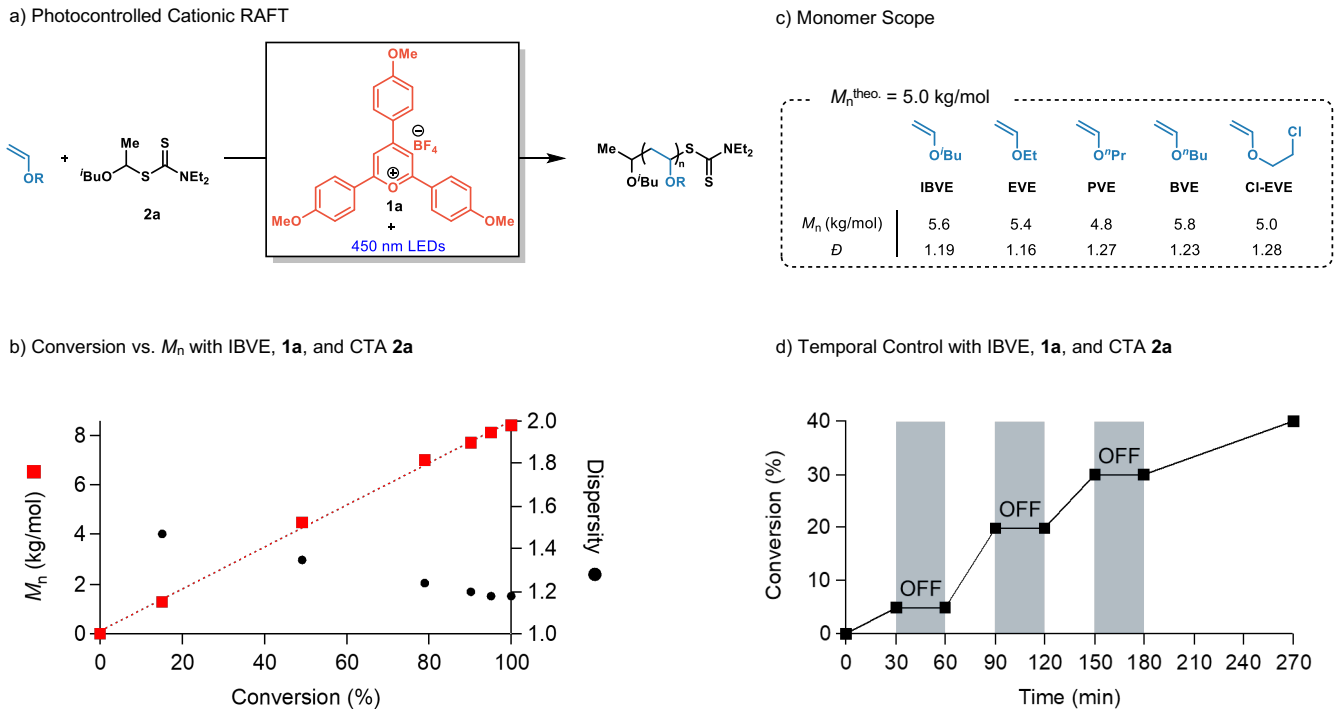


Fig. 2. a) Reaction scheme of a photocontrolled cationic polymerization of vinyl ethers using blue light and **1a**. b) Conversion vs. M_n shows our system exhibits living behavior. c) Monomer scope of a photocontrolled cationic RAFT process using **1a**. d) On/Off studies reveal that temporal control can be achieved (shaded regions represent the absence of light). Reproduced with permission from ref 1. Copyright 2016 American Chemical Society.

studies provided good control over polymer chain initiation, regulation over chain growth was still not possible.

In a separate effort, Boyer and Xu utilized a photochromic merocyanine-based photoacid (PAH), to regulate the cationic ring-opening polymerization (CROP) of lactones.[57] This method did provide temporal control; however, there was still some background polymerization in the absence of irradiation. Later, the Read De Alaniz group[58] optimized the architecture of these PAHs and successfully enhanced their solubility and reversion rate, achieving improved temporal control of CROP.

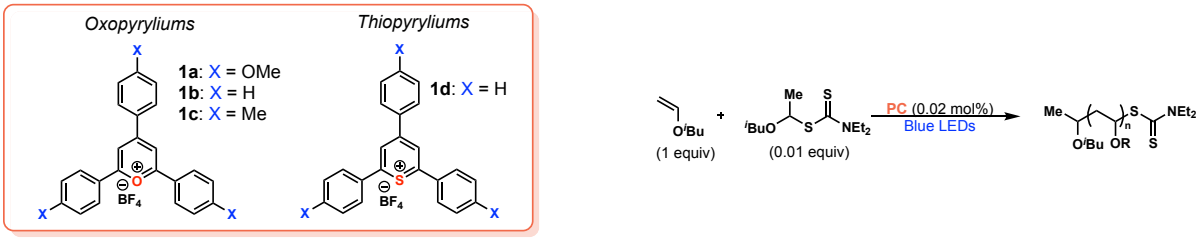
In this Account, we will discuss our recent developments in photocontrolled cationic polymerizations of vinyl ethers, and we will detail our mechanistic understanding of these polymerization systems (Scheme 1). In particular, our group has focused on the polymerizations of vinyl ethers for two main reasons: first, there is a deep understanding of vinyl ether polymerizations using acid initiators, providing us with the inspiration and fundamental knowledge to develop photocontrolled cationic polymerizations; second, poly(vinyl ether)s are often used in coatings and adhesives that are industrially relevant.[59] We will further examine how this work led to the external stimuli-controlled switching of polymerization mechanism *in situ* to give on demand regulation of monomer selectivity with light. We will conclude with insight into the future of photocontrolled cationic polymerizations and its role in the synthesis of advanced materials.

PHOTOCONTROLLED CATIONIC RAFT

To develop a photocontrolled cationic polymerization of vinyl ethers we needed to photoreversibly shuttle cations into a controlled polymerization process. We were inspired by the cationic reversible addition fragmentation chain transfer polymerizations (RAFT) using thiocarbonylthio chain transfer agents developed by Kamigaito and Sugihara (Figure 1a).[60,61] In these polymerizations, trace acid initiated the RAFT polymerization. We hypothesized that replacement of the acid initiator in these systems with an oxidizing photocatalyst could render these processes photocontrolled. Specifically, the thiocarbonylthio CTA could be directly oxidized with an excited photocatalyst and undergo a mesolytic cleavage to yield a carbocation that could participate in the RAFT process (Figure 1b).[1] Control over the polymerization would occur as the system enters a cationic degenerate chain transfer equilibrium with unoxidized thiocarbonylthio species. Finally, photocontrol over the polymerization would be achieved through photocatalyst turnover to recap propagating chains, allowing carbocations to form reversibly with light.

We began probing our hypothesis by exposing a solution of isobutyl vinyl ether (IBVE) and CTA **2a** with 0.02 mol% photocatalyst **1a** to blue light emitting diodes (LEDs) (Figure 2a). Irradiation for 3 h led full monomer conversion giving a polymer with a number average molar mass (M_n) of 5.6 kg/mol and a low dispersity ($Đ$) of 1.19. Importantly, the experimental and theoretical M_n values in these polymerizations were in good agreement. In monitoring the polymerization over time, we observed a linear relationship between M_n and conversion and first order kinetic behavior, showing that this was indeed a controlled chain growth process (Figure 2b). Furthermore, we were able to expand this system to a vast range of other vinyl ether monomers (Figure 2c). Additionally, the excellent fidelity of the

Table 1. Photophysical properties of and polymerization rate comparison using pyrylium photocatalyst derivatives. Reproduced with permission from ref 2. Copyright 2017 American Chemical Society.



Entry	PC	$E_{PC^{*}/PC^{\bullet}}$ (V vs SCE)	$E_{PC^{+}/PC^{\bullet}}$ (V vs SCE)	ε_{450} ($L \cdot mol^{-1} \cdot cm^{-1}$)	Φ_f	Φ_{ISC}	Time (min)	$M_n^{theo.}$ (kg/mol)	$M_n^{exp.}$ (kg/mol)	$Đ$
1	**1a**	+1.84[a]	−0.50	67,300	0.95	0.03	450	10.1	10.7	1.19
2	**1b**	+2.55[a]	−0.32	6,350	0.58	0.42	10	10.1	10.5	1.23
3	**1c**	+2.33	−0.55	32,100	-	-	10	10.1	11.1	1.17
4	**1d**	+2.45[a]	−0.19	7,330	0.03	0.94	300	10.1	10.3	1.21

[a] Potential of the singlet excited state. Φ_f = quantum yield of fluorescence. Φ_{ISC} = quantum yield of intersystem crossing.

thiocarbonylthio chain ends in these reactions allowed us to synthesize vinyl ether di-block copolymers.

The above results showed that we had a controlled cationic polymerization; however, key experiments were needed to show that this method gave temporal control over chain-growth with light. To test if the polymerization was photocontrolled, we first exposed a solution of IBVE, the dithiocarbamate CTA **2a,** and photocatalyst **1a** to blue LEDs for 30 min and then stirred the reaction in the dark for 30 min. This "on"/ "off" cycle was repeated 3 times an each cycle was monitored for polymer conversion and molecular weight. As hypothesized, we only observed polymerization when our system was exposed to light. Then, in the dark, we observe no monomer conversion, indicating temporal regulation of chain growth of vinyl ethers through light irradiation (Figure 2d).

Mechanistic studies on photocontrolled RAFT polymerizations. After our initial report of this new chemistry, we wanted to further study the mechanism of our method. There are 4 major mechanistic steps that we reasoned were responsible for the photocontrolled cationic RAFT polymerization (Figure 1b). First, upon excitation by light, the photocatalyst oxidizes the CTA to generate a radical cation intermediate (Figure 1b, step I). This radical cation undergoes a mesolytic cleavage to generate an active cationic chain end and a stable dithiocarbamate or trithiocarbonate radical (Figure 1b, Step II). Polymerization proceeds while the active cationic chain end engages in a RAFT equilibrium (Figure 1b, Step III), responsible for the predicted molecular weights and narrow $Đ$ we observe. Finally, turnover of the photocatalyst via a one-electron reduction of the thiocarbonylthio radical results in a thiocarbonylthio anion which caps the polymer chain end and deactivates chain growth (Figure 1b, Step IV). The next subsection of this Account will summarize the experimental findings that provide evidence for our mechanistic hypothesis.

Step I. *Photooxidation of the CTA.* Initially, we investigated the photomediated oxidation of the CTA with the excited catalyst using photoluminescence quenching experiments. It was revealed that in the excited state, **1a*** is quenched by both CTA **2a** and IBVE (Figure 3). However, we found that quenching of **1a*** by the CTA was significantly faster (k_q = 7.52 x 10^9 M^{-1} s^{-1}) than quenching by IBVE (k_q = 1.23 x 10^8 M^{-1} s^{-1}), suggesting that direct oxidation of CTA from PC* is kinetically favored.[2] Furthermore, electrochemical analysis shows that the onset of oxidation potential of CTA **2a** ($E^{o}_{2a/2a^{\bullet+}}$ = +1.19 V vs SCE) is lower than the oxidation potential of monomer ($E^{o}_{3a/3a^{\bullet+}}$ = +1.46 V vs SCE), providing further evidence that it is easier to oxidize the CTA over monomer. These experiments support our hypothesis that

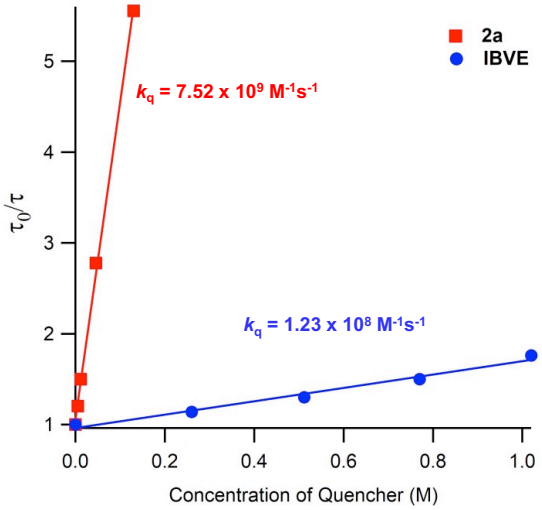


Fig. 3. Photoluminescence quenching studies of photocatalyst **1a** with CTA **2a** and IBVE. Reproduced with permission from ref 2. Copyright 2017 American Chemical Society.

the excited state photocatalyst selectively oxidizes the CTA over IBVE.

To further support the direct oxidation of the CTA with the photocatalyst, we looked for evidence of the formation of the reduced pyrylium radical (PC•). Photocatalyst **1a** in the presence of CTA **2a** under constant blue light irradiation resulted in an electron spin resonance (ESR) absorption signal consistent with formation of pyrylium radical intermediate, PC•.[2] However, steady-state irradiation of a mixture of **1a** and IBVE displayed a very different ESR spectra compared to **1a** with CTA **2a**, indicating other radical species were created instead of PC•. These experiments provide supporting evidence for the oxidation of the CTA by the excited photocatalyst.

We also set out to test our hypothesis that the rate of polymerization should be directly proportional to the intensity of irradiation. Using neutral density filters, we were able to observe the changes in initial polymerization rates as a function of light intensity. A linear relationship between light intensity and initial reaction rate demonstrated that the polymerization is first-order in light intensity.[1] This result shows that the cation concentration in the reaction can be precisely controlled by the external stimulus, which is key for temporal control over polymer chain growth.

We subsequently investigated the influence of the photocatalyst structure and redox potentials on the polymerization.[2] Surveying a series of aryl pyrylium photocatalysts with a range of excited state oxidation potentials, we observed that the higher oxidation potentials of photocatalysts **1b** and **1c** resulted in a faster polymerization rates, reaching full conversion in 10 min (Table 1, entries 2-3) instead of 8 hours using **1a** (Table 1, entry 1). However, switching to thiopyrylium **1d** with an oxidation potential of +2.45 V vs SCE (Table 1), we observe a significantly slower rate than its oxopyrylium counterpart **1b** (Table 1, entry 4), suggesting catalyst structure and oxidation potential both play an important role in the polymerization. Importantly, all these catalysts led to controlled polymerization processes with low dispersity values and good agreement between the experimental and theoretical M_n.

Step II*. Mesolytic cleavage of CTA*$^{+\bullet}$. The observation of a controlled cationic RAFT polymerization alone provides good evidence that mesolytic cleavage is occurring to give an oxocarbenium ion and a thiocarbonylthio radical. Additionally, we posited that in the absence of monomer, we would observe dimerization of the thiocarbonylthio radical to generate a thiuram disulfide. As expected, subjecting CTA **2a** and catalytic amounts of photocatalyst **1a** to blue LEDs, we observe the formation of thiuram disulfide **3,** providing evidence for the formation of the thiocarbonylthio radical (Figure 4).[2]

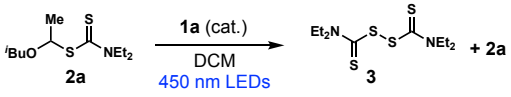
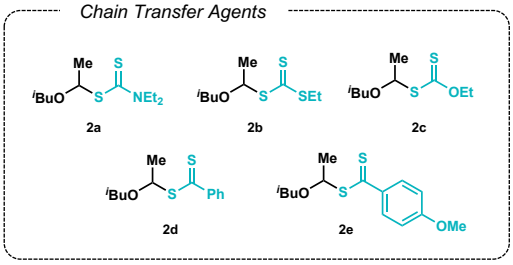


Fig. 4. Experimental evidence of the formation of thiocarbonylthio radicals**.** Reproduced with permission from ref 2. Copyright 2017 American Chemical Society.

Table 2. Cationic polymerization of isobutyl vinyl ether with various chain transfer agents. Reproduced with permission from ref 2. Copyright 2017 American Chemical Society.



Entry	CTA	$M_n^{theo.}$ (kg/mol)	$M_n^{exp.}$ (kg/mol)	$Đ$
1	**2a**	10.1	9.11	1.16
2	**2b**	10.1	10.1	1.43
3	**2c**	10.1	15.1	1.98
4	**2d**	10.1	15.0	2.10
5	**2e**	10.1	9.43	1.49

Step III*: CTA structure provides polymerization control.* Provided that the CTA acts as both the initiator and RAFT agent in our system, understanding the effects of CTA derivatives is essential for probing our mechanistic hypothesis. In general, we observed the best control over the polymerization using CTA **2a.** The use of **2b**, on the other hand, provided slightly higher dispersities but was found to be applicable to a wider monomer scope. Other CTAs derived from IBVE (Figure 2) led to broad $Đ$s but still achieved a match between the theoretical and experimental M_n values (Table 2). This result follows a similar trend in Kamigaito's initial

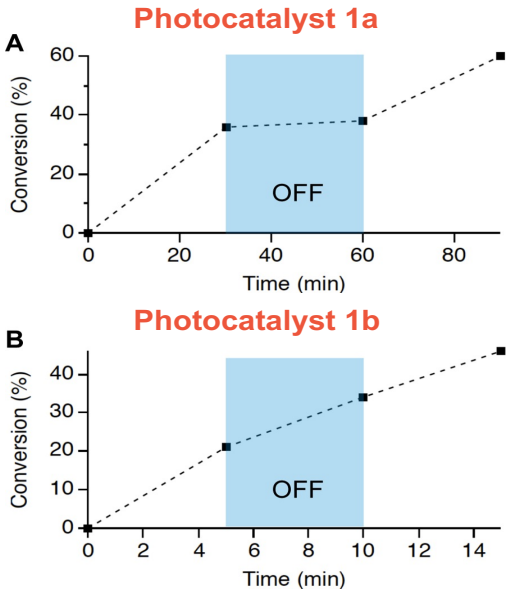


Fig. 5. Monomer conversion vs time with intermittent light exposure with photocatalysts **1a** (A) and **1b** (B). Reproduced with permission from ref 2. Copyright 2017 American Chemical Society.

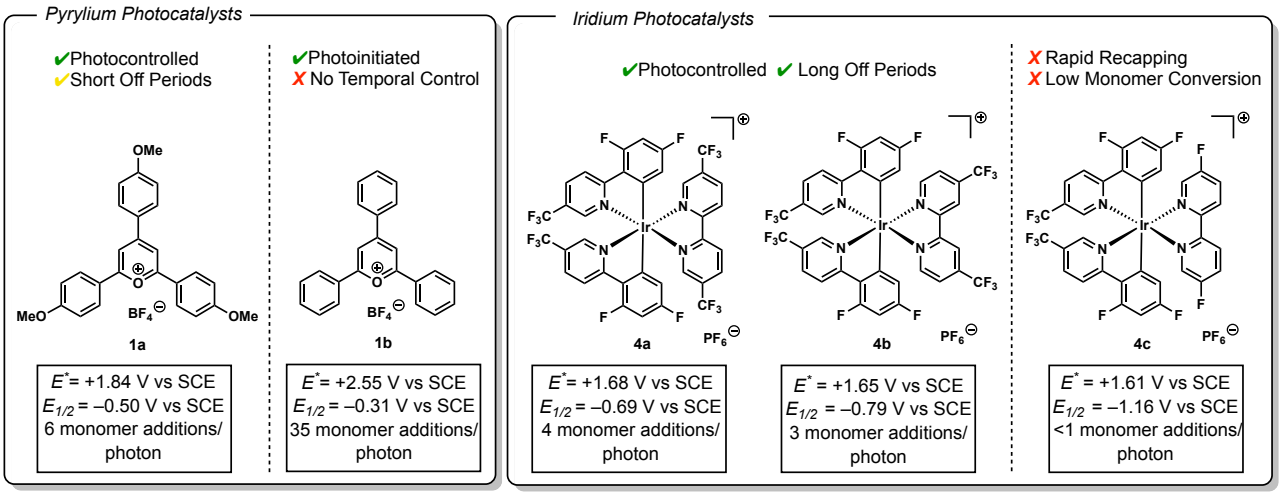


Fig. 6. Comparison of pyrylium and Iridium photocatalysts for photocontrolled cationic RAFT polymerizations. Reproduced with permission from ref 66. Copyright 2018 John Wiley and Sons.

study of cationic RAFT using a triflic acid initiator, thus suggesting that the control over the polymerization is coming from the RAFT equilibrium.[2]

***Step IV**: Turnover of PC* •. To confirm the catalyst turnover and polymer recapping, ESR experiments coupled with UV-vis spectroscopy were performed. The ESR signal of **1a**• in the presence of disulfide **3** resulted in instantaneous depletion of signal in the ESR and appearance of a UV-vis absorbance peak corresponding to ground state photocatalyst **1a**. This reveals that the photocatalyst turnover occurs through reduction of the thiocarbonylthio radical or disulfide species produced during the polymerization process.

Photocatalyst Quantum Yield Determines Temporal Control. Using a potassium ferrioxalate actinometer, we observed 6 monomer additions per photon absorbed when using catalyst **1a**. In contrast, photoinitiated cationic polymerizations typically lead to 200 monomer additions per photon absorbed,[62] suggesting that these lower quantum yields provide photocontrol. While we are able to achieve excellent "on"/ "off" control with catalyst **1a**, catalyst **1b** did not give temporal control over chain growth (Figure 5). The quantum yield for **1b** is roughly 6 times higher than that of **1a** (35 monomer additions per photon), suggesting that the recapping step (step IV) is much slower for **1b**. Thus, the polymerization using **1b** was photoinitiated. This can be further explained by the difference in ground state redox potentials (Table 1, $E^{\circ}_{1a+/1a\bullet}$ = –0.50 V versus SCE, and $E^{\circ}_{1b+/1b\bullet}$ = –0.32 V versus SCE).[62] Overall, the oxidation of the PC• by the thiocarbonyl radical is the key step to recap the cationic polymer chain and turnover the photocatalyst. Importantly, the redox characteristics of the photocatalyst in the ground state determine the temporal control of polymerization process.

Enhancing Temporal Control in Photocontrolled Cationic RAFT Polymerizations. Based on our mechanistic understanding of our photocontrolled cationic RAFT polymerization using pyrylium based photocatalysts, we concluded that the foundation for achieving photocontrol depends heavily on the interplay between chain activation (Step I) and deactivation (Step IV).

First, it is important that the excited state photocatalyst oxidizes the thiocarbonylthio chain end to generate carbocations (Figure 1b, Step I). Second, to render the polymer chains dormant in the absence of light, turnover of the photocatalyst must occur efficiently to reduce the thiocarbonylthio radical and recap the propagating cations (Figure 1b, Step IV). As mentioned previously, this was clearly observed when comparing photocatalysts **1a** and **1b**. While **1b** led to faster polymerization, the reaction could not be temporally controlled because of the inefficient chain recapping due to the low reduction potential of the photocatalyst in the ground state, **1b**• ($E_{1/2}$ = -0.31 V vs SCE).

While **1a** was able to achieve temporal control, at high conversions we started to observe some monomer conversion in the dark. This, in part, is due to pyrylium catalyst decomposition[2,63–65] and can be mitigated by switching to more stable photocatalysts. For this reason, we investigated polypyridyl Ir complexes, which have been extensively used as catalysts in small-molecule transformations. Not only are these Ir complexes more stable, but modification of the pyridyl ligands allows us to fine tune the excited state oxidation and ground state reduction potentials to achieve more efficient temporal control over the polymerization. Specifically, we turned our attention to photocatalysts, **4a**, **4b**, and **4c** since these complexes had a sufficiently high excited state oxidation potential to oxidize the CTA and were more reducing in the ground state than our initial pyrylium catalyst **1a** (Figure 6).[66]

4a and **4b** led to improved temporal control over the polymerization, with no monomer conversion observed during an off period of >20 hours and at high conversions. As expected for systems with good temporal control, the quantum yields for polymerizations using **4a** and **4b** were similar to that of **1a** (4 and 3

monomer additions/photon absorbed, respectively). Interestingly, attempts to polymerize IBVE using **4c** led to very low monomer conversion. We propose that recapping outcompetes efficient chain propagation for this catalyst, which is supported by a quantum yield for the polymerization that is less than 1 monomer addition per photon absorbed.

Overall, we found the outstanding stability of these Ir photocatalysts offered improved temporal control over polymer growth. By tuning the excited and ground state potentials of these Ir catalysts, we were able to regulate monomer additions and control the polymerization processes.

Expanding to Thioacetal Mediated Photocontrolled Cationic Degenerate Chain Transfer Polymerizations. Our understanding of the photocontrolled cationic RAFT process suggested that we could expand our system to other cationic polymerizations. In 2015, Kamigaito reported that thioacetals could be used to achieve a controlled cationic degenerate chain transfer (DCT) polymerization at low temperatures initiated by triflic acid.[67] While thioacetal species are generally easier to synthesize and more stable than their thiocarbonylthio counter parts, control over thioacetal mediated cationic polymerizations could only be achieved using non-hindered thioacetals derived from short alkyl chains.

We hypothesized that employing photoredox catalysis for this process would allow us to expand the scope of thioacetals that could be used to achieve a controlled polymerization.[4] Direct oxidation of a thioacetal chain end by a photocatalyst in the excited state would result in a radical cation that would undergo a mesolytic cleavage to form a thiyl radical and an oxocarbenium chain end. The oxocarbenium chain end could initiate polymer propagation and control over the polymerization could be acquired through a degenerate chain transfer process. Furthermore, we suspected that enhanced control of the polymerization would be achieved via efficient recapping of propagating cations through photocatalyst turnover, analogous to the photocontrolled polymerizations developed by Hawker and co-workers (Figure 7).[32]

We surveyed a series of thioacetal initiators and tested the polymerization of IBVE under blue LEDs using photocatalysts **1a** and **4a**. While we observe a match in the theoretical and experimental M_ns and narrow $Đ$ values

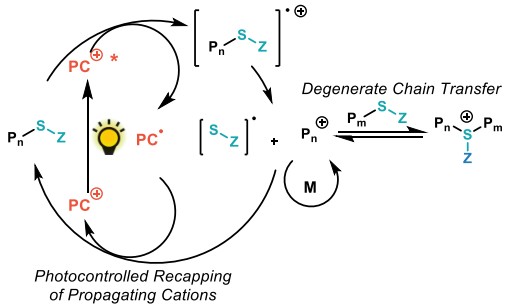


Fig. 7. Proposed mechanism for cationic photocontrolled degenerate chain transfer polymerization. Reproduced with permission from ref 4. Copyright 2020 Royal Society of Chemistry.

using photocatalyst **1a** and thioacetal **5a**, we did not observe temporal control during on/off studies (Figure 8a). Based on our previous mechanistic understanding, we suspected that the lack of photocontrol using **1a** was due to an insufficient reduction potential of **1a**• to turnover the photocatalyst and recap propagating chains. In switching to catalyst **4a**, which is 200 mV more reducing than **1a** in the ground state (Figure 6), we observed excellent temporal control, with the ability to turn off the polymerization for long periods of time in the dark (Figure 8a).

Taking advantage of the highly reducing ground state potential of **4a**, we were able to further improve on the degenerate chain transfer process by expanding the scope of thioacetals that could be used to achieve narrow $Đ$s. As compared to the acid initiated degenerate chain transfer developed by Kamigaito[67], a photocontrolled process provided greater control over a vast range of initiators. For example, in the acid-initiated polymerization, use of thioacetal

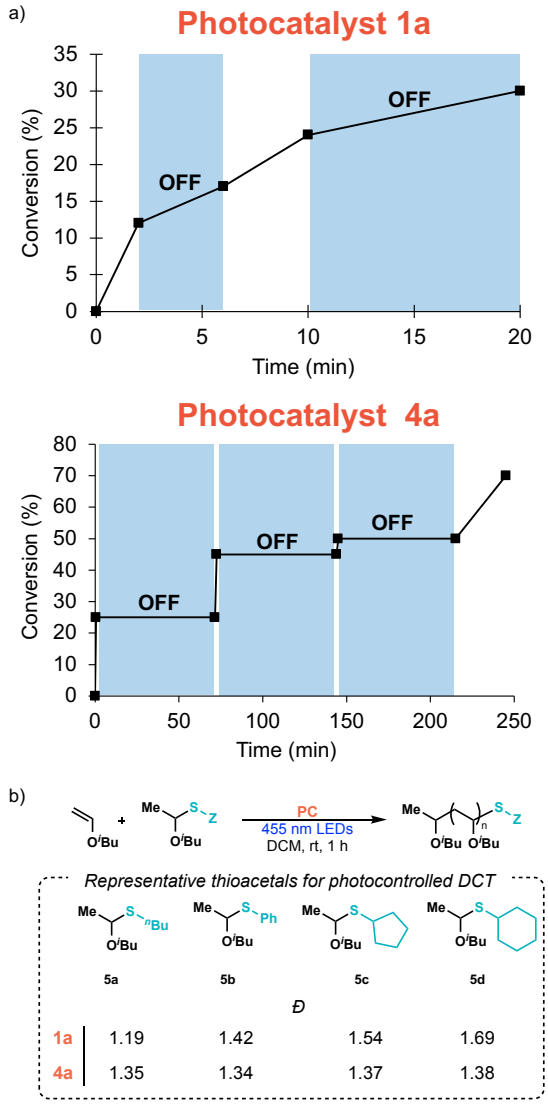


Fig. 8. a) On/off studies with IBVE and thioacetal **5a** with photocatalysts **1a** (top) and **4a** (bottom). b) Representative thioacetals that lead to polymerization control using more reducing **4a.** Reproduced with permission from ref 4. Copyright 2020 Royal Society of Chemistry.

5b to polymerize IBVE results in a broad $Đ$ of ~ 2.0. On the other hand, our photocontrolled process allows us to achieve p(IBVE) with $Đ$ of 1.42 using **1a** and a $Đ$ of 1.34 using **4a**, thus providing further evidence that photocatalyst turnover to recap propagating chains contributes to the control achieved in this photocontrolled degenerate chain transfer polymerization (Figure 8b).

Photocontrol Over Monomer Selectivity for One-Pot Synthesis of Multiblock Copolymers. Next, we looked to take advantage of the photocontrolled cationic polymerizations to control polymer structure on demand using light. We envisaged that we could merge our photocontrolled cationic polymerization with a photocontrolled radical polymerization to switch monomer selectivity in situ with light. Boyer[7,35,37,68,69] and others[70,71] have previously developed photocontrolled radical polymerizations using reducing photocatalysts and trithiocarbonate chain transfer agents. Moreover, Satoh and Kamigaito[72] have reported simultaneous cationic and radical polymerizations to make statistical block polymers, demonstrating that a single polymer chain can toggle between a cationic and radical chain end to change monomer selectivity. Based on these reports, we hypothesized that we could selectively excite either an oxidizing or a reducing photocatalyst in a single system through the appropriate selection of the wavelength of irradiation to change monomer selectivity–excitation of the oxidizing photocatalyst would promote the cationic polymerization of vinyl ethers and excitation of the reducing photocatalyst would lead the radical polymerization of acrylates (Figure 9a).[73]

We chose to use **1a** as our oxidizing photocatalyst and **Ir(ppy)$_3$** as the reducing photocatalyst. **Ir(ppy)$_3$** has been shown to give well-controlled radical polymerizations. Looking at the UV-Vis spectra of **1a** and **Ir(ppy)$_3$**, we observed a window at 520 nm where we could selectively excite **1a** and promote the cationic polymerization (Figure 9a). Then, upon switching to 450 nm light we posited that we would excite both catalysts and promote both the radical and cationic polymerizations. Using this to our advantage, we combined CTA **2b**, IBVE, methyl acrylate (MA), **1a**, and **Ir(ppy)$_3$** and irradiated with green LEDs to promote the cationic polymerization of IBVE. Switching to blue light after 80% conversion of IBVE, led to excitation of **Ir(ppy)$_3$** and the radical polymerization of MA to form a tapered diblock copolymer of poly(IBVE-*b*-MA) (Figure 9b(i)). Importantly, this experiment demonstrated that we could indeed switch the incorporation of different monomers by simply changing the wavelength of irradiation. Additionally, when the same reaction conditions were irradiated with just blue light, both photocatalyst were excited for the entire reaction and a multiblock copolymer of IBVE and MA was formed (Figure 9b(ii)).

This initial study showed that we could indeed switch polymerization mechanism at a growing chain end by changing wavelength of light. However, this two-photocatalyst system was still limited because the two polymerizations were not completely orthogonal–blue light excites both photocatalysts and promotes both polymerization mechanisms. The development of completely orthogonal switching between cationic and radical polymerizations still remained a challenge.

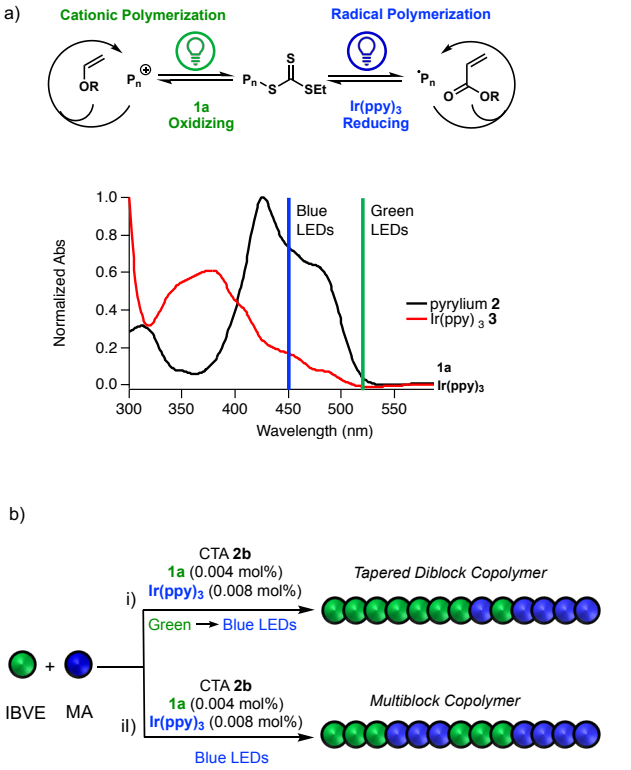


Fig. 9. a) General scheme depicting mechanistic switching to generate block copolymers (top) and UV-vis spectra of oxidizing catalyst **1a** and reducing catalyst **Ir(ppy)$_3$** (bottom). b) Examples of various block copolymers that can be synthesized by controlling light source and ratio of photocatalysts in solution. Reproduced with permission from ref 73. Copyright 2017 American Chemical Society.

Photoswitching Polymerizations for Spatiotemporal Control of Thermoset Properties. We posited that our photoswitchable polymerizations could be used to make multi material thermosets with spatiotemporally controlled physical properties. The Hawker and Boydston groups previously reported the use of photoinitiated polymerizations to spatially control epoxy-acrylate thermoset properties from a single resin.[74,75] However, these methods did not provide temporal control over crosslinking because they were photoinitiated and additives were necessary to covalently connect the two crosslinked networks to improve the properties at the material interfaces. We proposed that we could overcome these challenges by using our photoswitchable polymerization to selectively and covalently crosslink vinyl ethers and acrylates at growing chain ends by switching the wavelength of light.[3] Specifically, irradiating a resin composed of CTA **2b**, vinyl ethers, acrylates, along with photocatalysts **1a** and Ir(ppy)$_3$ with green light would selectively promote cationic polymerization and form a crosslinked vinyl ether film, while switching to blue light would induce radical polymerization and covalently incorporate acrylates into the vinyl ether film. Critically, the amount of acrylate cross-linker incorporated can be temporally tuned by varying blue light dosage. This method allows us to both

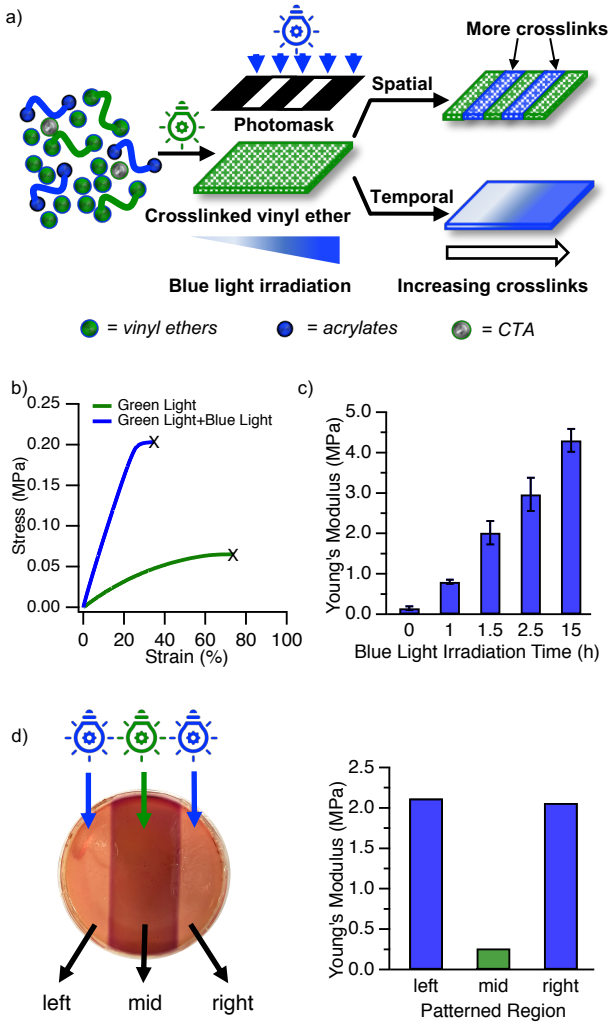


Figure 10. a) General scheme of spatiotemporal control of thermoset properties using photoswitchable polymerization. b) Stress-strain curves of crosslinked vinyl ether films synthesized under different light exposures. c) Young's modulus of crosslinked vinyl ether films using different amount of blue light exposure. *d)* Spatial control of crosslinked vinyl ether properties. Reproduced with permission from ref 3. Copyright 2021American Chemical Society.

spatially and temporally control the crosslink density of the thermoset by simply modulating the wavelength and dosage of light (Figure 10a).

To study the influence of light on thermoset properties, we first irradiated the vinyl ether-acrylate resin with green light for 30 min. This afforded a crosslinked vinyl ether film with Young's modulus (E) of 0.2 MPa. After switching to blue light irradiation for another 15 h, the E of the film increased to_0.8 MPa (Figure 10b), indicating that blue light promoted the radical polymerization and incorporated acrylate cross-linkers into the vinyl ether film. To demonstrate temporal control of thermoset properties, we varied the amount of blue light irradiation applied to the film after green light exposure. We found that the Young's modulus of vinyl ether film increased from 0.1 MPa to 4.3 MPa when the blue light irradiation time increased from 0-15 h (Figure 10c). These results are consistent with our hypothesis that by using photocontrolled switchable polymerizations, we can temporally control the incorporation of acrylate cross-linkers and tune the mechanical properties of the thermoset material.

In addition to temporal control, we also investigated the spatial control of crosslink density by using photomasks. We hypothesized that only the area receiving blue light irradiation would incorporate acrylate cross-linking. After 30 min green light exposure, we covered the mid-section of the vinyl ether film with a photomask and subjected the rest of the film to blue light irradiation for 2.5 h (Figure 10d). The E of mid-section (0.3 MPa) was significantly lower than the sections exposed to blue light (2 MPa). This result demonstrated that we can spatially create domains with different acrylate crosslink densities by patterning the blue light.

Overall, we successfully applied photoswitching polymerizations to gain both spatial and temporal control of vinyl ether thermoset properties. We expect to expand this methodology to 3D printing in the future.

Dual Stimuli controlled polymerizations for multi-block copolymer synthesis. As mentioned above, while switching between two wavelengths of light provided simple block copolymer structures derived from cationic and radical mechanisms, it was difficult to gain complete control over the polymer structure since blue light was able to initiate both radical and cationic polymerizations. Thus, we believed that finding a stimulus orthogonal to light would provide a better handle over block copolymer synthesis.

Our first attempts took advantage of a chemical oxidant ferrocenium tetrafluoroborate ($FcBF_4$) to directly oxidize CTA **2a** or **2b** to initiate cationic RAFT polymerization of IBVE.[76] The growing polymer chain can be reversibly terminated by adding a dithiocarbamate anion to recap the propagating cations and reduce ferrocene to ferrocenium. By alternating the addition of $FcBF_4$ and a dithiocarbamate anion, we achieved excellent temporal control over the polymer growth (Figure 11). We paired this chemically regulated cationic polymerization with photocontrolled radical polymerization to switch between the polymerization of IBVE and MA in one pot. Specifically, we mixed CTA **2b**,

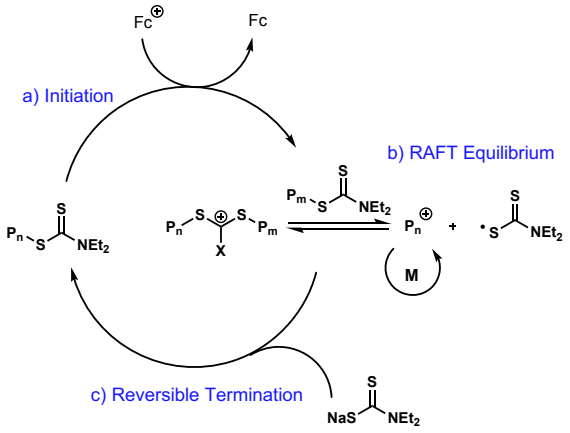


Fig. 11. Mechanism of chemically regulated cationic polymerization. Reproduced with permission from ref 76. Copyright 2018 American Chemical Society.

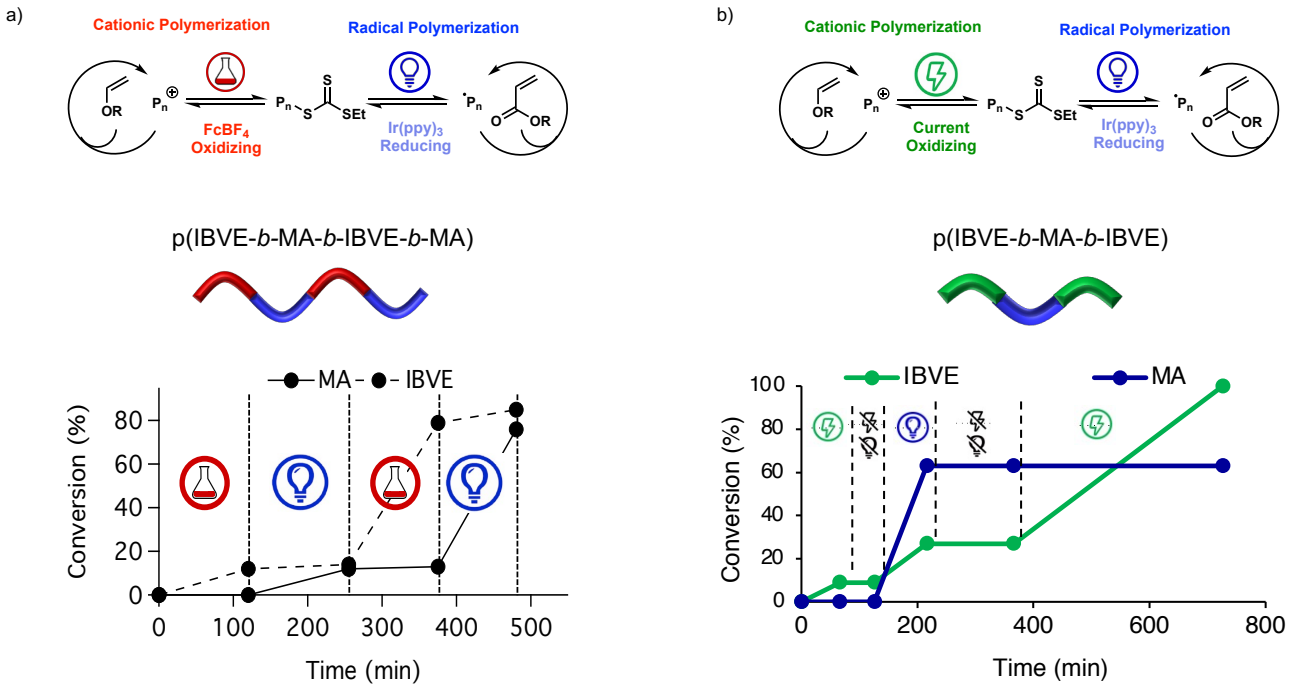


Figure 12. a) The use of chemical and photochemical orthogonal stimuli to generate block copolymers of IBVE and MA. b) The use of electrochemical and photochemical external stimuli to generate block copolymers of IBVE and MA. Reproduced with permission from ref 76,77. Copyright 2018 American Chemical Society and Copyright 2020 Elsevier.

IBVE, MA and **Ir(ppy)$_3$** in a single reaction. Irradiation of this mixture with blue light initiated the polymerization of MA, while addition of $FcBF_4$ promoted the polymerization of IBVE. This development of using orthogonal external stimuli allowed us to switch between photocontrolled radical polymerization and chemically controlled cationic polymerization, facilitating the synthesis of block copolymers in one pot (Figure 12a).

More recently, we sought to adapt this system to incorporate electrochemical methods by replacing the chemical oxidant, $FcBF_4$, with an oxidizing current or potential.[77] Using an electrochemical/photochemical switching method, we can toggle between electric current and light to produce well defined multi-block copolymers derived from MA and IBVE through a radical and cationic RAFT polymerization, respectively (Figure 12b). Both the electrochemical and chemical methods used to generate block copolymers are advantageous because they have allowed us to precisely generate multiblock copolymers of acrylates and vinyl ethers. This was unlike the dual photochemical switching in which we were limited by the use of blue light, which initiates both radical and cationic polymerizations.

Perspective and Future Outlook. Photocontrolled polymerizations have led to outstanding advances in polymer science and will continue to provide use for the development of advanced materials and complex architectures. While our current photocontrolled cationic systems have generated block copolymers of IBVE and MA, we are still limited to a narrow monomer scope. The structure of our CTAs which enable a controlled cationic polymerization limits our ability to polymerize other radical monomers outside of acrylates. This opens doors to new opportunities to develop other photocontrolled cationic polymerizations which could expand the types of monomers and mechanisms that can be used to generate block copolymers.

In fact, Kamigaito's recent work on photocontrolled cationic polymerizations using alkoxyamine initiators is an excellent example of alternative chain ends that could be leveraged for block copolymer synthesis.[78] Taking advantage of poly(vinyl ether)s and poly(*p*-methoxystyrene) capped with an alkoxyamine could enable mechanistic switching between cationic and nitroxide mediate polymerizations. We anticipate that these early developments in photocontrolled cationic polymerizations will inspire future work in external stimuli-controlled block copolymer synthesis.

Moreover, we would like to explore the solvent compatibility to extend the applications of our photocontrolled polymerization systems. So far, dichloromethane has been the best organic media to give controlled polymerizations. Studies on other organic solvents or aqueous media would open new doors for industrial and biomedical applications. Furthermore, besides using blue and green light, we would look at photocatalysts that could initiate polymerizations under other wavelengths of light such as violet or red light. In our current photocontrolled systems, blue light excites both iridium and pyrylium photocatalysts, inducing both radical and cationic polymerizations. The ability to use photocatalysts with non-overlapping absorbance would promote orthogonal photochemical switching of radical and cationic polymerizations.

We also believe that our photoswitchable crosslinking methodology will enable multimaterial 3D printing using green and blue light. Switching cationic and radical polymerizations at growing chain ends gives covalent formation of acrylate and vinyl ether thermosets, generating materials with spatiotemporally controlled crosslink

density. We expect that with 3D printing techniques, we could selectively incorporate different monomers in one resin and form three-dimensional multimaterial networks with controlled mechanical properties.

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Notes

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Biographical Information

Renee J. Sifri received her B.Sc. in chemistry from the University of California, Berkeley in 2016. Afterwards, she went on to complete her Ph.D. in synthetic polymer chemistry with Prof. Brett P. Fors at Cornell University. While in the Fors group, she focused on developing new synthetic methods to influence polymer properties. One subset of her work focused on achieving a photocontrolled cationic polymerization of vinyl ethers initiated by thioacetals. In 2021, she joined Process Research & Development at Merck & Co., Inc. where she is now using state-of-the-art organic and organometallic chemistry to address critical problems in drug discovery and drug development.

Yuting Ma received her B.Sc. from Nanjing University in 2014 and went to Cornell University to pursue her Ph.D. with Prof. Brett P. Fors. Her current research focuses on development of photoswitchable polymerization mechanisms for spatiotemporal control of thermoset properties.

Brett P. Fors is currently a professor at Cornell University. He received his B.Sc. from Montana State University in 2006 and earned his Ph.D. with Stephen L. Buchwald at the Massachusetts Institute of Technology (2011). After that, he went on to do postdoctoral research with Craig J. Hawker at the University of California, Santa Barbara. Brett started his independent career in 2014 at Cornell University and his research focuses on the development of new polymerization methodologies to control polymer structures and functions.

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