

# Combining Cationic and Anionic Polymerizations using a Universal Mediator: Enabling Access to Two- and Three-Mechanism Block Copolymers

Brandon M. Hosford<sup>‡,[a]</sup> William Ramos<sup>‡,[a]</sup> and Jessica R. Lamb<sup>\*[a]</sup>

<sup>[a]</sup>Department of Chemistry, University of Minnesota—Twin Cities, 207 Pleasant Street SE, Minneapolis, MN 55455, United States

<sup>‡</sup>B.M.H. and W.R. contributed equally to this work

**ABSTRACT:** The combination of multiple polymerization mechanisms and monomer classes to make block copolymers is an ongoing challenge. In particular, the combination of cationic and anionic polymerization mechanisms commonly requires extra compatibilization steps or the use of multi-functional initiators. Herein, we report the use of thiocarbonyl thio compounds (TCTs) as universal mediators to sequentially polymerize ethyl vinyl ether via photocontrolled cationic polymerization (photo-CP) and the thiirane phenoxy propylene sulfide via thioacyl anionic group transfer polymerization (TAGT). Thermal analyses of the resulting block copolymers provide evidence of microphase separation of the blocks. The resulting diblocks can be further chain extended using photoinduced electron/energy transfer reversible addition-fragmentation chain transfer polymerization (PET-RAFT) of *N*-isopropylacrylamide to make a triblock terpolymer from three different monomer classes incorporated via three different mechanisms without any end group modification steps. The development of this simple, sequential synthesis using a universal mediator opens up new possibilities by providing facile access to diverse block copolymers of vinyl ethers, thiiranes, and acrylamides.

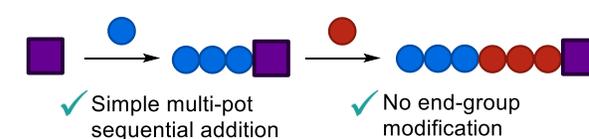
Block copolymers (BCPs) are important and versatile materials because of their unique properties and functions, which are dictated by their composition and microstructure.<sup>1,2</sup> Most BCPs are made from a single polymerization mechanism where compatible monomers are added sequentially,<sup>3</sup> but the accessible chemical space is limited to similar monomer classes or to a prescribed addition order to maintain the active chain-end.<sup>4</sup> Ideally, polymer chemists would not be confined to this paradigm, such that disparate monomers could be combined to access an expanded property space. To make this dream a reality, it is necessary to develop new ways to incorporate different polymerization mechanisms (e.g., cationic, anionic, radical) into a single material.

Polymer chemists can combine multiple mechanisms into a single polymer chain through a variety of strategies. Common methods – such as the coupling of two homopolymer chains,<sup>5–7</sup> end-group modification,<sup>8–21</sup> or the use of multi-functional initiators<sup>22–25</sup> – require additional synthetic steps and/or are limited in the architecture and number of blocks in the final material. The use of a universal mediator that can support multiple mechanisms without modification is an elegant solution to these challenges (Figure 1A). Once synthesized, the mediator can facilitate multiple mechanisms via a simple sequential addition of the respective monomers and reaction conditions. Due to the fact that the mediator stays at the chain end, the user is not limited in the number of blocks accessible. Thiocarbonyl thio compounds (TCTs) have been utilized as universal mediators to combine radical and cationic<sup>26–31</sup> as well as radical and anionic polymerizations<sup>32–37</sup> (Figure 1B), but this strategy has not

yet been applied to the historically more-challenging cationic and anionic mechanisms. Due to the rich literature of cationic<sup>27,38–43</sup> and anionic<sup>32,44,45</sup> homopolymerizations using TCTs, we hypothesized that proper selection of the R and Z groups on the mediator would fill this gap.

Herein, we report a simple multi-pot sequential polymerization that combines photocontrolled cationic polymerization (photo-CP) and thioacyl anionic group transfer polymerization (TAGT) to generate novel BCPs of poly(vinyl

## A Multi-mechanism BCPs via a universal mediator



## B

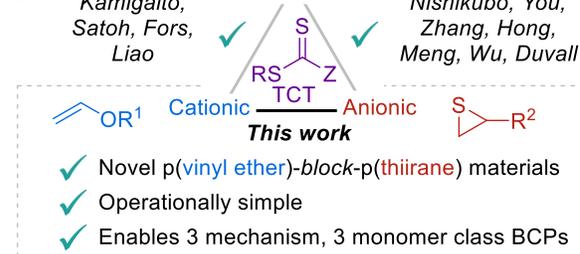


Figure 1. (A) General scheme for the synthesis of BCPs using a universal mediator. (B) Previous TCT universal mediator reports for radical/cationic and radical/anionic and this work on cationic/anionic polymerization.

ether)s and poly(thiirane)s. We explored the effect of [monomer]:[TCT] on polymerization control and thermal properties of the new BCPs via thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), which supports microphase separation of the two blocks. Taking advantage of the versatility of radical polymerization, we further chain extended the BCPs with *N*-isopropylacrylamide (NIPAM) using photoinduced electron/energy transfer reversible addition-fragmentation chain transfer polymerization (PET-RAFT). This novel triblock terpolymer is produced from three different mechanisms and three monomer classes without any end-group modification using this universal mediator approach.

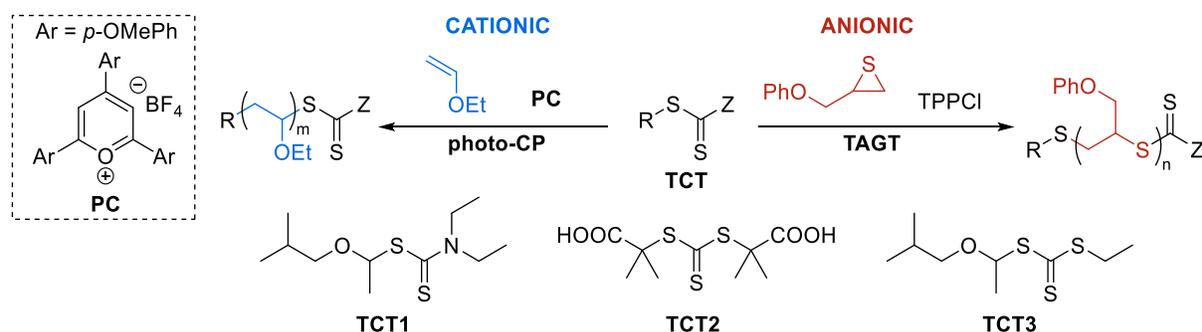
We began our compatibilization efforts by adapting reported reaction conditions for photo-CP<sup>46</sup> and TAGT.<sup>33</sup> For the cationic system, we used the classic oxidizing photocatalyst, 2,4,6-tri-(*p*-methoxyphenyl)pyrylium tetrafluoroborate (**PC**), in DCM. For the anionic polymerization, we used tetraphenyl phosphonium chloride (TPPCL) as the nucleophilic catalyst in DMAc. We chose ethyl vinyl ether (EVE) as the monomer for photo-CP due to the solubility of p(EVE) in DMAc.<sup>47</sup> Phenoxy propylene sulfide (POPS) was chosen as the TAGT monomer due to its precedence in compatibilized systems<sup>33,35,36,44,45</sup> and its high boiling point allowing for ease of manipulation. All runs were characterized by <sup>1</sup>H NMR spectroscopy and size-exclusion chromatography (SEC).

We screened a variety of TCT mediators, varying the R and Z groups. For photo-CP, the identity of the R group is vital for initiation of the cationic process – requiring a thioacetal chain end.<sup>31,48,49</sup> We screened **TCT1** first because it has been used to mediate photo-CP compatibilized with radical polymerization,<sup>46</sup> though it is important to note that a high degree of purity is required for good control when

polymerizing EVE.<sup>50</sup> As expected, **TCT1** gave good conversion, molar mass that matches closely with the theoretical value, and low dispersity for photo-CP (Table 1, entry 1a) but resulted in poor control and very broad dispersity (3.55) for TAGT (entry 1b). Similarly, the symmetrical mediator **TCT2**, which is commonly used for TAGT,<sup>33,35</sup> resulted in well-controlled polymerization for TAGT (entry 2b) but poor control over molar mass and a broad dispersity (2.51) for photo-CP (entry 2a). Excitingly, combining the vinyl ether-derived R group of **TCT1** and the trithiocarbonate Z group into **TCT3** resulted in moderate control of both photo-CP and TAGT (entries 3a and 3b). These data validate that the R group is very important for photo-CP and that the identity of the Z group plays an important role in control of both mechanisms.

While the high solubility of p(EVE) was beneficial for the compatibilization with the TAGT conditions, it also made purification difficult. While both residual monomer and DCM were volatile enough to be removed in vacuo, the **PC** is a solid that we wanted to remove via precipitation. Unfortunately, we found p(EVE) was soluble in a wide range of solvents – such as methanol, water, ethyl acetate, diethyl ether, and hexanes. Purification via dialysis was also unsuccessful. These purification challenges meant we were unable to effectively remove the **PC** from the photo-CP polymers. Therefore, we tested the effect of varying amounts of **PC** on the TAGT (see Supporting Information, Section S2.A). We found at high loadings, **PC** inhibits the anionic polymerization (10% conversion is seen at 5 mol % relative to TCT). However, at 3.3 mol % relative to TCT, most of the activity is retained (Table 1, entry 4b). During this exploration, we discovered the photo-CP still achieved 98% conversion at half of our standard loading (entry 4a). Therefore, in order

**Table 1. Optimization and identification of an appropriate universal mediator for cationic polymerization of EVE and anionic polymerization of POPS.**



TCT	entry	cationic <sup>[a]</sup>				anionic <sup>[b]</sup>				
		conv. (%) <sup>[c]</sup>	$M_{n,theo.}$ (kDa)	$M_n$ (kDa) <sup>[d]</sup>	$\mathcal{D}$	entry	conv. (%) <sup>[c]</sup>	$M_{n,theo.}$ (kDa)	$M_n$ (kDa) <sup>[d]</sup>	$\mathcal{D}$
<b>TCT1</b>	1a	95	3.7	3.8	1.13	1b	92	15.8	97.2	3.55
<b>TCT2</b>	2a	>99	3.9	6.2	2.51	2b	>99	17.4	16.5	1.22
<b>TCT3</b>	3a	>99	3.8	3.8	1.34	3b	88	15.6	19.5	1.35
<b>TCT3</b>	4a <sup>[e]</sup>	98	3.8	4.5	1.17	4b <sup>[f]</sup>	79	12.2	15.2	1.35
<b>TCT3</b>	5a <sup>[g]</sup>	<1	-	-	-	5b	-	-	-	-
-	6a	99	-	10.1	1.95	6b	73	-	289.6	1.87

[a] Cationic standard conditions: **TCT** (1 eq.), EVE (50 eq.), **PC** (2 mol % relative to **TCT**), DCM, RT, 456 nm LED, 6 h. [b] Anionic standard conditions: **TCT** (1 eq.), POPS (100 eq.), TPPCL (0.33 eq.), DMAc (1 mL), 60 °C, 6 h. [c] Conversion measured via <sup>1</sup>H NMR spectroscopy. [d] Measured via SEC in DMF against PMMA standards. [e] Polymerization run with 1 mol % of **PC** relative to **TCT**. [f] Polymerization run with 3.3 mol % of **PC** added relative to **TCT**. [g] Polymerization run with no **PC**.

to minimize the amount of **PC** contamination for chain extensions, we continued using the halved **PC** loading moving forward.

Control experiments show that no p(EVE) was made in the absence of **PC** (entry 5a) and that TCT is necessary for controlled polymerization in both cases (entries 6a and 6b). Successful polymerization of EVE without the presence of a mediator is evidence of direct oxidation of the vinyl ether monomer by **PC**, but previous studies have shown that TCT oxidation occurs much faster than direct monomer oxidation at low [vinyl ether]:[TCT] ratios.<sup>50</sup>

With standard conditions determined for each mechanism, we performed a monomer to **TCT3** ratio screen for both photo-CP and TAGT to determine control over a wide molar mass range (Figure 2, for tabulated data, see Section S2.B). Photo-CP performed well when [EVE]:[TCT] was 50 and 100 – resulting in a close match of  $M_n$  to  $M_{n,theo}$  and a low dispersity. However, at larger [EVE]:[TCT], the molar masses begin to deviate from theoretical, which is common for photo-CP due to the direct oxidation of monomer by **PC** being more prevalent when increased amounts of monomer are present. This oxidation acts as a competing initiation pathway, leading to more chains and resulting in a lower  $M_n$ .<sup>51</sup> TAGT performed well for all [POPS]:[TCT] screened and resulted in good agreement with calculated theoretical  $M_n$  achieving molar masses up to 53 kDa while maintaining a low-to-moderate dispersity (<1.55). These results show good control over each homopolymerization using **TCT3**, validating its promise as a universal mediator for these two mechanisms.

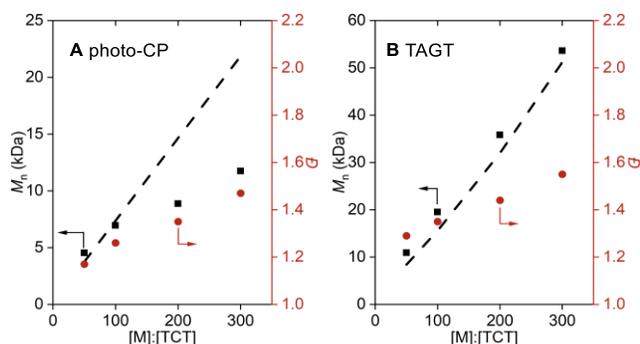


Figure 2. Molecular weight screen of (A) photo-CP and (B) TAGT homopolymerizations. Black square: number-average molecular weight ( $M_n$ ). Red circle: Dispersity ( $D$ ).

After simple removal of remaining EVE monomer and DCM via drying in vacuo, the p(EVE) samples were used as macro-mediators for chain extension via TAGT. Initially, we performed a chain extension screen using 50, 100, 200, and

300 equivalents of monomer to TCT for both the p(EVE) and p(POPS) blocks (Figure 3A, for tabulated data, see Supporting Information Section S2.C). After 6 hours of heating the samples, we observed peaks in the <sup>1</sup>H NMR spectra corresponding to p(POPS). Excitingly, the SEC traces of the obtained polymers showed a clean shift of the peak to a lower retention time compared to the starting p(EVE) peak, demonstrating clean chain extension to form p(EVE)-*b*-p(POPS) BCPs (Figure 3B). For polymers starting with p(EVE)<sub>200</sub> or p(EVE)<sub>300</sub>, a bimodal peak was observed in the SEC, which is explained by the increased level of direct oxidation of EVE monomer, leading to p(EVE) chains without the TCT chain ends (Section S2.C). Despite some loss of control at high molar masses, these chain extensions represent the first examples of sequential cationic-anionic polymerization using a TCT universal mediator.

Unfortunately, during the purification process via precipitation in methanol, we encountered fractionation of the p(EVE)-*b*-p(POPS) BCPs on the basis of the relative composition of the p(EVE) and p(POPS) blocks (Section S2.D). To avoid this fractionation from interfering with the polymer characterization, the chain extension screen was repeated – focusing on the block lengths that retained control (i.e., 50 and 100 equivalents of monomer relative to TCT) – and the resulting BCPs were purified using preparative SEC (prepSEC) (Table 2). As the ratio of [POPS]:[p(EVE)] went up from 50 to 100, the conversion of chain extension went up as well (compare entries 1 and 2 or 3 and 4), which we hypothesize is due to the higher concentration of monomer resulting in a chemical environment more similar to a POPS homopolymerization. Additionally, we observe lower conversion of POPS when using larger p(EVE) macro-mediators, which we hypothesize is due to the larger amount of residual **PC**, along with mass transport limitations. Similar to our initial chain extension screen, all BCPs showed clean peak shifts to lower retention times in the SEC relative to p(EVE) homopolymer (Section S2.E).

We next investigated the thermal characteristics of the BCPs purified by prepSEC. TGA revealed multi-stage degradations corresponding to the different blocks. Extrapolated onset temperatures of degradation ( $T_0$ ) were measured for these BCPs and compared to the corresponding homopolymers (Section S2.F). All BCPs have a moderately high thermal stability, possessing an initial major  $T_0$  from 271–283 °C, corresponding to the p(POPS) block, followed by a second  $T_0$  from 373–379 °C, corresponding to the p(EVE) block (Figure 4A). As expected, the % mass loss attributed to each of these degradation events corresponds to the size of the respective blocks. For example, the p(POPS)  $T_0$  accounts for

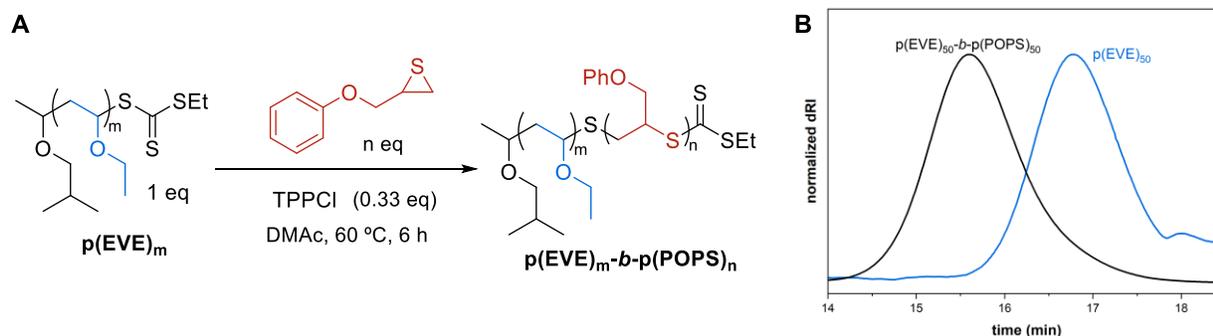


Figure 3. (A) Reaction scheme for chain extension of p(EVE) with POPS via TAGT. (B) Representative SEC traces showing chain extension from p(EVE) homopolymer to p(EVE)-*b*-p(POPS).

**Table 2. Select chain extensions of p(EVE) with TAGT**

entry	starting polymer	[POPS]:[p(EVE)]	conv. (%) <sup>[b]</sup>	$M_n$ (kDa) <sup>[c]</sup>	$M_w$ (kDa) <sup>[c]</sup>	$\bar{D}$ <sup>[c]</sup>	$T_o$ (°C) <sup>[d]</sup>	$T_g$ (°C) <sup>[e]</sup>
1	p(EVE) <sub>50</sub>	50:1	55%	10.3	14.7	1.43	283, 376	-30, 18
2		100:1	61%	18.7	27.4	1.47	272, 375	-32, 19
3	p(EVE) <sub>100</sub>	50:1	36%	10.4	15.2	1.46	271, 373	-41, 4
4		100:1	44%	18.0	27.2	1.51	277, 379	-49, 4

[a] Standard reaction conditions: p(EVE) (4.0  $\mu$ mol, 1 eq.), POPS (n eq.), TPPCl (0.33 eq.), DMAc (15  $\mu$ M p(EVE)), 6 h, 60 °C [b] conversion measured via <sup>1</sup>H NMR spectroscopy. [c] Measured via SEC in DMF with 0.025 M LiBr against PMMA standards. [d] Measured using TGA. [e] Measured using DSC.

approximately 25%, 50%, and 75% of the total mass loss for p(EVE)<sub>100</sub>-*b*-p(POPS)<sub>50</sub> (Figure S20), p(EVE)<sub>100</sub>-*b*-p(POPS)<sub>100</sub> (Figure 4A), p(EVE)<sub>50</sub>-*b*-p(POPS)<sub>100</sub> (Figure S19), respectively. A small mass loss event is seen for each BCP around 150 °C which we attribute to an unidentified small molecule mass loss in the p(EVE) blocks that was also observed in the multi-stage degradation of the p(EVE) homopolymer (Figure S16).

Next, DSC revealed two glass-transition temperature ( $T_g$ ) features for each BCP (Figure 4B), indicating that microphase separation between the two blocks has occurred.<sup>52</sup> The two  $T_g$ 's match closely to their respective homopolymers (Figure S22 and S23): the lower  $T_g$  (-49--30 °C) originates from the p(EVE) block, and the higher  $T_g$  (4--19 °C) originates from the p(POPS) block.

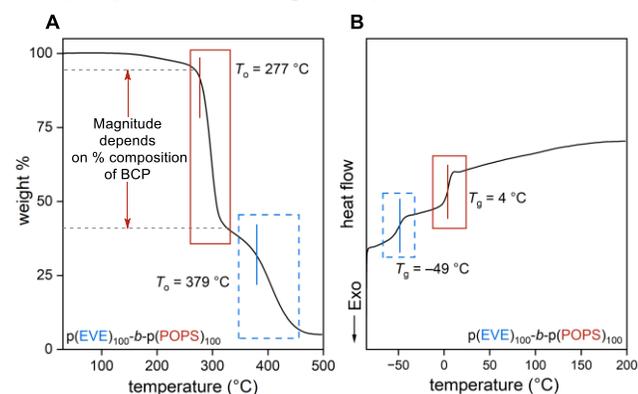


Figure 4. (A) TGA and (B) DSC of p(EVE)<sub>100</sub>-*b*-p(POPS)<sub>100</sub> with  $T_o$  and  $T_g$  features corresponding to p(POPS) (solid red box) and p(EVE) (dashed blue box).

The utility of the universal mediator is the fact that it supports multiple mechanisms while staying at the chain end. This end-group fidelity allows for the incorporation of a radical polymerization on our newly synthesized cationic-anionic BCPs to make a novel terpolymer. TCT compounds have also been reported to serve as a mediators in PET-RAFT utilizing a reducing photocatalyst.<sup>33,53–62</sup> Thus, we performed PET-RAFT using tris[2-phenylpyridinato-C2,N]iridium(III) [Ir(ppy)<sub>3</sub>] as the photocatalyst to extend our p(EVE)<sub>100</sub>-*b*-p(POPS)<sub>100</sub> macro-mediator with NIPAM (Figure 5). Excitingly, we observed a complete shift of the SEC peak corresponding to the diblock to a higher molar mass, indicating successful triblock formation. Due to the low molar mass tailing, we hypothesize that the shorter chains of the macro-mediator did not extend as cleanly as the higher molar mass chains. To the best of our knowledge, the only other example of combining radical, cationic, and

anionic polymerization sequentially was reported by the Kamigaito group in 2019,<sup>63</sup> but this system did not use a different monomer class for each mechanism, and the end group was modified after anionic polymerization to access the cationic and radical mechanisms. Therefore, our protocol represents the first report of combining cationic, anionic, and radical polymerizations in a single chain without any intermediate compatibilization or end-group modification steps to synthesize block copolymers of three different monomer classes.

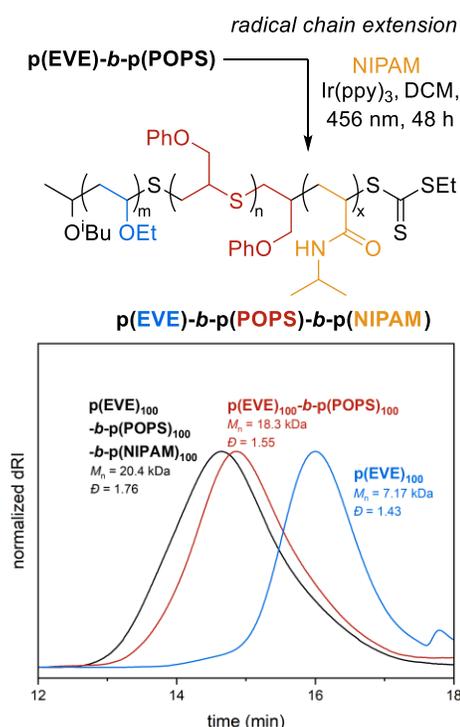


Figure 5. Radical chain extension from p(EVE)-*b*-p(POPS) diblock to make a block terpolymer from three different mechanisms and three different monomer classes.

In summary, we identified and applied **TCT3** as a universal mediator for photo-CP of vinyl ethers and TAGT of thiiranes in a simple, sequential procedure. The choice of TCT and monomer compatibilized the two mechanisms, allowing for complete chain extension of p(EVE) with POPS to form novel p(vinyl ether)-*b*-p(thiirane) diblock copolymers with a range of block lengths. These materials exhibited two  $T_g$  features in the DSC thermograms, suggesting microphase separation into two distinct domains. The utility of **TCT3** was further demonstrated by successfully extending the p(EVE)-*b*-p(POPS) diblock using PET-RAFT of NIPAM to

form a p(EVE)-*b*-p(POPS)-*b*-p(NIPAM) triblock terpolymer. Future work will focus on expanding the utility of this system as well as further characterization and application of these novel materials.

## ASSOCIATED CONTENT

Additional polymer characterization, including SEC chromatograms, TGA and DSC thermograms, tabulated data, experimental details, methods, reagent sources, synthetic procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

**Jessica R. Lamb** – Department of Chemistry, University of Minnesota–Twin Cities, Minneapolis, Minnesota 55455, United States; [orcid.org/0000-0001-9391-9515](https://orcid.org/0000-0001-9391-9515);  
Email: [jrlamb@umn.edu](mailto:jrlamb@umn.edu)

### Authors

Brandon M. Hosford<sup>‡</sup> – Department of Chemistry, University of Minnesota–Twin Cities, Minneapolis, Minnesota 55455, United States; [orcid.org/0000-0002-2349-0095](https://orcid.org/0000-0002-2349-0095)

William Ramos<sup>‡</sup> – Department of Chemistry, University of Minnesota–Twin Cities, Minneapolis, Minnesota 55455, United States; [orcid.org/0000-0002-7953-1212](https://orcid.org/0000-0002-7953-1212)

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENT

This work was supported by the National Science Foundation (NSF) Materials Research Science and Engineering Centers (MRSEC) (DMR-2011401) and the University of Minnesota (UMN). We thank Prof. Aleksandr Zhukhovitskiy and Hilary Djomnang-Fokwa for assistance with running prepSEC. NMR analyses were supported by the Research and Innovation Office (RIO), College of Science and Engineering (CSE), the Department of Chemistry at UMN, and the Office of the Director, National Institutes of Health (NIH, S10OD011952). Part of this work was carried out in the College of Science and Engineering Polymer Characterization Facility, UMN, which has received capital equipment funding from the National Science Foundation through the UMN MRSEC. The content of this paper is the sole responsibility of the authors and does not represent the official views of or endorsement by the NIH or NSF.

## REFERENCES

- (1) Harwood, H. J. Sequence Distribution in Copolymers. *Angew. Chem., Int. Ed.* **1965**, *4*, 1051–1060. <https://doi.org/10.1002/anie.196510511>.
- (2) Lutz, J.-F. An Introduction to Sequence-Controlled Polymers. In *Sequence-Controlled Polymers: Synthesis, Self-Assembly, and Properties*; ACS Symposium Series; American Chemical Society,

2014; Vol. 1170, pp 1–11. <https://doi.org/10.1021/bk-2014-1170.ch001>.

- (3) Grubbs, R. B.; Grubbs, R. H. 50th Anniversary Perspective: Living Polymerization—Emphasizing the Molecule in Macromolecules. *Macromolecules* **2017**, *50*, 6979–6997. <https://doi.org/10.1021/acs.macromol.7b01440>.

- (4) Ekizoglou, N.; Hadjichristidis, N. Synthesis of Model Linear Tetrablock Quaterpolymers and Pentablock Quintopolymers of Ethylene Oxide. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2166–2170. <https://doi.org/10.1002/pola.10288>.

- (5) Guo, X.-H.; Gu, G.-G.; Yue, T.-J.; Ren, W.-M. Orthogonal Polymerization of Aziridine with Cyclic Carbonates for Constructing Amphiphilic Block Copolymers. *Polym. Chem.* **2023**, *14*, 5034–5039. <https://doi.org/10.1039/D3PY01045G>.

- (6) Creutz, S.; Vandooren, C.; Jérôme, R.; Teyssié, P. Coupling of Living Polystyryllithium Anions and Living Polyethyl Vinyl Ether Cations. *Polym. Bull.* **1994**, *33*, 21–28. <https://doi.org/10.1007/BF00313469>.

- (7) Verma, A.; Nielsen, A.; McGrath, J. E.; Riffle, J. S. Preparation of Ester Terminated Poly(Alkyl Vinyl Ether) Oligomers and Block Copolymers Using a Combination of Living Cationic and Group Transfer Polymerization. *Polym. Bull.* **1990**, *23*, 563–570. <https://doi.org/10.1007/BF01033099>.

- (8) Puglisi, A.; Murtezi, E.; Yilmaz, G.; Yagci, Y. Synthesis of Block Copolymers by Mechanistic Transformation from Photoinitiated Cationic Polymerization to a RAFT Process. *Polym. Chem.* **2017**, *8*, 7307–7310. <https://doi.org/10.1039/C7PY01707C>.

- (9) Kahveci, M. U.; Acik, G.; Yagci, Y. Synthesis of Block Copolymers by Combination of Atom Transfer Radical Polymerization and Visible Light-Induced Free Radical Promoted Cationic Polymerization. *Macromol. Rapid Commun.* **2012**, *33*, 309–313. <https://doi.org/10.1002/marc.201100641>.

- (10) 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. <https://doi.org/10.1021/ma101420u>.

- (11) Schäfer, M.; Wieland, P. C.; Nuyken, O. Synthesis of New Graft Copolymers Containing Polyisobutylene by a Combination of the 1,1-Diphenylethylene Technique and Cationic Polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3725–3733. <https://doi.org/10.1002/pola.10472>.

- (12) Feldthusen, J.; Iván, B.; Müller, A. H. E. Stable Carbanions by Quantitative Metalation of Cationically Obtained Diphenylvinyl and Diphenylmethoxy Compounds: New Initiators for Living Anionic Polymerizations. *Macromolecules* **1997**, *30*, 6989–6993. <https://doi.org/10.1021/ma9704166>.

- (13) Yoshida, E.; Sugita, A. Synthesis of Poly(Tetrahydrofuran) with a Nitroxyl Radical at the Chain End and Its Application to Living Radical Polymerization. *Macromolecules* **1996**, *29*, 6422–6426. <https://doi.org/10.1021/ma9605210>.

- (14) Nomura, R.; Narita, M.; Endo, T. Block Copolymerization of Tetrahydrofuran and Tert-Butyl Methacrylate. Polarity Inversion of Cationic Propagation Ends into Anionic Ones via Two-Electron Reduction by Samarium Iodide. *Macromolecules* **1994**, *27*, 4853–4854. <https://doi.org/10.1021/ma00095a034>.

- (15) Liu, Q.; Konas, M.; Davis, R. M.; Riffle, J. S. Preparation and Properties of Poly(Alkyl Vinyl Ether-2-Ethyl-2-Oxazoline) Diblock Copolymers. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1709–1717. <https://doi.org/10.1002/pola.1993.080310709>.

- (16) Nemes, S.; Kennedy, J. P. Synthesis and Characterization of Polyisobutylene–Polybutadiene Diblocks. *J. Macromol. Sci., Chem.* **1991**, *28*, 311–328. <https://doi.org/10.1080/00222339108052145>.

- (17) Kitayama, T.; Nishiura, T.; Hatada, K. PMMA-Block-Polyisobutylene-Block-PMMA Prepared with  $\alpha,\omega$ -Dilithiated Polyisobutylene and Its Characterization. *Polym. Bull.* **1991**, *26*, 513–520. <https://doi.org/10.1007/BF01032676>.

- (18) Souel, T.; Schu e, F.; Abadie, M.; Richards, D. H. Block Copolymers Prepared by an Anion to Free Radical Transformation Process. 1. Kinetics and Efficiency of Initiation by Polyisoprene-Lead Trimethyl. *Polymer* **1977**, *18*, 1292–1294. [https://doi.org/10.1016/0032-3861\(77\)90298-1](https://doi.org/10.1016/0032-3861(77)90298-1).
- (19) Burgess, F. J.; Cunliffe, A. V.; MacCallum, J. R.; Richards, D. H. Reactions to Effect the Transformation of Anionic Polymerization into Cationic Polymerization: 2. Synthesis and Reactivities of Anionically Generated Xylelene Bromide-Terminated Polymers. *Polymer* **1977**, *18*, 726–732. [https://doi.org/10.1016/0032-3861\(77\)90241-5](https://doi.org/10.1016/0032-3861(77)90241-5).
- (20) Burgess, F. J.; Cunliffe, A. V.; MacCallum, J. R.; Richards, D. H. Reaction to Effect the Transformation of Anionic Polymerization into Cationic Polymerization: 1. Synthesis and Reactivities of Anionically Generated Bromine Terminated Polymers. *Polymer* **1977**, *18*, 719–725. [https://doi.org/10.1016/0032-3861\(77\)90240-3](https://doi.org/10.1016/0032-3861(77)90240-3).
- (21) Burgess, F. J.; Cunliffe, A. V.; Dawkins, J. V.; Richards, D. H. Reaction to Effect the Transformation of Anionic Polymerization into Cationic Polymerization: 3. Analysis of Block Copolymer Formation by Gel Permeation Chromatography. *Polymer* **1977**, *18*, 733–740. [https://doi.org/10.1016/0032-3861\(77\)90242-7](https://doi.org/10.1016/0032-3861(77)90242-7).
- (22) Zhang, K.; Bai, T.; Ling, J. Iron(III) Triflate as a Green Catalyst for Janus Polymerization to Prepare Block Polyesters. *Macromolecules* **2023**, *56*, 7389–7395. <https://doi.org/10.1021/acs.macromol.3c01359>.
- (23) Qiu, H.; Shen, T.; Yang, Z.; Wu, F.; Li, X.; Tu, Y.; Ling, J. Janus Polymerization: A One-Shot Approach towards Amphiphilic Multiblock Poly(Ester-Acetal)s Directly from 1,3-Dioxolane with  $\epsilon$ -Caprolactone. *Chin. J. Chem.* **2022**, *40*, 705–712. <https://doi.org/10.1002/cjoc.202100782>.
- (24) Dong, H.; Zhu, Y.; Li, Z.; Xu, J.; Liu, J.; Xu, S.; Wang, H.; Gao, Y.; Guo, K. Dual Switching in Both RAFT and ROP for Generation of Asymmetric A2A1B1B2 Type Tetrablock Quaterpolymers. *Macromolecules* **2017**, *50*, 9295–9306. <https://doi.org/10.1021/acs.macromol.7b01784>.
- (25) Hepuzer, Y.; Yagci, Y.; Biedron, T.; Kubisa, P. Photoactive Epichlorohydrin, 2. Photoinitiated Free-Radical and Promoted Cationic Polymerization by Using Polyepichlorohydrin with Benzoin Terminal Groups. *Die Angewandte Makromolekulare Chemie* **1996**, *237*, 163–171. <https://doi.org/10.1002/apmc.1996.052370109>.
- (26) Guerre, M.; Uchiyama, M.; Folgado, E.; Semsarilar, M.; Am eduri, B.; Satoh, K.; Kamigaito, M.; Ladmiral, V. Combination of Cationic and Radical RAFT Polymerizations: A Versatile Route to Well-Defined Poly(Ethyl Vinyl Ether)-Block-Poly(Vinylidene Fluoride) Block Copolymers. *ACS Macro Lett.* **2017**, *6*, 393–398. <https://doi.org/10.1021/acsmacrolett.7b00150>.
- (27) Uchiyama, M.; Satoh, K.; Kamigaito, M. Cationic RAFT Polymerization Using Ppm Concentrations of Organic Acid. *Angew. Chem., Int. Ed.* **2015**, *54*, 1924–1928. <https://doi.org/10.1002/anie.201410858>.
- (28) Ma, Q.; Zhang, X.; Jiang, Y.; Lin, J.; Graff, B.; Hu, S.; Lalev e, J.; Liao, S. Organocatalytic PET-RAFT Polymerization with a Low Ppm of Organic Photocatalyst under Visible Light. *Polym. Chem.* **2022**, *13*, 209–219. <https://doi.org/10.1039/D1PY01431E>.
- (29) Kottisch, V.; Michaudel, Q.; Fors, B. P. Photocontrolled Interconversion of Cationic and Radical Polymerizations. *J. Am. Chem. Soc.* **2017**, *139*, 10665–10668. <https://doi.org/10.1021/jacs.7b06661>.
- (30) 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. <https://doi.org/10.1021/jacs.1c09523>.
- (31) 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. <https://doi.org/10.1016/j.chempr.2020.05.003>.
- (32) Nagai, A.; Koike, N.; Kudo, H.; Nishikubo, T. Controlled Thioacyl Group Transfer (TAGT) Polymerization of Cyclic Sulfide: Novel Approach to AB Diblock Copolymers by the Combination of RAFT and TAGT Polymerizations. *Macromolecules* **2007**, *40*, 8129–8131. <https://doi.org/10.1021/ma071533w>.
- (33) 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. <https://doi.org/10.1038/s41467-018-05000-2>.
- (34) Li, J.-W.; Chen, M.; Zhang, Z.; Pan, C.-Y.; Zhang, W.-J.; Hong, C.-Y. Hybrid Copolymerization of Acrylate and Thirane Monomers Mediated by Trithiocarbonate. *Polym. Chem.* **2022**, *13*, 402–410. <https://doi.org/10.1039/D1PY01031J>.
- (35) Zhang, Z.; Xia, L.; Zeng, T.-Y.; Wu, D.-C.; Zhang, W.-J.; Hong, C.-Y.; You, Y.-Z. Hybrid Copolymerization via Mechanism Interconversion between Radical Vinyl-Addition and Anion Ring-Opening Polymerization. *Polym. Chem.* **2019**, *10*, 2117–2125. <https://doi.org/10.1039/C9PY00230H>.
- (36) Wang, C.-H.; Fan, Y.-S.; Zhang, Z.; Chen, Q.-B.; Zeng, T.-Y.; Meng, Q.-Y.; You, Y.-Z. Synthesis of Dual-Responsive Polymer via Convertible RAFT and Ring-Opening Polymerizations in One-Pot. *Applied Surface Science* **2019**, *475*, 639–644. <https://doi.org/10.1016/j.apsusc.2019.01.033>.
- (37) Gupta, M. K.; Meyer, T. A.; Nelson, C. E.; Duvall, C. L. Poly(PS-*b*-DMA) Micelles for Reactive Oxygen Species Triggered Drug Release. *J. of Controlled Release* **2012**, *162*, 591–598. <https://doi.org/10.1016/j.jconrel.2012.07.042>.
- (38) Spring, S. W.; Cerione, C. S.; Hsu, J. H.; Shankel, S. L.; Fors, B. P. Scalable, Green Chain Transfer Agent for Cationic RAFT Polymerizations. *Chin. J. Chem.* **2023**, *41*, 399–404. <https://doi.org/10.1002/cjoc.202200557>.
- (39) Shankel, S. L.; Lambert, T. H.; Fors, B. P. Moisture Tolerant Cationic RAFT Polymerization of Vinyl Ethers. *Polym. Chem.* **2022**, *13*, 5974–5979. <https://doi.org/10.1039/D2PY00780K>.
- (40) Peterson, B. M.; Lin, S.; Fors, B. P. Electrochemically Controlled Cationic Polymerization of Vinyl Ethers. *J. Am. Chem. Soc.* **2018**, *140*, 2076–2079. <https://doi.org/10.1021/jacs.8b00173>.
- (41) Li, J.; Kerr, A.; Song, Q.; Yang, J.; H akkinen, S.; Pan, X.; Zhang, Z.; Zhu, J.; Perrier, S. Manganese-Catalyzed Batch and Continuous Flow Cationic RAFT Polymerization Induced by Visible Light. *ACS Macro Lett.* **2021**, *10*, 570–575. <https://doi.org/10.1021/acsmacrolett.1c00180>.
- (42) Matsuda, M.; Uchiyama, M.; Itabashi, Y.; Ohkubo, K.; Kamigaito, M. Acridinium Salts as Photoredox Organocatalysts for Photomediated Cationic RAFT and DT Polymerizations of Vinyl Ethers. *Polym. Chem.* **2022**, *13*, 1031–1039. <https://doi.org/10.1039/D1PY01568K>.
- (43) Zhang, X.; Jiang, Y.; Ma, Q.; Hu, S.; Liao, S. Metal-Free Cationic Polymerization of Vinyl Ethers with Strict Temporal Control by Employing an Organophotocatalyst. *J. Am. Chem. Soc.* **2021**, *143*, 6357–6362. <https://doi.org/10.1021/jacs.1c02500>.
- (44) Zhang, Z.; Nie, X.; Wang, F.; Chen, G.; Huang, W.-Q.; Xia, L.; Zhang, W.-J.; Hao, Z.-Y.; Hong, C.-Y.; Wang, L.-H.; You, Y.-Z. Rhodanine-Based Knoevenagel Reaction and Ring-Opening Polymerization for Efficiently Constructing Multicyclic Polymers. *Nat. Commun.* **2020**, *11*, 3654. <https://doi.org/10.1038/s41467-020-17474-0>.
- (45) Takahashi, A.; Tsunoda, S.; Yuzaki, R.; Kameyama, A. Thioacyl-Transfer Ring-Expansion Polymerization of Thiranes Based on a Cyclic Dithiocarbamate Initiator. *Macromolecules* **2020**, *53*, 5227–5236. <https://doi.org/10.1021/acs.macromol.0c00711>.
- (46) Kottisch, V.; Michaudel, Q.; Fors, B. P. Cationic Polymerization of Vinyl Ethers Controlled by Visible Light. *J. Am. Chem. Soc.* **2016**, *138*, 15535–15538. <https://doi.org/10.1021/jacs.6b10150>.
- (47) Commonly, isobutyl vinyl ether (IBVE) and *n*-butyl vinyl ether (NBVE) are used for photo-CP due to their increased compatibility with a range of TCTs. However, the resulting polymers were found to be insoluble in DMAc, preventing the ability to chain extend using TAGT.

- (48) 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. <https://doi.org/10.1021/acscentsci.8b00401>.
- (49) 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. <https://doi.org/10.1002/anie.201406590>.
- (50) 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. <https://doi.org/10.1021/jacs.7b09539>.
- (51) Kottisch, V.; Supej, M. J.; Fors, B. P. Enhancing Temporal Control and Enabling Chain-End Modification in Photoregulated Cationic Polymerizations by Using Iridium-Based Catalysts. *Angew. Chem., Int. Ed.* **2018**, *57*, 8260–8264. <https://doi.org/10.1002/anie.201804111>.
- (52) Daimon, H.; Okitsu, H.; Kumantani, J. Glass Transition Behaviors of Random and Block Copolymers and Polymer Blends of Styrene and Cyclododecyl Acrylate. I. Glass Transition Temperatures. *Polym. J.* **1975**, *7*, 460–466. <https://doi.org/10.1295/polymj.7.460>.
- (53) Xu, J.; Fu, C.; Shanmugam, S.; Hawker, C. J.; Moad, G.; Boyer, C. Synthesis of Discrete Oligomers by Sequential PET-RAFT Single-Unit Monomer Insertion. *Angewandte Chemie International Edition* **2017**, *56*, 8376–8383. <https://doi.org/10.1002/anie.201610223>.
- (54) Chen, M.; Deng, S.; Gu, Y.; Lin, J.; MacLeod, M. J.; Johnson, J. A. Logic-Controlled Radical Polymerization with Heat and Light: Multiple-Stimuli Switching of Polymer Chain Growth via a Recyclable, Thermally Responsive Gel Photoredox Catalyst. *J. Am. Chem. Soc.* **2017**, *139*, 2257–2266. <https://doi.org/10.1021/jacs.6b10345>.
- (55) Xu, J.; Shanmugam, 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. <https://doi.org/10.1021/jacs.5b12408>.
- (56) Shanmugam, 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. <https://doi.org/10.1002/anie.201510037>.
- (57) Xu, J.; Shanmugam, S.; Duong, H. T.; Boyer, C. Organo-Photocatalysts for Photoinduced Electron Transfer-Reversible Addition-Fragmentation Chain Transfer (PET-RAFT) Polymerization. *Polym. Chem.* **2015**, *6*, 5615–5624. <https://doi.org/10.1039/C4PY01317D>.
- (58) Shanmugam, 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. <https://doi.org/10.1039/C4SC03342F>.
- (59) Shanmugam, S.; Xu, J.; Boyer, C. Exploiting Metalloporphyrins for Selective Living Radical Polymerization Tunable over Visible Wavelengths. *J. Am. Chem. Soc.* **2015**, *137*, 9174–9185. <https://doi.org/10.1021/jacs.5b05274>.
- (60) Shanmugam, S.; Boyer, C. Stereo-, Temporal and Chemical Control through Photoactivation of Living Radical Polymerization: Synthesis of Block and Gradient Copolymers. *J. Am. Chem. Soc.* **2015**, *137*, 9988–9999. <https://doi.org/10.1021/jacs.5b05903>.
- (61) 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. <https://doi.org/10.1021/acsmacrolett.5b00241>.
- (62) 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. <https://doi.org/10.1021/ja501745g>.
- (63) Satoh, K.; Mori, Y.; Kamigaito, M. Direct through Anionic, Cationic, and Radical Active Species: Terminal Carbon-Halogen Bond for “Controlled”/Living Polymerizations of Styrene. *J. Polym. Sci., Part A: Polym. Chem.* **2019**, *57*, 465–473. <https://doi.org/10.1002/pola.29261>.

---

## Table of Contents graphic:

