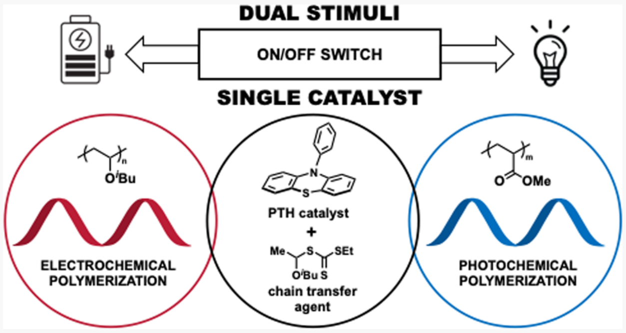
JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
pubs.acs.org/JACS
Article

Interconvertible Living Radical and Cationic Polymerization using a Dual Photoelectrochemical Catalyst

Andrei Nikolaev,† Zhipeng Lu,† Arunavo Chakraborty, Lior Sepunaru,* and Javier Read de Alaniz*

Cite This: J. Am. Chem. Soc. 2021, 143, 12278−12285
Read Online

ABSTRACT: The necessity of well-tuned reactivity for successful controlled polymer synthesis often comes with the price of limited monomer substrate scope. We demonstrate here the on-demand interconversion between living radical and cationic polymerization using two orthogonal stimuli and a dual responsive single catalyst. The dual photo- and electrochemical reactivity of 10-phenyl-phenothiazine catalyst provides control of the polymer's molar mass and composition by orthogonally activating the common dormant species toward two distinct chemical routes. This enables the synthesis of copolymer chains that consist of radically and cationically polymerized segments where the length of each block is controlled by the duration of the stimulus exposure. By alternating the application of photochemical and electrochemical stimuli, the on-demand incorporation of acrylates and vinyl ethers is achieved without compromising the end-group fidelity or dispersity of the formed polymer. The results provide a proof-of-concept for the ability to substantially extend substrate scope for block copolymer synthesis under mild, metal-free conditions through the use of a single, dual reactive catalyst.



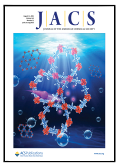
INTRODUCTION

The development of "living" polymerization has a profound impact on polymer synthesis, enabling control over polymer architecture, polymer sequence, and chain-end fidelity.[1−5] Recent advances in controlling the reversible interconversion between dormant and active species with an external stimulus have provided the ability to molecularly control polymer synthesis with high spatial and temporal resolution.[6,7] This external stimulus is commonly either photochemical or electrochemical excitation.[8−13] Thanks to advances in catalyst design, these methodologies are compatible with modern cationic and radical polymerization techniques that enable the use of monomers ranging from electron-deficient acrylates to electron-rich vinyl ethers. The end products of polyacrylates and poly(vinyl ethers) have a broad range of applications such as adhesives, lubricants, anticorrosion agents, textiles, and high-temperature-resistant elastomers.[14,15] However, at the moment, the synthesis of block copolymers encompassing both acrylates and vinyl ether-based polymers either requires the use of multiple catalysts or suffers from the inability to selectively activate each catalyst, which compromises exclusive activation of either the cationic or radical polymerization mechanism (vide infra).[16] Similar challenges were found in interconvertible living cationic and radical polymerizations.[17,18] Block copolymers are an important class of soft materials in which the molecular design and properties of distinct polymer chains affects the formation of well-defined mesophases on the nanometer length scale.[19] Control over these properties through synthesis of new block copolymers creates opportunities in a variety of applications ranging from drug delivery to microelectronic materials.[20−22]

We, therefore, sought to incorporate divergent "trigger-induced" chemical pathways into one-pot polymerization that will provide a new approach to synthesize complex block copolymers with a broader range of monomer scope. However, accomplishing this requires a novel design of multi-stimuli-responsive systems that can readily control the polymerization mechanism by turning "on" or "off" the desired stimuli for chemically orthogonal pathways.[23]

Fundamentally, the stimuli-controlled polymerization strategies can be classified into two main categories: those controlled by endogenous chemical additives (e.g., the addition of acid and bases to shift the equilibrium position) and those that utilize exogenous triggering that consequently causes a change in the system's chemical potential (e.g., photochemical, electrochemical, and thermal). Kamigaito and co-workers have demonstrated the ability to switch between reversible addition−fragmentation chain transfer (RAFT) of acrylates

Received: May 26, 2021
Published: July 27, 2021



https://doi.org/10.1021/jacs.1c05431
J. Am. Chem. Soc. 2021, 143, 12278−12285

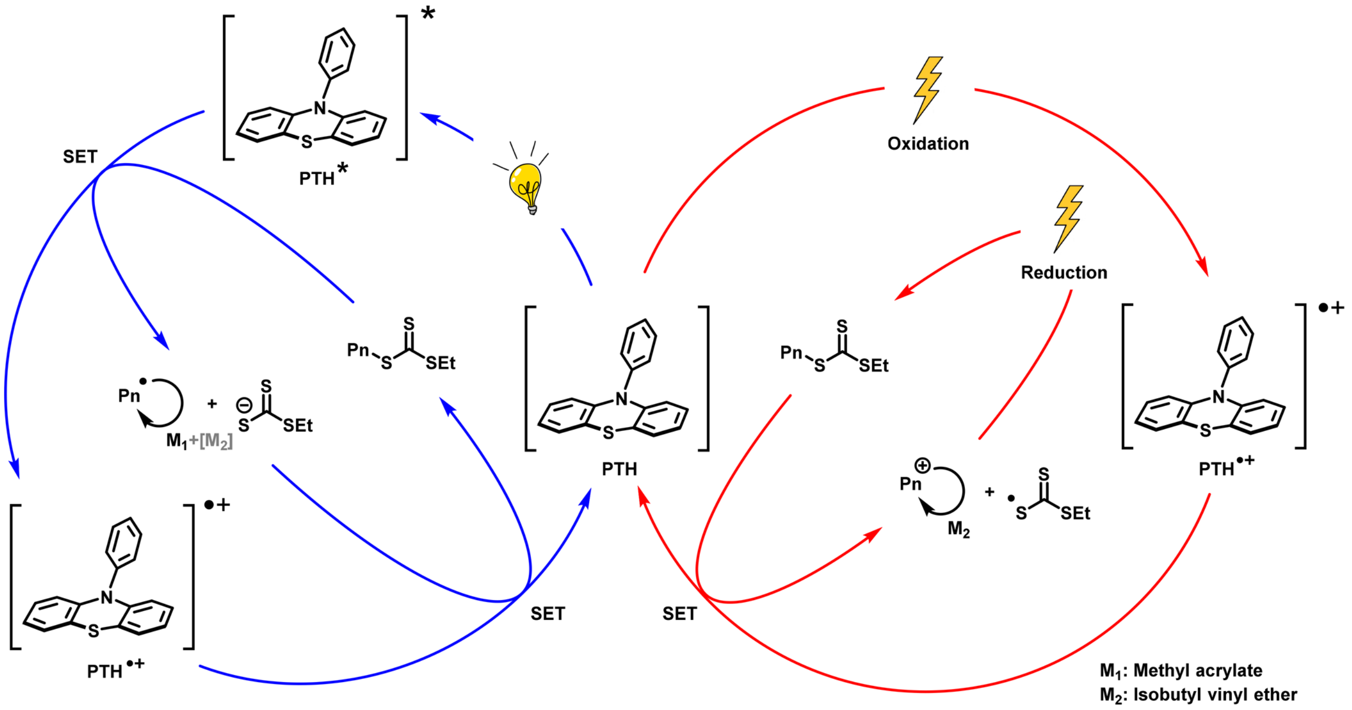


Figure 1. Proposed mechanism of PTH-controlled electrochemical and photochemical polymerization.

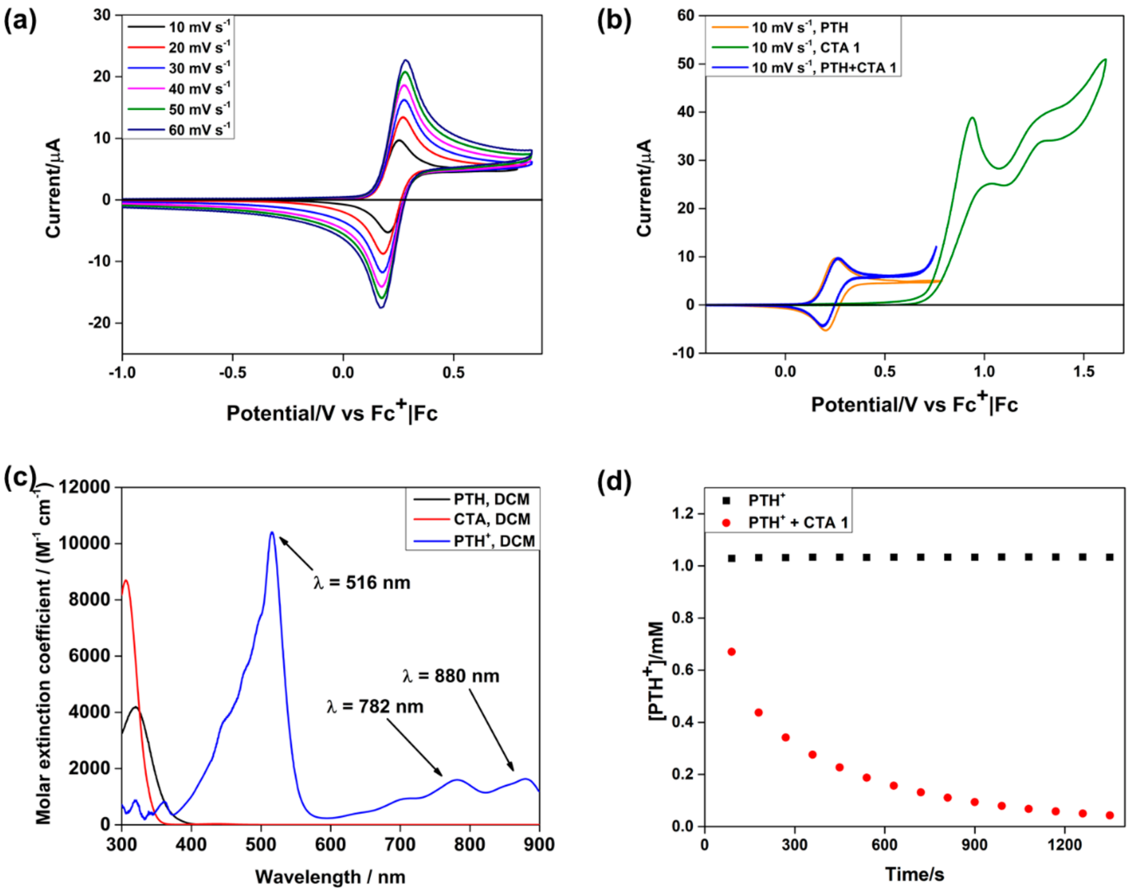


Figure 2. PTH can be oxidized electrochemically to PTH$^{\bullet +}$, which in turn oxidizes CTA **1** homogeneously in solution. (a) Scan-rate-dependent voltammograms of 1.0 mM PTH in 0.1 M [^{n}Bu$_4$N][PF$_6$] electrolyte in DCM solvent. (b) Overlay of CVs of 1 mM PTH, 10 mM CTA **1**, and 1 mM PTH + 10 mM CTA **1** mixture at 10 mV s^{-1} under identical solvent and electrolyte conditions. (c) UV−vis spectra of PTH, PTH$^{\bullet +}$, and CTA **1**. (d) [PTH$^{\bullet +}$] vs time plot determined from UV−vis spectra of PTH$^{\bullet +}$ in the absence of any CTA **1** (black squares) and upon addition of CTA **1** (red circles). See Figures S8−S11 for more details.

(radical) and vinyl ethers (cationic) by adding an appropriate, yet orthogonal, chemical stimulus.[24−27] Specifically, 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) was used to initiate the radical polymerization and tin(IV) chloride was used as the Lewis acid to mediate the cationic polymerization of isobutyl vinyl ether (IBVE).[25] In separate reports, the same group recently showed a similar approach using triflic acid (Brønsted acid) and aluminum-based Lewis acid to initiate the cationic-RAFT polymerization of IBVE.[26−28] The use of endogenous chemical stimuli, however, generates additional byproducts that may complicate sequential reactions or purification and the use of strong Brønsted and Lewis acids requires special handling that pose safety issues. In parallel, Fors and co-workers recently demonstrated an elegant noninvasive approach based on photochemical stimuli, where the polymerization RAFT pathway is switched between vinyl ethers (cationic) and acrylates (radical) by changing the irradiation wavelength.[16] Here, 2,4,6-tri-(*p*-methoxyphenyl)-pyrylium catalyst was used to mediate the cationic polymerization, and tris[2-phenylpyridinato-C^2,*N*]iridium(III) catalyst was used to mediate the acrylate polymerization. Despite the pioneering dual photo-mediated pathway, the use of this method suffers from the high cost of iridium catalyst and large absorption spectra overlap of both photocatalysts, which limit the ability to exclusively activate either the cationic or radical polymerization mechanism. To address some of these challenges, Fors subsequently developed orthogonal radical and cationic strategies that rely on the combination of chemical oxidation or electrochemical excitation with photo-activation.[29,30] The advantage of the last approach stems from the use of a single photocatalyst and improved control over block copolymer synthesis. However, the ferrocene (Fc) catalyst used to mediate the electrochemical excitation also quenches the excited photocatalyst $Ir(ppy)_3$. The concentration of Fc had to be carefully tuned to prevent inhibition or substantially slowing down photochemical polymerization through inhibition. The challenge of balancing reactivity and selectivity remains at the forefront of this emerging field that seeks to leverage the use of multistimuli responsive systems.

Here, we demonstrate the application of a single, metal-free catalyst platform that can selectively mediate monomer addition by controlling the electro- or photochemical stimuli of either cationic (vinyl ethers) or radical (acrylates) polymerization, respectively, using 10-phenylphenothiazine (PTH) as the dual-responsive catalyst. Furthermore, we discovered that under optimized conditions we can selectively synthesize homo-, diblock-, triblock,- or tetrablock polymer by alternating the external stimuli source (photons or electrochemical potential). PTH, therefore, constitutes an effective catalyst in controlling both cationic and radical-based polymerization, providing new opportunities for polymer synthesis, enabling control over polymer architecture and polymer sequence.

■ RESULTS AND DISCUSSION

Design of Dual-Responsive System. To achieve on-demand controlled polymerization in one-pot, we aimed to take advantage of photo and electrochemical orthogonal stimuli for regulating cationic and radical polymerization processes in situ. We hypothesize that PTH can initiate and reversibly terminate both polymerization pathways, leading to precise spatiotemporal control over polymer growth (Figure 1). To achieve this, several conditions must be met to make a single catalyst system work. First, the extrinsically activated catalyst must selectively activate the chain transfer agent (CTA) and be inert to all the other species in the reaction to avoid undesired pathways that would result in uncontrolled polymerization. Second, the catalyst has to respond to two orthogonal stimuli to fulfill on-demand mechanism switching. In addition, the single catalyst approach should not compromise the end-group fidelity or high monodispersity of the formed polymer. Finally, the catalyst must reversibly interconvert between the dormant and active species on the polymer chain-end to control chain growth for both cationic and radical polymerization processes.

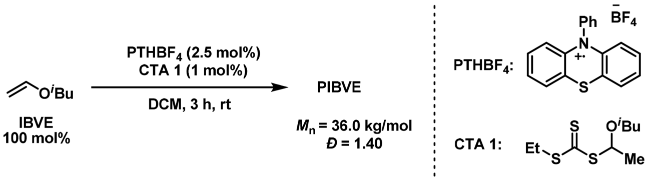


Figure 3. $PTH^{•+}BF_4^-$ initiated polymerization of IBVE in the presence of CTA **1**.

Electrochemical Pathway with PTH. We started our electrochemical investigation by first studying the thermodynamic properties (formal reduction potential) of the phenothiazine catalyst. PTH may serve as a mediator only if the electrochemically generated radical cation, $PTH^{•+}$, oxidizes CTA **1** at potentials that are lower than that needed to oxidize CTA **1** directly on the electrode surface.[31] Then, the $PTH^{•+}$ radical, if long-lived, can facilitate cationic RAFT polymerization in the presence of a vinyl ether monomer (Figure 1, right side). To gain insight into the feasibility of this approach, we turned to cyclic voltammetry investigations (CV). As shown in Figure 2a, reversible voltammograms are recorded for PTH in DCM at various scan rates, indicating fast heterogeneous electron transfer between the PTH species and the glassy carbon working electrode (further details are in the Supporting Information). The reversibility of the voltammograms suggests the long-lived feature of $PTH^{•+}$. Full analysis of the formal reduction potential of PTH (E_f^0 = 0.226 V vs Fc^+ |Fc), and the diffusion coefficient (D_{PTH} = 2.28 × 10^{-5} cm^2 s^{-1}) was done by fitting the experimental results to the Randles−Sevcik semi-infinite diffusion model (see Figure S2 and discussion within).[32] Of note, irreversible oxidation of CTA **1** (Figure 2b, green trace, and Figure S2) on the glassy carbon electrode is seen only at higher potentials (E_p = 0.938 V vs Fc^+ |Fc). These results demonstrate that PTH will be preferentially oxidized over CTA **1** on the electrode surface, supporting that it can work as a mediator to oxidize CTA **1** in solutions.[31]

Encouraged by our thermodynamic insights, we sought to determine whether the electrochemically generated PTH radical cation can oxidize CTA **1**. For this, cyclic voltammetry was used as the investigative tool. We used a relatively slow scan rate (10 mV s^{-1}) to allow the generated radical to interact homogeneously in solution with the CTA agent (for other scan rates, please refer to Figures S3−S7).[33] However, Figure 2b (blue CV trace) shows no clear current amplification and the voltammogram did not transform into an irreversible wave as expected from a fast electrocatalytic process. The results indicate that the CTA **1** oxidation by $PTH^{•+}$ radical is too slow to observe with slow scan rates, if the oxidation occurs at all. Note, we could not perform CV measurements at lower scan

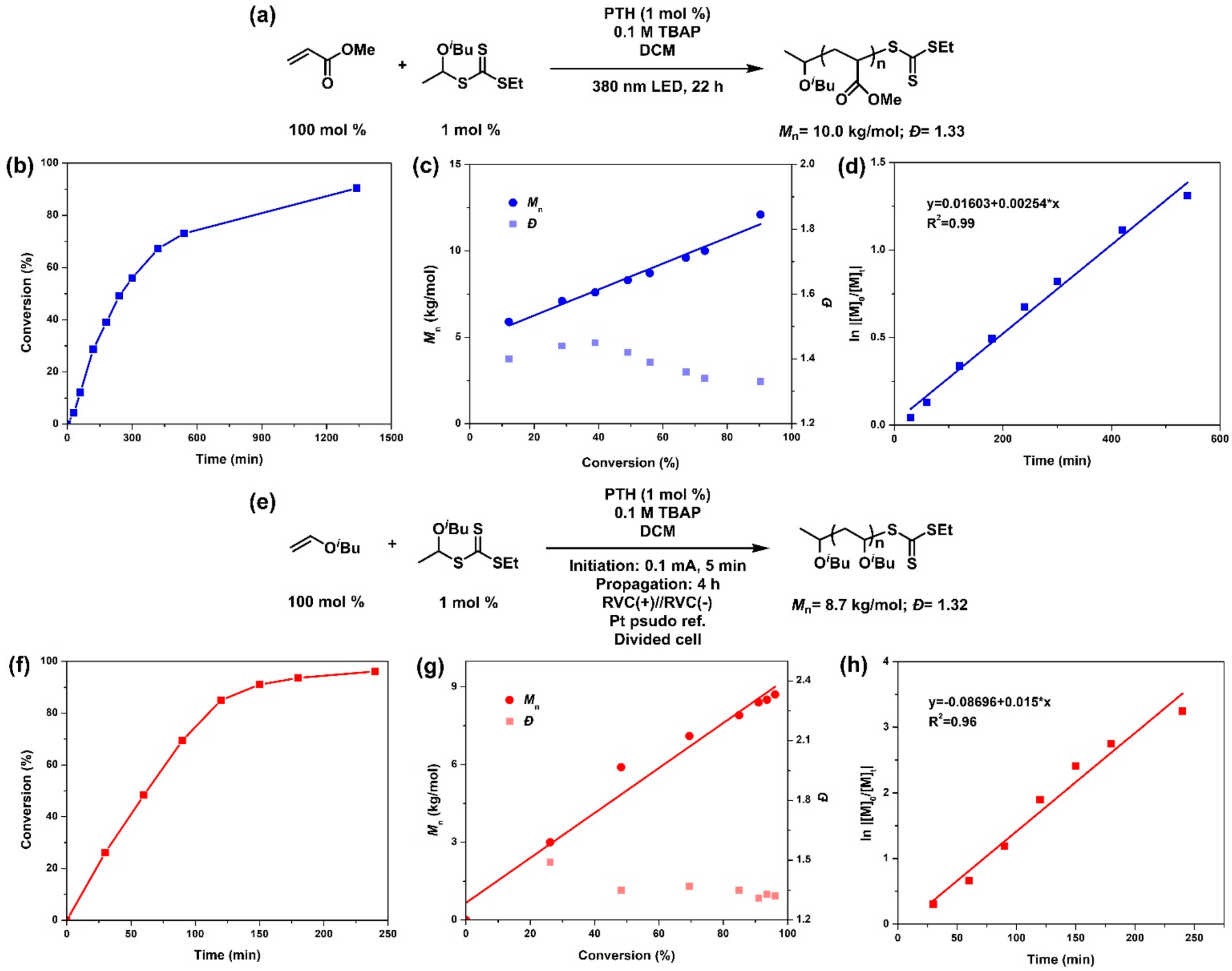


Figure 4. PTH can mediate polymer synthesis via electrochemical or photochemical triggering. (a) General schematic of the photochemical polymerization of methyl acrylate (MA); (b) conversion versus time for MA (blue); (c) M_n and Đ versus conversion for MA (blue); (d) semilogarithmic kinetic plots ($\ln[M]_0/[M]_t$ versus polymerization time) for radical polymerization of MA (blue); (e) general schematic of the electrochemical polymerization of isobutyl vinyl ether (IBVE); (f) conversion versus time for IBVE (red); (g) M_n and Đ versus conversion for IBVE (red); (h) semilogarithmic kinetic plots ($\ln[M]_0/[M]_t$ versus polymerization time) for cationic polymerization of IBVE (red).

rates <10 mV s^{-1} because the time scale for the measurement induces analyte convection and the obtained voltammograms are no longer analytical.[34] Because CVs could not be used to ascertain the kinetics of CTA **1** oxidation, we turned to UV−vis absorption studies to resolve the kinetic process. In this case, electrochemically generated $PTH^{•+}$ reacts with CTA **1** and the concentration of $PTH^{•+}$ is monitored using UV−vis spectroscopy. The absorption spectra of PTH, electrochemically generated $PTH^{•+}$, and CTA **1** are shown in Figure 2c. We chose to track the change in concentration of the $PTH^{•+}$ radical during the homogeneous interaction with CTA **1** via the 782 nm maxima (the absorption feature at 782 nm has been reported in prior work for phenothiazine radical cation) under conditions used later for the full electro-polymerization process (vide infra).[35−37] We found no change in the UV−vis spectrum of the $PTH^{•+}$ radical in absence of CTA **1** over the time scale of ∼25 min (Figure 2d, black squares), and hence no measurable decomposition of the $PTH^{•+}$ radical (Figure S8). When CTA was added to the long-lived $PTH^{•+}$ radical in solution the absorption signal at 782 nm decayed over the course of ∼25 min (Figure 2d, red circles). From this data, we were able to resolve the reaction rate of CTA **1** oxidation by $PTH^{•+}$. The overall order of reaction was determined to be second order (first-order in PTH and first-order in CTA **1**) with a rate constant $k = 0.272 \pm 0.017\ M^{-1}\ s^{-1}$ (see Figures S8−S14 and associated details in the Supporting Information for the kinetic analysis). From these experiments, we surmised that the electrogenerated PTH radical cation can oxidize CTA **1** slowly and posit that it may be the rate-limiting step for the initiation of chain transfer polymerization.

To validate whether PTH radical cation can initiate cationic polymerization in the presence of CTA **1**, we first demonstrated that $PTH^{•+}BF_4^-$ can oxidize CTA **1** in dichloromethane (DCM) to generate 80% of bis(ethylsulfanyl thiocarbonyl)disulfide as shown in Figure S19. Next, we reacted pregenerated $PTH^{•+}BF_4^-$ (2.5 mol %), CTA **1** (1 mol %), and IBVE (100 mol %) in DCM at ambient temperature. To our satisfaction, full conversion to PIBVE (M_n = 36 kg/mol, polydispersity Đ = 1.40) was observed after 3 h (Figure 3). These results along with the CV data (Figure 2)

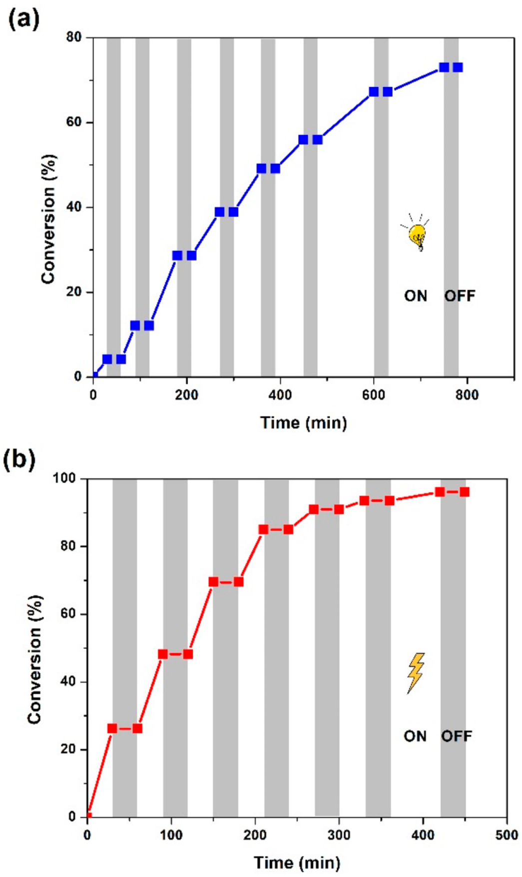


Figure 5. Temporal control of polymer growth initiation and reversible termination using PTH catalyst under the optimized reaction conditions with (a) light stimulus (see Table S2, entry 1) or (b) electrochemical stimulus (see Table S1, entry 1).

demonstrate the ability of PTH to undergo reversible electrochemical oxidation and initiate the cationic polymerization of IBVE via selective oxidation of CTA **1**.

Development of Orthogonal Polymerization Conditions Using PTH. Encouraged by these results, we turned our attention to identifying conditions that would favor polymer growth via photochemically controlled radical polymerization of methyl acrylate (MA) and electrochemically controlled cationic polymerization of isobutyl vinyl ether (IBVE), catalyzed by PTH. The use of PTH for photomediated, controlled radical polymerization has seen tremendous growth since the introduction in 2014,[38] with a number of important contributions continuing to expanding the utility of metal-free photoredox catalysis.[39−43] To test the feasibility of the photochemically controlled strategy using CTA **1**, we irradiated a mixture of PTH (9.68 mM), CTA **1**, (10 mM) and MA (1000 mM) (monomer commonly used in radical polymerization) in DCM with 365 nm LED light, polymer with a broad dispersity *Đ* of 1.56 was obtained after 22 h. We attributed the lack of polymerization control to absorption overlap at 365 nm, which precluded a selective excitation of PTH in the presence of CTA **1** (Figure 2c). Hence, we sought further improvement by switching to longer wavelengths to avoid an absorbance overlap between CTA **1** and PTH and to avoid a potential background iniferter polymerization that might lead to a competing background reaction. Indeed, switching to a 380 nm LED (≈ 3 mW/cm^2) light source yielded a polymer with a narrower dispersity *Đ* of 1.33 after 22 h (Figure 4a). Under the optimized reaction conditions, 50% monomer conversion was observed within 4 h, reaching 90% conversion over 22 h (Figure 4b). Importantly, the number-average molecular weight M_n linearly increased and *Đ* decreased as the reaction extended, suggesting tuned control of polymer growth using the optically excited PTH catalyst (Figure 4c). Moreover, a linear dependence of $\ln[M]_0/[M]_t$ on time was observed (Figure 4d), suggesting a pseudo-first-order kinetic behavior characteristic of a living radical polymerization. Series of control experiments confirmed that PTH, CTA **1**, and light excitation are all necessary for achieving controlled radical polymerization (Table S2).

To test the ability of PTH to mediate the electrochemically controlled cationic polymerization, we began with constant current conditions (galvanostatic rather than potentiostatic control) to oxidize PTH using a divided electrochemical cell (Figure S21). In this way, a constant and known flux of PTH radical cation was generated prior to the polymerization initiation process. Applying an anodic current of 1.0 mA for 5 min to a solution of PTH, IBVE, CTA **1**, and tetra-*n*-butylammonium perchlorate ([^{n}Bu$_4$N][ClO$_4$]) in DCM furnished a poly(isobutyl vinyl ether) PIBVE with a *Đ* of 1.40 after 22 h. The polymer dispersity was further improved by lowering the applied constant current to 0.1 mA for 5 min, yielding polymers with a narrow dispersity (*Đ* = 1.32) within 4 h (Figure 4e). Next, we monitored the progress of the polymerization as a function of time to demonstrate the control over polymer growth (Figure 4f). The polymer polydispersity decreased and M_n linearly increased as expected for a controlled chain growth process (Figure 4g). It is worth noting that the polymers obtained from direct electrolysis of the CTA **1** displayed broad dispersity *Đ* = 2.48 and a lack of control, which highlights the critical role of the PTH catalyst for the successful electromediated synthesis (see Table S1, entry 7). Without PTH, the CTA **1** will be directly oxidized on the electrode surface, resulting in a large number of locally generated cations and leading to unwanted side reactions. Instead, by having PTH as a mediator, PTH was oxidized preferentially rather than CTA **1**, and the in situ generated PTH$^{\bullet+}$ could distribute into the solution to form a homogeneous solution. Then, PTH$^{\bullet+}$ will slowly react with CTA **1** (k = 0.272 ± 0.017 M^{-1} s^{-1}) to initiate the polymerization in a slower but more controllable way. This spatial (heterogeneous vs homogeneous) and kinetics (fast vs slow) difference between mediated and direct electrolysis highlights the advantage of using a mediator.[31,44] Of note, similar to photochemically controlled radical polymerization of MA, a linear dependence of $\ln[M]_0/[M]_t$ on polymerization time was observed (Figure 4h), suggesting a pseudo-first-order kinetic behavior characteristic of a living cationic polymerization.

Temporal Control of Both the Photo- and Electrostimuli. The ability to control when and where a monomer addition takes place is critical for tailored synthesis of new polymers. To demonstrate temporal control over polymer growth, we subjected CTA **1**, MA, and PTH to on/off irradiation cycles with the light stimulus. We expect chain growth to occur only during the light-on stage and remain dormant during the light-off stage. Indeed, irradiating the reaction mixture for 30 min resulted in a monomer to polymer conversion that was completely halted in the absence of a photonic stimulus. This cycle was repeated several times, with

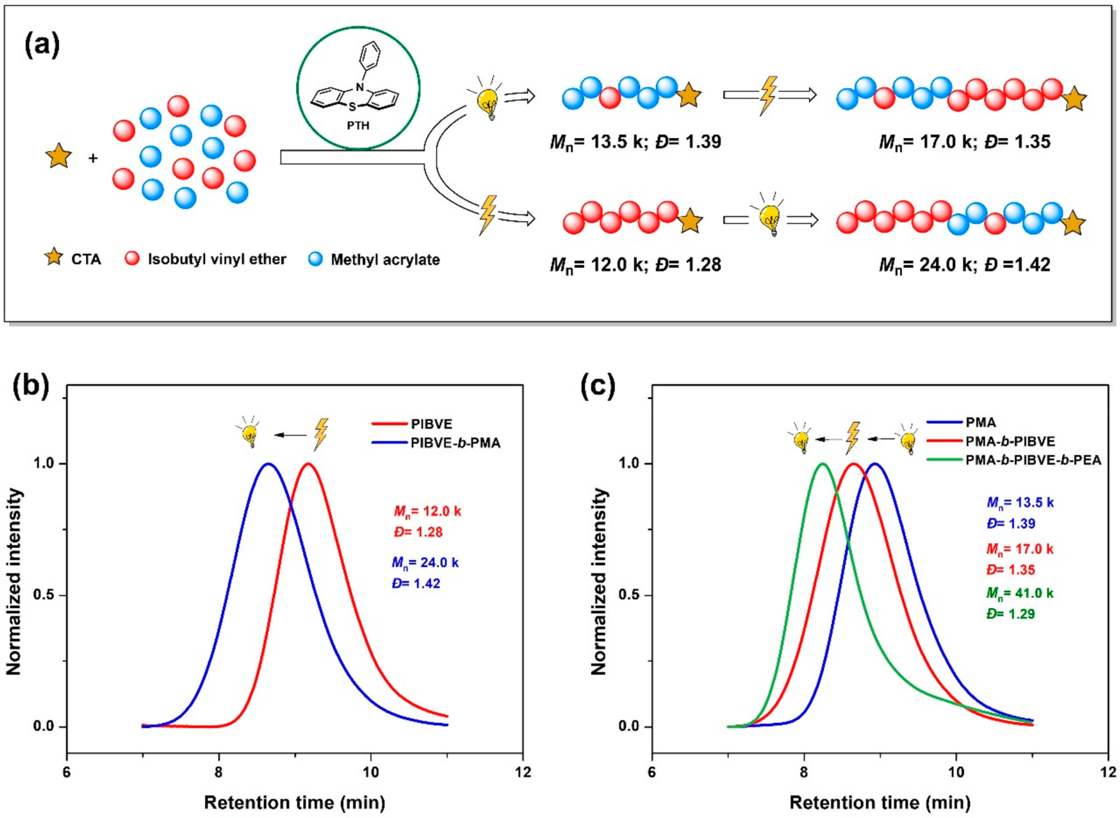


Figure 6. On-demand synthesis of di- and triblock copolymers using orthogonal electro- or photochemical stimulus. (a) PTH catalyzed orthogonal stimuli controlled on-demand polymerization mechanism switching; (b) GPC traces of PIBVE homopolymer (red trace) and PIBVE-*b*-PMA) diblock copolymer (blue trace); (c) GPC traces of PMA homopolymer (blue trace), PMA-*b*-PIBVE diblock copolymer (red trace), and PMA-*b*-PIBVE-*b*-PEA triblock copolymer (green trace).

polymer growth observed only when the light stimulus was applied (Figure 5a). These data show an excellent temporal control of the polymerization process under the photochemical conditions that we have carefully found.

To gain insight into temporal control over polymer chain growth using electrochemical stimulus, we galvanostatically triggered a mixture of PTH, IBVE, CTA **1**, and$[^n\mathrm{Bu}_4\mathrm{N}][\mathrm{ClO}_4]$ in DCM solvent to +0.1 mA anodic current for 5 min. This induced a fixed flux of PTH toward the electrode surface, consequently controlling the amount of generated PTH radical cation. After forming the radical cation in solution, we reasoned that electrochemically controlled polymerization could self-propagate, even without applying oxidizing current, and could be terminated by applying the opposite polarity using −0.1 mA current. As hypothesized, applying an oxidizing galvanostatic current followed by open circuit potential reinitiated the cationic-RAFT polymerization in contrast to reductive currents that rapidly terminated the polymer propagation (Figure 5b). Importantly, the "on-demand" on and off switching phenomenon of the cationic polymerization was demonstrated during the monomer to polymer synthesis, regardless of the extent of conversion.

Sequence Controlled Polymerization. We have so far demonstrated the ability of PTH to serve as a single catalyst platform to mediate both electrochemical and photochemical polymerization of IBVE and MA, respectively. With these optimized conditions in hand, we directed our attention to the synthesis of di- and triblock copolymers using an orthogonal-stimuli strategy. By this, we aimed to demonstrate the on-demand switching between the radical and cationic polymerization mechanisms at any given point during the extent of reaction. Specifically, through modulation of the two stimuli, block copolymer structures consisting of PMA and PIBVE can be accessed. The success of this approach hinges on the ability to switch between radical (MA) and cationic (IBVE) mechanisms, initiated by either the reduction (photochemical) or the oxidation (electrochemical) of the trithiocarbonate chain end. Operationally, we envisioned switching from cationic to radical polymerization mechanism by simply irradiating PIBVE under the optimized conditions in the presence of MA monomer (Figure 6a, bottom path). However, switching from radical to cationic mechanism is hampered by the formation of the unfavorable ester α-cation (Figure 6a, top path). Previously, Fors and Kamigaito have independently shown the ability to circumvent this limitation by simply adding small amounts of IBVE to generate the S, O-mixed acetal chain-end that enables subsequent cationic polymerization.[26,29]

Starting with the equimolar ratio of IBVE and MA monomers, we first synthesized the PIBVE homopolymer through electrochemically controlled cationic polymerization of IBVE and analyzed this polymer by gel permeation chromatography (GPC) (Figure 6b, red GPC trace). As expected, no MA monomer incorporation is observed during this polymerization step. Importantly, when the electrochemical excitation is stopped and the photochemical process is turned on using 380 nm light excitation, we observed efficient chain extension of the MA-based monomer, furnishing

PIBVE-*b*-PMA diblock copolymer (Figure 6b, blue GPC trace).

Finally, we set out to demonstrate the ability to change the order of the two applied stimuli by synthesizing a well-defined triblock and tetra-block copolymers. Irradiating an equimolar solution of MA (100 mol %) and IBVE (100 mol %) with 380 nm light provided PMA polymer with 34% IBVE incorporation (Figure 6c, blue GPC trace). The incorporation of IBVE during the radical polymerization is consistent with prior results.[29] Importantly, switching off the light and switching on the electrochemical stimulus successfully initiated the cationic RAFT-polymerization to form PMA-*b*-PIBVE diblock copolymer as illustrated by the gradual shift in GPC trace (Figure 6c, red GPC trace) which reflected a gradual increase in the polymer molecular weight. To monitor the formation of the triblock, ethyl acrylate (EA) was used, because it can easily distinguish from MA by ^{1}H NMR spectroscopy. As seen by the ^{1}H NMR (Figure S26) and by the shift in the GPC trace (Figure 6c, green GPC trace), a well-defined triblock bearing three distinct repeat polymers segments was prepared in a single pot. Interestingly, by altering the sequence of the two applied stimuli and adding extra polymerization step using ethyl vinyl ether (EVE), PIBVE-*b*-PMA-*b*-PEVE-*b*-PEA tetrablock copolymer was synthesized (Figures S27 and S28). Taken together, these examples demonstrate the ability to control the precise polymer architecture by an on-demand control of the polymerization mechanism through the application of external orthogonal stimuli using PTH as the dual catalyst, in a single pot.

CONCLUSION

In summary, we have developed a single catalyst platform that allows on-demand switching between radical and cationic reversible addition−fragmentation chain transfer (RAFT)-polymerization mechanisms by simply applying photo or electrochemical stimuli. The orthogonal nature of the two stimuli was critical for the ability to switch between the two mechanistic pathways required to polymerize both electron-rich vinyl-based monomers and electron-deficient acrylate-based monomers. We show that the presence of catalytic amounts of 10-phenylphenothiazine (PTH), a metal-free catalyst, reversibly initiates the radical polymerization mechanism of methyl acrylate upon irradiation with an adequate wavelength. Moreover, we showed that the same catalyst can initiate the cationic polymerization of isobutyl vinyl ether when exposed to anodic oxidation in a divided electrochemical cell. Under the optimized reaction conditions, several well-defined multiblock copolymers were synthesized in a single pot by simply switching between the two stimuli. Significantly, the length of each polymer block was dependent on the duration of the applied stimulus and polyblock architecture was dependent on the number of times each stimulus is applied. These results demonstrate the remarkable ability of PTH to function as a photo- and electroresponsive catalyst to initiate and reversibly terminate both radical and cationic polymerization. This work also highlights the advantage of using a metal-free organic catalyst and sets the stage for discovery of other metal-free catalysts for use in sequence-controlled polymerization with traceless stimuli.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c05431.

> Additional information including reagent information, analytical information, experimental protocols, ^{1}H NMR spectra, and kinetic studies (PDF)

AUTHOR INFORMATION

Corresponding Authors

Javier Read de Alaniz − *Department of Chemistry and Biochemistry, University of California at Santa Barbara, Santa Barbara, California 93106, United States;* orcid.org/0000-0003-2770-9477; Email: javier@chem.ucsb.edu

Lior Sepunaru − *Department of Chemistry and Biochemistry, University of California at Santa Barbara, Santa Barbara, California 93106, United States;* orcid.org/0000-0002-4716-5035; Email: sepunaru@ucsb.edu

Authors

Andrei Nikolaev − *Department of Chemistry and Biochemistry, University of California at Santa Barbara, Santa Barbara, California 93106, United States*

Zhipeng Lu − *Department of Chemistry and Biochemistry, University of California at Santa Barbara, Santa Barbara, California 93106, United States*

Arunavo Chakraborty − *Department of Chemistry and Biochemistry, University of California at Santa Barbara, Santa Barbara, California 93106, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.1c05431

Author Contributions

[†]A.N. and Z.L. authors contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from UC Santa Barbara is gratefully acknowledged. This work utilized NMR instruments supported by the National Science Foundation under award MRI-1920299. We thank Rachel Behrens for helpful discussions. We thank Richard Bock, UC Santa Barbara Department of Chemistry glass shop manager, for making custom H cells for the electrochemical work in this paper.

REFERENCES

(1) Matyjaszewski, K.; Spanswick, J. Controlled/Living Radical Polymerization. *Mater. Today* **2005**, *8*, 26−33.

(2) Szwarc, M. Living” Polymers. *Nature* **1956**, *178*, 1168−1169.

(3) Braunecker, W. A.; Matyjaszewski, K. Controlled/Living Radical Polymerization: Features, Developments, and Perspectives. *Prog. Polym. Sci.* **2007**, *32*, 93−146.

(4) Perrier, S. 50th Anniversary Perspective: RAFT Polymerization - A User Guide. *Macromolecules* **2017**, *50*, 7433−7447.

(5) Grubbs, R. B.; Grubbs, R. H. 50th Anniversary Perspective: Living Polymerization - Emphasizing the Molecule in Macromolecules. *Macromolecules* **2017**, *50*, 6979−6997.

(6) Leibfarth, F. A.; Mattson, K. M.; Fors, B. P.; Collins, H. A.; Hawker, C. J. External Regulation of Controlled Polymerizations. *Angew. Chem., Int. Ed.* **2013**, *52*, 199−210.

(7) Zhou, Y. N.; Li, J. J.; Wu, Y. Y.; Luo, Z. H. Role of External Field in Polymerization: Mechanism and Kinetics. *Chem. Rev.* **2020**, *120*, 2950−3048.

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

(9) Xu, J.; Jung, K.; Atme, A.; Shanmugam, 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*, 5508−5519.

(10) Qi, 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.

(11) Magenau, A. J. D.; Strandwitz, N. C.; Gennaro, A.; Matyjaszewski, K. Electrochemically Mediated Atom Transfer Radical Polymerization. *Science* **2011**, *332*, 81−84.

(12) Peterson, B. M.; Lin, S.; Fors, B. P. Electrochemically Controlled Cationic Polymerization of Vinyl Ethers. *J. Am. Chem. Soc.* **2018**, *140*, 2076−2079.

(13) Sang, W.; Yan, Q. Electro-Controlled Living Cationic Polymerization. *Angew. Chem.* **2018**, *130*, 5001−5005.

(14) Kirillov, E.; Rodygin, K.; Ananikov, V. Recent Advances in Applications of Vinyl Ether Monomers for Precise Synthesis of Custom-Tailored Polymers. *Eur. Polym. J.* **2020**, *136*, 109872.

(15) Ali, U.; Karim, K. J. B. A.; Buang, N. A. A Review of the Properties and Applications of Poly (Methyl Methacrylate) (PMMA). *Polym. Rev.* **2015**, *55*, 678−705.

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

(17) Zhang, Z.; Zeng, T.-Y.; Xia, L.; Hong, C.-Y.; Wu, D.-C.; You, Y.-Z. Synthesis of Polymers with On-Demand Sequence Structures via Dually Switchable and Interconvertible Polymerizations. *Nat. Commun.* **2018**, *9*, 2577.

(18) Zhu, J.; Hao, X.; Yan, Q. Electro-Selective Interconversion of Living Cationic and Radical Polymerizations. *Sci. China: Chem.* **2019**, *62*, 1023−1029.

(19) Bates, F. S.; Hillmyer, M. A.; Lodge, T. P.; Bates, C. M.; Delaney, K. T.; Fredrickson, G. H. Multiblock Polymers: Panacea or Dandora's Box? *Science* **2012**, *336*, 434−440.

(20) Cabral, H.; Miyata, K.; Osada, K.; Kataoka, K. Block Copolymer Micelles in Nanomedicine Applications. *Chem. Rev.* **2018**, *118*, 6844−6892.

(21) Bates, C. M.; Maher, M. J.; Janes, D. W.; Ellison, C. J.; Willson, C. G. Block Copolymer Lithography. *Macromolecules* **2014**, *47*, 2−12.

(22) Luo, M.; Epps, T. H. Directed Block Copolymer Thin Film Self-Assembly: Emerging Trends in Nanopattern Fabrication. *Macromolecules* **2013**, *46*, 7567−7579.

(23) Teator, A. J.; Lastovickova, D. N.; Bielawski, C. W. Switchable Polymerization Catalysts. *Chem. Rev.* **2016**, *116*, 1969−1992.

(24) Aoshima, H.; Uchiyama, M.; Satoh, K.; Kamigaito, M. Interconvertible Living Radical and Cationic Polymerization through Reversible Activation of Dormant Species with Dual Activity. *Angew. Chem., Int. Ed.* **2014**, *53*, 10932−10936.

(25) 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 Copolymers. *Macromolecules* **2010**, *43*, 7523−7531.

(26) Satoh, K.; Hashimoto, H.; Kumagai, S.; Aoshima, H.; Uchiyama, M.; Ishibashi, R.; Fujiki, Y.; Kamigaito, M. One-Shot Controlled/Living Copolymerization for Various Comonomer Sequence Distributions: Via Dual Radical and Cationic Active Species from RAFT Terminals. *Polym. Chem.* **2017**, *8*, 5002−5011.

(27) Uchiyama, M.; Satoh, K.; McKenzie, T. G.; Fu, Q.; Qiao, G. G.; Kamigaito, M. Diverse Approaches to Star Polymers via Cationic and Radical RAFT Cross-Linking Reactions Using Mechanistic Transformation. *Polym. Chem.* **2017**, *8*, 5972−5981.

(28) Satoh, K.; Sun, Z.; Uchiyama, M.; Kamigaito, M.; Xu, J.; Boyer, C. Interconvertible and Switchable Cationic/PET-RAFT Copolymerization Triggered by Visible Light. *Polym. J.* **2020**, *52*, 65−73.

(29) Peterson, B. M.; Kottisch, V.; Supej, M. J.; Fors, B. P. On Demand Switching of Polymerization Mechanism and Monomer Selectivity with Orthogonal Stimuli. *ACS Cent. Sci.* **2018**, *4*, 1228−1234.

(30) Supej, M. J.; Peterson, B. M.; Fors, B. P. Dual Stimuli Switching: Interconverting Cationic and Radical Polymerizations with Electricity and Light. *Chem.* **2020**, *6*, 1794−1803.

(31) Francke, R.; Little, R. D. Redox Catalysis in Organic Electrosynthesis: Basic Principles and Recent Developments. *Chem. Soc. Rev.* **2014**, *43*, 2492−2521.

(32) Messersmith, S. J. Cyclic Voltammetry Simulations with DigiSim Software: An Upper-Level Undergraduate Experiment. *J. Chem. Educ.* **2014**, *91*, 1498−1500.

(33) Compton, R. G.; Banks, C. E. *Understanding Voltammetry*; World Scientific, 2018; pp 245−297.

(34) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; John Wiley & Sons, 2001; pp 28−29.

(35) Christensen, J. A.; Phelan, B. T.; Chaudhuri, S.; Acharya, A.; Batista, V. S.; Wasielewski, M. R. Phenothiazine Radical Cation Excited States as Super-Oxidants for Energy-Demanding Reactions. *J. Am. Chem. Soc.* **2018**, *140*, 5290−5299.

(36) Odom, S. A.; Ergun, S.; Poudel, P. P.; Parkin, S. R. A Fast, Inexpensive Method for Predicting Overcharge Performance in Lithium-Ion Batteries. *Energy Environ. Sci.* **2014**, *7*, 760−767.

(37) Sun, D.; Rosokha, S. V.; Kochi, J. K. Donor-Acceptor (Electronic) Coupling in the Precursor Complex to Organic Electron Transfer: Intermolecular and Intramolecular Self-Exchange between Phenothiazine Redox Centers. *J. Am. Chem. Soc.* **2004**, *126*, 1388−1401.

(38) Treat, N. J.; Sprafke, 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.

(39) Szczepaniak, G.; Fu, L.; Jafari, H.; Kapil, K.; Matyjaszewski, K. Making ATRP More Practical: Oxygen Tolerance. *Acc. Chem. Res.* **2021**, *54*, 1779−1790.

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

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

(42) Mccarthy, B.; Miyake, G. M. Organocatalyzed Atom Transfer Radical Polymerization Catalyzed by Core Modified N-Aryl Phenoxazines Performed under Air. *ACS Macro Lett.* **2018**, *7*, 1016−1021.

(43) Discekici, E. H.; Anastasaki, A.; Read De Alaniz, J.; Hawker, C. J. Evolution and Future Directions of Metal-Free Atom Transfer Radical Polymerization. *Macromolecules* **2018**, *51*, 7421−7434.

(44) Savéant, J. M. Molecular Catalysis of Electrochemical Reactions. Mechanistic Aspects. *Chem. Rev.* **2008**, *108*, 2348−2378.