On Demand Switching of Polymerization Mechanism and Monomer Selectivity with Orthogonal Stimuli

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Supporting Information

ABSTRACT: The development of next-generation materials is coupled with the ability to predictably and precisely synthesize polymers with well-defined structures and architectures. In this regard, the discovery of synthetic strategies that allow on demand control over monomer connectivity during polymerization would provide access to complex structures in a modular fashion and remains a grand challenge in polymer chemistry. In this Article, we report a method where monomer selectivity is controlled during the polymerization by the application of two orthogonal stimuli. Specifically, we developed a cationic polymerization where polymer chain growth is controlled by a chemical stimulus and paired it with a compatible photocontrolled radical polymerization. By alternating the application of the chemical and photochemical stimuli the incorporation of vinyl ethers and acrylates could be dictated by switching between cationic and radical polymerization mechanisms, respectively. This enables the synthesis of multiblock copolymers where each block length is governed by the amount of time a stimulus is applied, and the quantity of blocks is determined by the number of times the two stimuli are toggled. This new method allows on demand control over polymer structure with external influences and highlights the potential for using stimuli-controlled polymerizations to access novel materials.

INTRODUCTION

Macromolecular properties are inherently influenced by polymer molar mass, monomer sequence, and architecture, as made evident by the diversity of functions observed among bio-macromolecules derived from a limited library of molecular building blocks. Therefore, the discovery of synthetic techniques that give increased control over monomer connectivity and structure in a polymer will broaden the range of applications of these materials. Chemists have made significant progress in making well-defined materials with the development of “living” polymerizations that enable the formation of macromolecules with predictable molar masses (M_n) and narrow molar mass distributions (dispersity, D) with high chain-end fidelity capable of postpolymerization modification. Even greater control over polymerization processes has recently been achieved through regulation of chain growth with various external stimuli (i.e., thermal, chemical, mechanoochemical, electrochemical, and photochemical). However, the ability to precisely control monomer connectivity during a polymerization remains a grand challenge.

Temporal control of polymer chain growth in externally regulated polymerizations provides an excellent opportunity to precisely control macromolecular structure and function. To exploit this unique level of control, we envisioned a system where monomer selectivity at a given polymer chain-end could be switched on demand with two different stimuli. This strategy would enable the one-pot synthesis of polymers where the monomer connectivity would be precisely dictated by external influences and would be a step closer to nature’s ability to perfectly control polymer sequence.

To achieve this goal, we were inspired by systems developed by Kamigaito and co-workers where both radical and cationic polymerization processes are active in a single reaction, allowing blocks of two monomers that react via different mechanisms to be randomly incorporated into the same polymer chain. We reasoned that temporal control over the cationic and radical mechanisms via two stimuli would allow on demand switching of polymerization mechanism in situ and lead to precise control over the block structure of the final polymer.

Taking a step toward this challenge, our group recently developed a two-photocatalyst system that took advantage of photocontrolled cationic and radical reversible addition–fragmentation chain transfer (RAFT) polymerizations (Figure 1a). Irradiating our system with green light led to promotion of the cationic polymerization of isobutyl vinyl ether (IBVE) through selective excitation of an oxidizing photocatalyst. Alternatively, irradiation with blue light excited both the reducing and oxidizing photocatalysts in solution leading to simultaneous radical polymerization of...
methyl acrylate (MA) and cationic polymerization of IBVE
(Figure 1a). Although this two-photocatalyst system
demonstrated that the polymerization mechanism could be changed
in situ, selective promotion of the radical mechanism was not
possible due to the overlap of the absorption spectra of the two
catalysts. In order to overcome this limitation, polymerization
processes where chain growth is regulated by two orthogonal
and compatible stimuli are necessary to allow selective
promotion of either the radical or cationic pathways (Figure
1b).

Herein, we report the development of a new chemically
controlled cationic polymerization of vinyl ether monomers.
Combining this cationic polymerization with a photocontrolled
radical process enables completely orthogonal switching of
polymerization mechanism at a single chain-end in situ. This
increased level of control is successfully applied to the one-pot
synthesis of multiblock copolymers of IBVE and MA, without
the need for subsequent polymer isolation, purification, or
chain-end modification (Figure 1c).

■ RESULTS AND DISCUSSION
To gain precise control over polymerization mechanism in situ,
we set out to develop a cationic polymerization regulated by a
stimulus orthogonal and compatible with the photocontrolled
radical polymerization process. In recent years, chemists have
investigated a number of stimuli compatible with light to
induce polymerization, including mechanical force, electricity,
redox events triggered by chemical additives, and temperature.
Among those, we opted for a chemical stimulus that could be
used to initiate and reversibly terminate the propagating cation.
We hypothesized that the cationic polymerization could be
initiated with a mild single electron oxidant (Figure 2a).

Specifically, we reasoned that the addition of ferrocenium
salts (FcX) should selectively oxidize the chain transfer agents
(CTA) 1a or 1b and, consequently, shuttle a predictable
amount of an oxocarbenium ion into the RAFT mechanism
(Figure 2b).57 Importantly, temporal control over chain
growth could be achieved through the addition of a
dithiocarbamate anion, 2a, to recap propagating cations as
well as reduce any remaining ferrocenium to ferrocene,
completely halting the polymerization (Figure 2c). This
process would provide a cationic polymerization that could
be reversibly activated/deactivated through the addition of two
chemical species. Moreover, the rate of polymerization could
be dictated by the concentration of FcX added.

To test our hypothesis, we examined the use of ferrocenium
tetrafluoroborate (FcBF4) to initiate the cationic polymer-
ization of vinyl ether monomers (M = monomer).

Table 1. Optimization of the Cationic Polymerization of
IBVE Using FcBF4

| entry | [IBVE]:[CTA]:[Fc+] conversion (%) | M_meth (kg/mol) | M_exp (kg/mol) | D |
|-------|---------------------------------|-----------------|----------------|---|
| 1     | 100:1:0.01                      | >99             | 10.2           | 10.3 | 1.11|
| 2     | 100:1:0                         | 0               | 0              | 0   | 0   |
| 3     | 100:0.0:0.01                    | 89              | 243            | 2.35|
| 4     | 100:1:0.0025                    | >99             | 10.2           | 14.7 | 1.14|
| 5     | 100:1:0.0025                    | 0               | 0              | 0   | 0   |
| 6     | 100:1:5.0                       | >99             | 10.2           | 11.1 | 1.45|
| 7     | 100:1:1.0                       | >99             | 10.2           | 10.6 | 1.10|
| 8     | 200:1:0.01                      | >99             | 20.2           | 19.0 | 1.11|
| 9     | 400:1:0.02                      | >99             | 40.2           | 35.1 | 1.16|
| 10    | 600:1:0.04                      | >99             | 60.5           | 54.6 | 1.28|
| 11    | 800:1:0.04                      | >99             | 80.5           | 65.3 | 1.24|
| 12    | 100:1:0.01                      | >99             | 10.2           | 10.1 | 1.25|

[(IVBE) = 3.1 M (in DCM); reaction volume = 0.65 mL. bM_meth = [M]/[CTA] × MW_monomer × conversion + MW_CTA. 12cM_exp determined by gel permeation chromatography with a multangle light scattering detector. 12cCTA = 1b. 12eOpen to air.}
Importantly, the experimental molar mass aligned well with the theoretical value, demonstrating that this system has excellent initiator efficiency. Control experiments demonstrated that performing the reaction in the absence of FcBF$_4$ gave no polymerization (Table 1, entry 2), while removal of 1a gave a broad dispersity, high molecular weight polymer (Table 1, entry 3). At higher loadings of FcBF$_4$ (5 mol % relative to IBVE), experimental $M_n$’s deviated from theoretical values (Table 1, entry 4), through promotion of uncontrolled polymerization pathways like those observed in the absence of 1a. Additionally, at very low concentrations of FcBF$_4$ (0.0025 mol %), no conversion of monomer is observed (Table 1, entry 5), unless the more active CTA 1b is used (Table 1, entry 6).

Interestingly, initiating the polymerization with FcBF$_4$ proved to be effective at synthesizing high molecular weight poly(IBMVE) up to 65 kg/mol with narrow $D$ values (Table 1, entries 7–11). This is a significant advantage over our previously reported photocontrolled cationic polymerizations where we observed a loss in control when targeting molar masses above 20 kg/mol. We attribute this increased efficiency to the lower oxidation potential of ferrocene (Fc) relative to 1a, creating milder polymerization conditions that limit the generation of new chains via direct oxidation of IBVE, a previously observed undesired pathway.$^{55}$ Under the reported reaction conditions, high degrees of polymerization were achieved within 3 h. Additionally, these conditions provide a polymerization robust enough to proceed under ambient atmosphere while maintaining low $D$ and excellent control over the final polymer $M_n$ (Table 1, entry 12).$^{58}$ This result demonstrates the practicality of the polymerization and avoids the requirement of advanced air and water free techniques.

Importantly, the new FcBF$_4$-initiated process delivered effective cationic polymerization of a range of vinyl ether monomers that had varied steric and electronic characteristics, along with para-methoxystyrene. In each case, excellent agreement between theoretical and experimental $M_n$’s was observed while maintaining narrow $D$ values (Figure 3).

To grow multiblock copolymers employing this method excellent chain-end fidelity is essential. To demonstrate that active chain-ends are maintained in these polymerizations, we synthesized a poly(IBMVE) macroinitiator under our standard conditions and then chain-extended it with ethyl vinyl ether (EVE) to give a well-defined poly(IBMVE-$b$-EVE) diblock copolymer (see the Supporting Information, Figures S7–S9).

Importantly, we observed a clear shift in the size exclusion chromatography trace to higher molar mass with no tailing, demonstrating that the dithiocarbamate chain-ends are intact after the polymerization.

Thus far, we have shown that ferrocenium is an effective mediator of the cationic polymerization vinyl ethers. However, the ability to temporally control chain growth on demand is required to pair this system with a photocontrolled radical polymerization and enable switching of polymerization.

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**Figure 3.** Substrate scope of vinyl monomers that can be polymerized via ferrocenium-mediated cationic RAFT polymerization.

**Figure 4.** Temporal control over polymer initiation and reversible termination via the addition of FcBF$_4$ and 2, respectively.

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mechanism. We hypothesized that the chemically controlled polymerization could be reversibly terminated through the addition of 1 equiv of the dithiocarbamate anion relative to the amount of FcBF₄ added to initiate polymerization (Figure 2c). Theoretically, the anion should cap propagating cations to generate a dormant chain-end, while reducing unreacted Fc⁺ to Fc, preventing the generation of new propagating cations. To test this hypothesis, polymerization of IBVE was initiated through the addition of FcBF₄ under our standard conditions (Figure 4). After 25 min, 2 was added, and conversion of the monomer immediately halted. Importantly, the subsequent addition of FcBF₄ once again initiated the cationic polymerization. This process was repeated multiple times, demonstrating excellent temporal control over the polymerization with a chemical stimulus.

Significantly, our new chemically regulated cationic polymerization method is orthogonal to visible light and should be compatible with the radical photoinduced electron transfer-RAFT (PET-RAFT) polymerizations employing Ir(ppy)₃ as the photocatalyst. Therefore, combining these two polymerizations in one pot should enable switching of polymerization mechanisms through modulation of the two stimuli, although consideration must be given to the mechanism of switching.

We have previously demonstrated efficient initiation of the radical polymerization of MA from a poly(IBVE) macroinitiator due to the favorable formation of an α-acyl cation, which will enable efficient chain extension of MA from poly(IBVE). Conversely, initiation of the polymerization of IBVE from the poly(MA) chain-end could be problematic because it requires the formation of a high energy α-acyl cation. However, we proposed that we could circumvent this issue by taking advantage of the small amounts of incorporation of IBVE during the radical copolymerization with MA. As previously shown by Kamigaito, the majority of dormant chain-ends are thioacetals derived from vinyl ether monomers due to the radical RAFT fragmentation kinetics. Thioacetals are effective at generating a cation and can promote vinyl ether homopolymerization.

Indeed, when exposing 1b, equimolar amounts of MA and IBVE, and 0.02 mol % Ir(ppy)₃ to blue light, poly(MA) is synthesized with 20−30% incorporation of IBVE (Figure 5a). Chain-end analysis by ¹H NMR of the final polymer revealed the presence of greater than 90% thioacetal chain-ends (Figure 5b). Gratifyingly, upon removal of blue light irradiation and addition of FcBF₄ to the crude reaction mixture, the polymer was successfully chain-extended via cationic polymerization to give a well-defined poly(MA-b-IBVE) block polymer (Figure 5a). This result demonstrates successful switching from radical to cationic polymerization in situ through modulation of the external stimuli, which is a key requirement for the controlled synthesis of multiblock copolymers. This approach represents a significant advance over our previously reported photocontrolled switching method, due to the orthogonal stimuli that enable us to selectively invoke the radical mechanism.

With the ability to switch polymerization mechanon demand, we set out to explore the range of copolymer sequences that can be targeted through modulation of the order of applied stimuli. Figure 6a shows the monomer conversion over time for the synthesis of poly(MA-b-IBVE) diblock copolymer, where we first promoted the radical polymerization with light followed by the chemically controlled cationic polymerization. This can be extended to triblock copolymers under the same conditions by adding an additional switching event. After the first mechanistic switch from radical...
to cationic polymerization to generate poly(MA-b-IBVE), vinyl ether polymerization can be successfully halted by the addition of 2. Subsequent re-exposure to blue light initiates radical polymerization of MA resulting in poly(MA-b-IBVE-b-MA) triblock with predictable molar mass and narrow dispersity (Figure 6b).

Interestingly, from the same solution conditions the inverse triblock copolymer can be synthesized by simply altering the sequence of the two applied stimuli. Specifically, initiating polymerization of IBVE, in the presence of MA and Ir(ppy)₃, by treatment with FcBF₄ in the absence of blue light (Figure 6c), we observed solely conversion of IBVE over the first hour. Addition of 2 resulted in termination of the cationic polymerization, followed by irradiation with blue light for 2 h to promote radical polymerization of the acrylate. Turning the light off and treating the reaction with 0.05 mol % FcBF₄ resulted in a clean mechanistic switch from radical polymerization of MA to the cationic polymerization of vinyl ethers, generating a well-defined poly(IBVE-b-MA-b-IBVE) triblock. This can be taken a step further, generating a poly(IBVE-b-MA-b-IBVE-b-MA) tetrablock copolymer (Figure 6d) by adding one additional switching event to the last triblock copolymer. It is worth noting that the length of each block can be controlled by the length of time the stimulus is applied, and the number of blocks can be dictated by the number of times the stimuli are toggled. These data clearly show that pairing orthogonal stimuli to control polymerization mechanism and monomer selectivity is a powerful approach toward the synthesis of advanced polymeric structures.

CONCLUSION

In conclusion, we have developed a system that enables switching of polymerization mechanism and monomer selectivity in situ with two external stimuli. The identification of a cationic polymerization controlled by a chemical stimulus that was both orthogonal and compatible with the phototriggered radical polymerization was key to achieving efficient switching. We demonstrated that ferrocenium salts were highly efficient initiators for the cationic RAFT polymerization of vinyl ethers and showed that reversible termination could be achieved through the addition of a dithiocarbamate anion. By pairing this new chemically controlled cationic polymerization with a photoswitched RAFT polymerization, we were able to selectively and reversibly promote the polymerization of vinyl ethers or acrylates. Under identical solution conditions, this enabled the synthesis of an array of well-defined multiblock copolymers where the final structure was dictated by the two stimuli; the length of each block was controlled by the amount of time the stimulus was applied, and the number of blocks was governed by the alternating application of the two stimuli. These results demonstrate the power of combining controlled polymerization processes that are regulated by different external stimuli and lay the groundwork for developing systems where polymer sequence, structure, and architecture are controlled on demand via external influences.

ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.8b00401.
Transfer Reactions for Macromolecular Syntheses. Nanoparticles to Cu Catalysts. ATRP by Promoting Interfacial Electron Transfer from Piezoelectric Polymeric Materials to Cu Catalysts. ACS Macro Lett. 2017, 6, 546–549.

(18) Chmielarz, P.; Fantin, M.; Park, S.; Isse, A. A.; Gennaro, A.; Maguen, A. J. D.; Sobkowiak, A.; Matyjaszewski, K. Electrochemically Mediated Atom Transfer Radical Polymerization (EATRP). Angew. Chem., Int. Ed. 2015, 54, 5172–5201.

(19) Chen, M.; Zhong, M.; Johnson, J. A. Light-Controlled Radical Polymerization: Mechanisms, Methods, and Applications. Chem. Rev. 2016, 116, 10167–10211.

(20) Corrigan, N.; Shannugam, S.; Xu, J.; Boyer, C. Photocatalysis in Organic and Polymer Synthesis. Chem. Soc. Rev. 2016, 45, 6165–6212.

(21) Ciftci, M.; Yoshikawa, Y.; Yagci, Y. Living Cationic Polymerization of Vinyl Ethers through a Photoinduced Radical Oxidation/Addition/Deactivation Sequence. Angew. Chem., Int. Ed. 2017, 56, 519–523.

(22) Kitahata, C.; Schmitz, C.; Strehel, V.; Yagci, Y.; Strehmel, B. Near-Infrared Sensitized Photoinduced Atom-Transfer Radical Polymerization (ATRP) with a Copper (II) Catalyst Concentration in the ppm Range. Angew. Chem., Int. Ed. 2018, 57, 7898–7902.

(23) Dadasi-Silat, S.; Doran, S.; Yagci, Y. Photoinduced Electron Transfer Reactions for Macromolecular Syntheses. Chem. Rev. 2016, 116, 10212–10275.

(24) Trott, J. T.; Fors, B. P. Organic Catalysts for Photocontrolled Polymerizations. Synlett 2016, 27, 702–713.

(25) McKenzie, T. G.; Fu, Q.; Uchiyama, M.; Sato, K.; Xu, J.; Boyer, C.; Kamigaito, M.; Qiao, G. G. Beyond Traditional RAFT: Alternative Activation of Thiacarbonyl Compounds for Controlled Polymerization. Adv. Sci. 2016, 3, 1500394.

(26) Fors, B. P.; Hawker, C. J. Control of a Living Radical Polymerization of Methacrylates by Light. Angew. Chem., Int. Ed. 2012, 51, 8850–8853.

(27) Konkolewicz, D.; Schröder, K.; Buback, J.; Bernhard, S.; Matyjaszewski, K. Visible Light and Sunlight Photoinduced ATRP with Ppm of Cu Catalyst. ACS Macro Lett. 2012, 1, 1219–1223.

(28) Anastasaki, A.; Nikolou, V.; Zhang, Q.; Burns, J.; Samanta, S. R.; Waldron, C.; Haddleton, A. J.; McHale, R.; Fox, D.; Percec, V.; et al. Copper(II)/Tertiary Amine Synergy in Photoinduced Living Radical Polymerization: Accelerated Synthesis of αω-Functional and αω-Heterofunctional Poly(Acrylates). J. Am. Chem. Soc. 2014, 136, 1141–1149.

(29) Treat, N. J.; Sprake, H.; Kramer, J. W.; Clark, P. G.; Barton, B. E.; Read de Alaniz, J.; Fors, B. P.; Hawker, C. J. Metal-Free Atom Transfer Radical Polymerization. J. Am. Chem. Soc. 2014, 136, 16096–16101.

(30) Pan, X.; Malhotra, N.; Simakova, A.; Wang, Z.; Konkolewicz, D.; Matyjaszewski, K. Photoinduced Atom Transfer Radical Polymerization with Ppm-Level Cu Catalyst by Visible Light in Aqueous Media. J. Am. Chem. Soc. 2015, 137, 15430–15433.

(31) Jones, G. R.; Whittlefield, R.; Anastasaki, A.; Haddleton, D. M. Aqueous Copper(II) Photoinduced Polymerization of Acrylates: Low Copper Concentration and the Importance of Sodium Halide Salts. J. Am. Chem. Soc. 2016, 138, 7346–7352.

(32) Theriot, J. C.; Lim, C.-H.; Yang, H.; Ryan, M. D.; Musgrave, C. B.; Miyake, G. M. Organocatalyzed Atom Transfer Radical Polymerization Driven by Visible Light. Science 2016, 352, 1082–1086.

(33) Pearson, R. M.; Lim, C.-H.; McCarthy, B. G.; Musgrave, C. B.; Miyake, G. M. Organocatalyzed Atom Transfer Radical Polymerization Using N-Aryl Phenoxazines as Photoinductive Catalysts. J. Am. Chem. Soc. 2016, 138, 11398–11407.

(34) Wang, Z.; Pan, X.; Yan, J.; Dadasi-Silat, S.; Xie, G.; Zhang, J.; Wang, Z.; Xia, H.; Matyjaszewski, K. Temporal Control in Mechanically Controlled Atom Transfer Radical Polymerization Using Low Ppm of Cu Catalyst. ACS Macro Lett. 2017, 6, 546–549.

(35) Ramsey, B. L.; Pearson, R. M.; Beck, L. R.; Miyake, G. M. Photoinduced Organocatalyzed Atom Transfer Radical Polymerization Using Continuous Flow. Macromolecules 2017, 50, 2668–2674.

(36) Xu, J.; Jung, K.; Atme, A.; Shannugam, S.; Boyer, C. A. Robust and Versatile Photoinduced Living Polymerization of Conjugated and Unconjugated Monomers and Its Oxygen Tolerance. J. Am. Chem. Soc. 2014, 136 (14), 5508–5519.

(37) Shannugam, S.; Xu, J.; Boyer, C. Exploiting Metalloporphyrins for Selective Living Radical Polymerization Tunable over Visible Wavelengths. J. Am. Chem. Soc. 2015, 137, 9174–9185.

(38) Shannugam, S.; Xu, J.; Boyer, C. Utilizing the Electron Transfer Mechanism of Chlorophyll a under Light for Controlled Radical Polymerization. Chem. Sci. 2015, 6, 1341–1349.

(39) Shannugam, S.; Xu, J.; Boyer, C. Light-Regulated Polymerization under Near-Infrared/Far-Red Irradiation Catalyzed by Bacteriochlorophyll a. Angew. Chem., Int. Ed. 2016, 55, 1036–1040.

(40) Xu, J.; Shannugam, S.; Fu, C.; Aguey-Zinsou, K.-F.; Boyer, C. Selective Photoactivation: From a Single Unit Monomer Insertion Reaction to Controlled Polymer Architectures. J. Am. Chem. Soc. 2016, 138, 3094–3106.

(41) Shannugam, S.; Boyer, C. Stereoo-, Temporal and Chemical Control through Photoactivation of Living Radical Polymerization: Synthesis of Block and Gradient Copolymers. J. Am. Chem. Soc. 2015, 137, 9988–9999.

(42) Chen, M.; MacLeod, M. J.; Johnson, J. A. Visible-Light-Controlled Living Radical Polymerization from a Trithiocarbonate Initiator Mediated by an Organic Photoredox Catalyst. ACS Macro Lett. 2015, 4, 566–569.

(43) Theriot, J. C.; Miyake, G. M.; Boyer, C. A. N,N-Diaril Dihydrophenazines as Photoredox Catalysts for PET-RAFT and Sequential PET-RAFT/O-ATRP. ACS Macro Lett. 2017, 7, 662–666.

(44) Shi, M.; Dong, Q.; Wang, D.; Byers, J. A. Electrochemically Switchable Ring-Opening Polymerization of Lactide and Cyclohexene Oxide. J. Am. Chem. Soc. 2018, 140, 5686–5690.

(45) Kituchi, S.; Saito, K.; Akita, M.; Inagaki, A. Nonradical Light-Controlled Polymerization of Styrene and Vinyl Ethers Catalyzed by an Iridium—Palladium Photocatalyst. Organometallics 2018, 37, 359–366.

(46) Guerre, M.; Uchiyama, M.; Lopez, G.; Améduri, B.; Sato, K.; Kamigaito, M.; Ladmiral, V. Synthesis of PEVE-b-P(CTFE-AHE-EVE) Block Copolymers by Sequential Cationic and Radical RAFT. Polym. Chem. 2018, 9, 352–361.

(47) Shannugam, S.; Kamigaito, M. Manganese-Based Controlled/Living Radical Polymerization of Vinyl Acetate, Methyl Acrylate, and Styrene: Highly Active, Versatile, and Photoresponsive Systems. Macromolecules 2008, 41, 7359–7367.

(48) Guerre, M.; Uchiyama, M.; Lopez, G.; Améduri, B.; Sato, K.; Kamigaito, M.; Ladmiral, V. Synthesis of PEVE-b-P(CTFE-AHE-EVE) Block Copolymers by Sequential Cationic and Radical RAFT. Polym. Chem. 2018, 9, 352–361.

(49) Aoshima, H.; Uchiyama, M.; Satoh, K.; Kamigaito, M. Manganese-Based Controlled/Living Radical Polymerization of Vinyl Acetate, Methyl Acrylate, and Styrene: Highly Active, Versatile, and Photoresponsive Systems. Macromolecules 2008, 41, 7359–7367.
Reversible Activation of Dormant Species with Dual Activity. Angew. Chem., Int. Ed. 2014, 53, 10932−10936.

(53) Kottisch, V.; Michaudel, Q.; Fors, B. P. Photocontrolled Interconversion of Cationic and Radical Polymerizations. J. Am. Chem. Soc. 2017, 139, 10665−10668.

(54) Previous work employing two wavelengths of light to promote PET-RAFT and ROP polymerization mechanisms from two different chain-ends can be found. Fu, C.; Xu, J.; Boyer, C. Photoacid-Mediated Ring Opening Polymerization Driven by Visible Light. Chem. Commun. 2016, 52, 7126−7129.

(55) Kottisch, V.; Michaudel, Q.; Fors, B. P. Cationic Polymerization of Vinyl Ethers Controlled by Visible Light. J. Am. Chem. Soc. 2016, 138, 15535−15538.

(56) Michaudel, Q.; Chauviré, 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.

(57) CTAs 1a and 1b were selected due to the control provided in cationic polymerizations and their potential to function in radical polymerizations: See ref 49.

(58) Yeow, J.; Chapman, R.; Gormley, A. J.; Boyer, C. Up in the Air: Oxygen Tolerance in Controlled/Living Radical Polymerisation. Chem. Soc. Rev. 2018, 47, 4357.

(59) Kumagai, S.; Nagai, K.; Satoh, K.; Kamigaito, M. In-Situ Direct Mechanistic transformation from RAFT to Living Cationic Polymerization for (Meth)acrylate-Vinyl Ether Block Copolymer. Macromolecules 2010, 43, 7523−7531.