Cationic Polymerization of Vinyl Ethers Controlled by Visible Light

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S *Supporting Information*

ABSTRACT: Photoinitiated cationic polymerizations are widely used in industrial processes; however, gaining photocontrol over chain growth would expand the utility of these methods and facilitate the design of novel complex architectures. We report herein a cationic polymerization regulated by visible light. This polymerization proceeds under mild conditions: a combination of a metal-free photocatalyst, a chain-transfer agent, and light irradiation enables the synthesis of various poly(vinyl ether)s with good control over molecular weight and dispersity as well as excellent chain-end fidelity. Significantly, photoreversible cation formation in this system enables efficient control over polymer chain growth with light.

Applications for polymers are constantly expanding, in part because of the increasing degree of control that can be exerted during the synthesis of these complex macromolecules. The recent merging of photoredox chemistry and controlled radical polymerizations has led to the development of novel reactions that produce polymers with precise average molar masses and narrow dispersities ($Đ$) and, most interestingly, afford spatiotemporal control over chain growth.[1] The implementation of these reactions for patterning has delivered a bottom-up alternative to classic top-down photolithography techniques and has the potential to provide unique polymer architectures.[2] Consequently, it remains highly desirable to broaden the scope of polymerizations that allow photoregulation over chain growth and increase the number of polymeric architectures that can be created with these methods.

The vast majority of the photocontrolled polymerizations developed to date are based on radical processes. Several elegant photocontrolled atom transfer radical polymerizations (ATRP),[3] photoinduced organotellurium-mediated radical polymerizations (TERP),[4] and photoinduced electron transfer reversible addition—fragmentation chain transfer (PET-RAFT)[5] polymerizations have enabled the polymerization of a variety of acrylate, methacrylate, and styrenic derivatives. In a different approach, Boydston and co-workers disclosed a metal-free ring opening metathesis polymerization (ROMP) based on photoredox catalysis.[6] Through light irradiation, these reactions can be turned on or off at will, paving the way for applications requiring spatiotemporal control.

Photocontrolled cationic polymerizations have yet to receive the attention of their radical counterparts despite an impressive body of work on the photoinitiation of cationic transformations. Photoinitiated cationic polymerizations of vinyl ethers and oxiranes are indeed industrially relevant, and such systems commonly rely on the generation of acids or reactive

cations through light irradiation.[7] More recently, Nicewicz[8a] and Spokoyny[8b] have separately reported new systems for photoinitiated cationic polymerizations. However, these methods provide control only over polymer chain initiation, and the regulation of chain growth with light remains a notable challenge. Herein we address this unmet need and report the discovery of a photocontrolled "living" cationic polymerization of vinyl ethers (Scheme 1).

**Scheme 1. Design of a Photoreversible Cationic Polymerization of Vinyl Ethers**
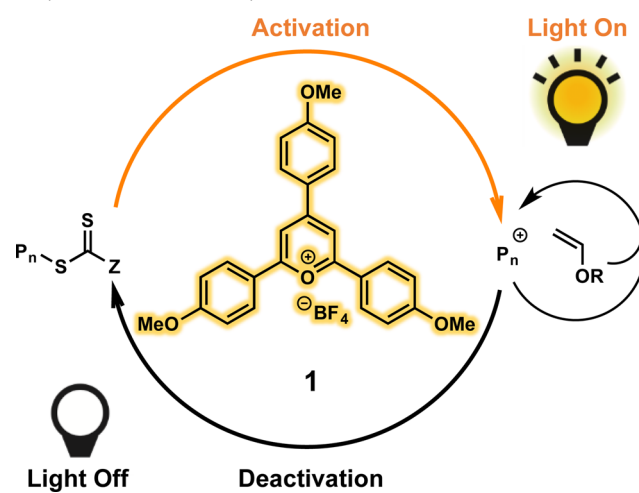
The ability to form carbocations reversibly in situ with light is the key to achieving photoregulation in cationic polymerizations. In 2015, Kamigaito and co-workers and Sugihara and co-workers independently disclosed controlled cationic RAFT polymerizations that used unique chain-transfer agents (CTAs) initiated with strong acids.[1c,9] We postulated that the oxidation of these CTAs with an appropriate photocatalyst followed by mesolytic cleavage would photoreversibly yield a carbocation that could participate in the RAFT process.[10] Significantly, this reaction would give rise to a "living" cationic polymerization process in which chain growth is regulated by light (Scheme 1).

To test our hypothesis, we investigated the polymerization of isobutyl vinyl ether (IBVE) with **2a** as the CTA (Table 1). An examination of strongly oxidizing photocatalysts showed that 0.01 mol % 2,4,6-tris(*p*-methoxyphenyl)pyrylium tetrafluoroborate (**1**)[11] converted 47% of the monomer after exposure to visible light for 3 h to yield a 2.6 kg/mol poly(IBVE) with a $Đ$

Table 1. Photocontrolled Cationic Polymerization of Isobutyl Vinyl Ether
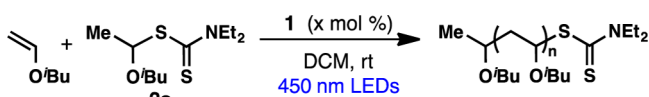
entry[a]	**1** (mol %)	M_n (exp) (kg/mol)	M_n (theo) (kg/mol)	Đ
1	0.01	2.6	2.3	1.29
2	0.02	5.6	5.0	1.19
3	0.02	10.0	10.0	1.21
4	0.02	17.5	20.0	1.21
5	0.01	35.0	40.0	1.30
6	0.02	26.0	40.0	1.37
7[b]	0.02	–	5.0	–
8[c]	–	–	5.0	–
9[d]	0.02	52.2	–	3.96

[a]Reaction conditions: IBVE (1 equiv), **1** (0.01−0.02 mol %), and **2a** (0.0025−0.02 equiv) at room temperature (rt) in DCM with blue light-emitting diode (LED) irradiation. [b]Carried out in the absence of light. [c]Carried out in the absence of **1**. [d]Carried out in the absence of **2a**.

Figure 1. Polymerization of IBVE: (a) conversion vs time; (b) M_n and Đ vs conversion.

of 1.29 (Table 1, entry 1). Increasing the concentration of **1** to 0.02 mol % led to full conversion and yielded 5.6 kg/mol polymer with a narrower Đ of 1.19 (Table 1, entry 2). These results demonstrate that a controlled cationic polymerization process promoted by light takes place. In further support of a controlled process, modulation of the CTA-to-monomer ratio enabled the synthesis of polymers with controlled number-average molecular weight (M_n) and narrow Đ values (Table 1, entries 2−5). Notably, all of the reactions were run to full conversion and showed excellent agreement between the theoretical and experimental molar masses. Furthermore, better control was observed at lower catalyst loadings when larger M_n values were targeted (Table 1, entries 5 and 6). Control experiments without light or **1** (Table 1, entries 7 and 8) did not yield any polymer. Additionally, reactions in the absence of **2a** led to uncontrolled polymerization, which we attributed to photoinitiation by direct oxidation of the monomer (Table 1, entry 9).[6,8a,12]

Monitoring the polymerization of IBVE under the optimized reaction conditions revealed a small induction period followed by fast monomer consumption to give full conversion after 2 h (Figure 1a). As expected for a system with living characteristics, M_n grew linearly with conversion and Đ steadily decreased from 1.41 to 1.19 as the reaction proceeded (Figure 1b). These data further corroborate the involvement of a controlled chain-growth process.

We next investigated our hypothesis that cation photo-activation is reversible, which would provide temporal control over the chain-growth process. A reaction mixture containing monomer, catalyst, and a CTA was exposed to light for 30 min and then stirred in the dark for the same time period. This cycle was repeated three times, and aliquots were obtained at each switching point for analysis by NMR spectroscopy and size-exclusion chromatography (SEC). The plot representing conversion versus time (Figure 2a) clearly shows that polymerization proceeded only under visible-light irradiation. Moreover, these results demonstrate that the reaction was arrested by removing the external stimulus and efficiently reinitiated by re-exposure to light. The SEC traces further support these data and show that the polymers grew only during periods of light exposure (Figure S12). These data
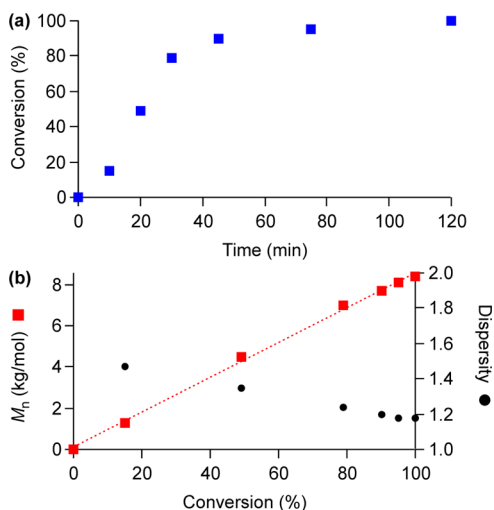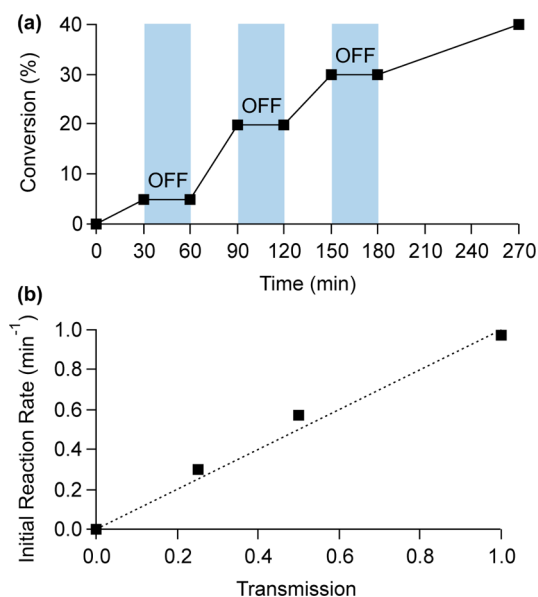
Figure 2. Temporal control of polymerization: (a) monomer conversion vs time with intermittent light exposure; (b) influence of light intensity on initial reaction rate.
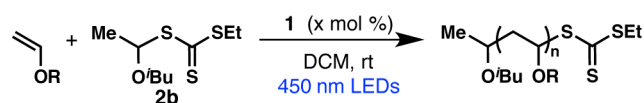
illustrate that the catalyst system provides photocontrol over polymer chain growth and that we have developed a truly photoregulated cationic polymerization process.[13]

To further demonstrate the temporal control of these polymerizations, we investigated the influence of the light intensity on the polymerization rate. Using neutral density filters, we observed a linear relationship between transmission and the initial reaction rate (Figure 2b), which shows that light intensity can be used to control the rate of polymer chain growth.

We then sought to apply this new methodology to other vinyl monomers. Interestingly, CTA **2a** yielded no polymer when used with other vinyl ethers. We therefore decided to use CTA **2b**, from which we expected to obtain a more active propagating cation.[9a] Gratifyingly, the use of **2b** under our standard conditions and low catalyst loadings of **1** led to the polymerization of ethyl vinyl ether (EVE), 2-chloroethyl vinyl ether (Cl-EVE), n-propyl vinyl ether (PVE), and n-butyl vinyl

ether (BVE). In all cases, good agreement between the experimental and theoretical M_n and narrow $Đ$ values were observed (Table 2).

Table 2. Optimized Polymerization Conditions for Other Vinyl Ethers with Photocatalyst 1 and CTA 2b

entry[a]	monomer	1 (mol %)	M_n (exp) (kg/mol)	M_n (theo) (kg/mol)	$Đ$
1	EVE	0.02	5.4	5.0	1.16
2	EVE	0.01	9.6	10.0	1.20
3	Cl-EVE	0.02	5.0	5.0	1.28
4	Cl-EVE	0.02	8.8	10.0	1.30
5	PVE	0.01	4.8	5.0	1.27
6	BVE	0.02	5.8	5.0	1.23

[a]Reaction conditions: vinyl ether (1 equiv), 1 (0.01−0.02 mol %), and 2b (0.01−0.02 equiv) at room temperature (rt) in DCM with blue light-emitting diode (LED) irradiation. Reactions were run to full conversion.

With conditions in hand that provide well-controlled vinyl ether homopolymers, we probed the chain-end fidelity of these materials through the synthesis of block copolymers. Using our standard conditions with 2b as the CTA, we synthesized 4.3 kg/mol poly(EVE) followed by the addition of IBVE to yield 10.7 kg/mol poly(EVE-b-IBVE) diblock copolymer (Figure 3).
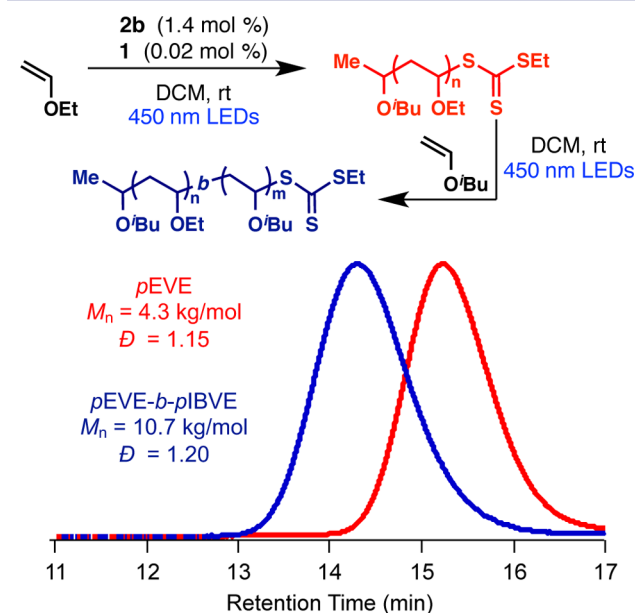

Figure 3. Synthesis of poly(ethyl vinyl ether) and poly(ethyl vinyl ether-*block*-isobutyl vinyl ether).

The SEC trace shows a monomodal distribution with low $Đ$ (1.20) and little to no tailing. This result demonstrates that our method can be used for the one-pot synthesis of block polymers and that the products maintain excellent chain-end fidelity even at full conversion.

Finally, photoluminescence quenching experiments were conducted to gain a better understanding of the polymerization mechanism. Strong quenching of 1* by 2a was observed at millimolar concentrations, and significant quenching by IBVE was measured at molar concentrations similar to those of the polymerization conditions (Figures S15−S19). These observations suggest that 1* may oxidize either the CTA or IBVE as previously reported by Nicewicz[8a] and Boydston.[6] Given these experimental data and literature precedents, we postulate that polymerization is activated by either direct oxidation of the CTA[14] with the excited catalyst or oxidation of the monomer[6,8a,12] followed by electron transfer from the CTA (Figure 4). Mesolytic fragmentation of the oxidized CTA[10]
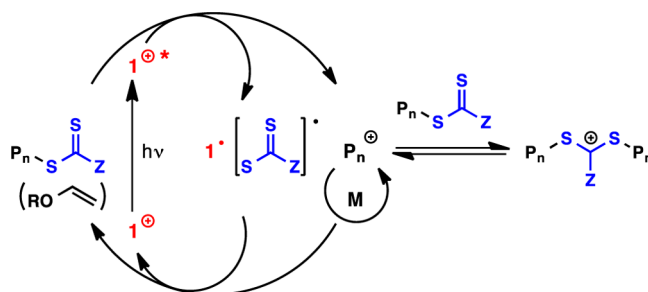

Figure 4. Postulated catalytic cycle for the photocontrolled polymerization of vinyl ethers.

would then result in a carbocation that would polymerize via a degenerative chain-transfer mechanism, thereby allowing for narrow $Đ$ and controlled M_n values. Reduction of the radical CTA with the reduced photocatalyst to the dithiocarbamate (for 2a) or trithiocarbonate (for 2b) anion would allow for the regeneration of 1 and concomitant chain capping. This final step closes the catalytic cycle and enables the photoreversible formation of a cation, which gives rise to temporal control over polymer chain growth.[15]

In summary, we have developed a cationic polymerization regulated by visible light that requires mild reaction conditions, parts per million concentrations of a metal-free photocatalyst,[16] and inexpensive blue light-emitting diodes. Narrow $Đ$ and predictable M_n values can be obtained for a variety of vinyl ether monomers, and block copolymers can be synthesized because of the high chain-end fidelity. Linear responses to light intensity and reversible photoactivation of the chain end allow temporal control over chain growth. This methodology therefore opens the field of photocontrolled reactions to a brand new class of monomers and should find numerous applications for the synthesis of complex polymeric architectures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b10150.

General experimental considerations, experimental procedures, pictures of experimental setups, and additional supporting data (PDF)

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Notes

The authors declare no competing financial interest.

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