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Metal-Free Ring-Opening Metathesis Polymerization

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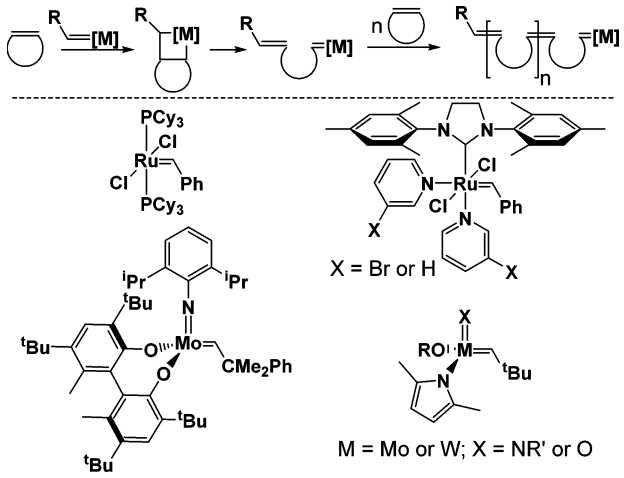
Supporting Information

ABSTRACT: We have developed a method to achieve ring-opening metathesis polymerization (ROMP) mediated by oxidation of organic initiators in the absence of any transition metals. Radical cations, generated via one-electron oxidation of vinyl ethers, were found to react with norbornene to give polymeric species with microstructures essentially identical to those traditionally obtained via metal-mediated ROMP. We found that vinyl ether oxidation could be accomplished under mild conditions using an organic photoredox mediator. This led to high yields of polymer and generally good correlation between M_n values and initial monomer to catalyst loadings. Moreover, temporal control over reinitiation of polymer growth was achieved during on/off cycles of light exposure. This method demonstrates the first metal-free method for controlled ROMP.

Ring-opening metathesis polymerization (ROMP, Scheme 1) is one of the most prevalent technologies that has emerged from the development of transition-metal-based olefin metathesis.[1,2] The widespread implementation of ROMP in both academic and industrial settings has led to breakthroughs in areas such as drug delivery, biomedical engineering, photovoltaics, and production of structural and engineering materials.[1,3] In general, ROMP can be used to achieve living polymerizations, provide polymers of narrow dispersity, enable excellent control over end group functionality, and incorporate a broad range of functional groups into polymer scaffolds and network materials.

Scheme 1. (Top) Generalized Depiction of ROMP Using Transition Metal Alkylidene Initiators, and (Bottom) Representative Metal Alkylidene Complexes Used in ROMP



These attributes are afforded by the highly optimized reactivities of primarily Ru- and Mo-based alkylidene initiators, as well as other transition metal complexes (Scheme 1, bottom). With such tremendous breakthroughs coming from *organometallic* developments, we became curious if a metal-free variant for ROMP could ever be achieved. Motivation for a departure from transition metal catalysts and initiators comes in part from recognition that metal-based byproducts can be difficult to remove from the polymeric materials,[4] and also by the promise of new synthetic capabilities stemming from unique polymerization strategies.

In general, metallic byproducts or residual complexes can lead to complications with biological studies, electronic properties measurements, or optical properties. Moreover, downstream reactivity of residual metallic species can be problematic,[5] often leading to untoward oxidative processes in the final material. At a minimum, the potential for metal contaminants often warrants quantitation by advanced techniques such as inductively coupled plasma mass spectrometry.[6] These issues have motivated a number of protocols for removing metal-based components,[4] which, even when successful, add additional processing steps for material production. Beyond circumventing issues directly related to metal species, moving toward organic initiators and potentially different polymerization mechanisms could offer unique control over polymer end group functionality, main chain microstructure, and methods for spatiotemporal control over polymer production.

We envisioned a method by which ROMP polymers could be obtained in a metal-free manner, using "all organic" initiators. A key to how this might be accomplished was first reported by Chiba and co-workers, in which an electrochemical intermolecular olefin cross metathesis reaction was achieved with an excess of terminal alkene in the presence of vinyl ethers (Scheme 2, top).[7] To our knowledge, however, this has only been demonstrated for a limited set of olefins, and without a *catalytic* role of the vinyl ether. More commonly, oxidation of the vinyl ethers leads to formation of a [2 + 2] complex that is reduced to give cyclobutanes.[8] Similar overall reactivity has also been reported using photoredox mediators,[9] as opposed to bulk electrolysis, to accomplish olefin dimerization (Scheme 2, bottom). Outcompeting the reduction to form cyclobutanes would be key to expanding the scope of this method and could unlock access to a new mechanism for ROMP.

As depicted in Scheme 3, we envisioned an approach to ROMP that would be initiated by one-electron oxidation of a

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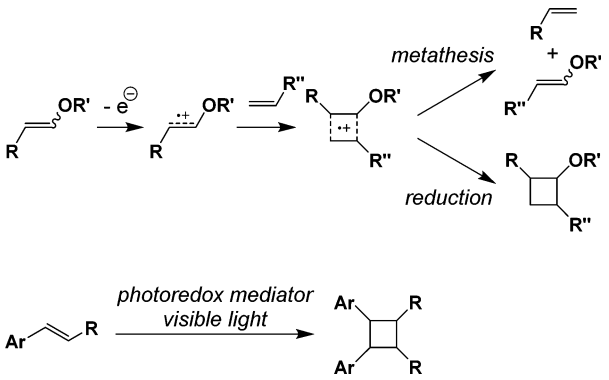
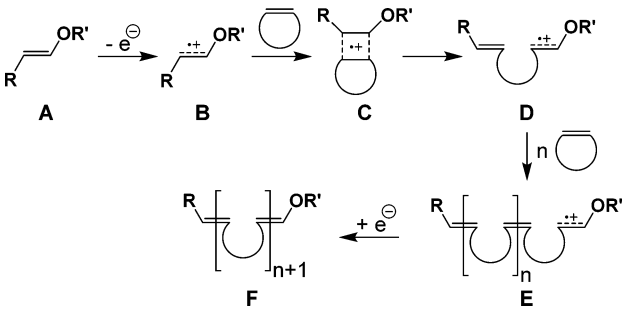
Scheme 2. (Top) Electrochemical Olefin Metathesis and Cyclobutane Formation, and (Bottom) Photoredox Mediated Cyclobutane Synthesis



Scheme 3. Idealized Mechanism of Redox-Initiated, Metal-Free ROMP



vinyl ether initiator (**A**) to produce the activated radical cation **B**. Subsequent reaction with a cycloalkene monomer would form a [2 + 2] complex (**C**). We hypothesized that reduction of **C** could be out-competed by rapid ring opening to alleviate ring strain in an appropriate cycloalkene. This would complete the ROMP initiation event arriving at **D**. Continued propagation with additional cycloalkene monomers would ultimately yield ROMP polymers, potentially bearing a reactive radical cation chain end (**E**). Reversible reductions of **D** and **E** are also likely, which would result in iterative termination−reinitiation cycles to arrive eventually at **F**. Encouraged by the propensity for ring strain in cycloalkene monomers to facilitate ROMP, we were inspired to develop an electro-organic approach to this widely used polymerization method. Herein, we report the initial development of a metal-free ROMP method.

We focused on norbornene (**1**) as a monomer, as this scaffold exhibits relatively high ring strain among common ROMP monomers (Figure 1). To investigate the direct oxidation of vinyl

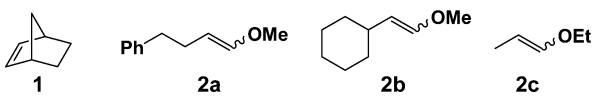


Figure 1. Monomers and initiators used in this study.

ethers and propensity for the ensuing radical cation to initiate ROMP, we conducted bulk electrolysis on solutions of **1** containing readily available vinyl ether initiators (**2a**−**c**). After electrolysis of **1** and **2a** for 3 h, the reaction solution and electrodes were analyzed for any presence of polynorbornene (PNB). A small amount of material was obtained (3% yield), and analysis by NMR spectroscopy revealed signals consistent with PNB. Moreover, end group signals consistent with the vinyl ether were observed even after precipitation of the polymer to remove any residual small molecule initiator. Gel permeation chromatography (GPC) analysis revealed a number-average molecular weight (M_n) of 11.8 kDa ($Đ$ = 2.2). Similar results were obtained using initiators **2b** and **2c**. Although the yields of PNB were consistently low, the confirmation that an anodic oxidation of **2** could initiate polymerization of **1** to give polymer structures consistent with a ROMP mechanism was encouraging.

The main challenges with further development of the electrochemical approach appeared to be poor solubility of **1** and PNB in nitromethane (a requisite solvent in Chiba's work), and heterogeneous oxidation of the initiator (**2**) at the electrode surface. To circumvent these issues, we pursued similar redox processes that were amenable to a broader solvent scope and homogeneous oxidations. We were inspired by recent breakthroughs in photoredox polymerizations, which have emerged as a powerful method for achieving metal-free protocols and spatiotemporal control over polymerizations.[10] Notably, photoredox polymerization strategies have focused almost exclusively on controlled radical addition polymerizations in which a redox process is inherent in the activation/deactivation of the polymer chain end. Traditional metal-mediated ROMP (Scheme 1), on the other hand, is redox-neutral at all stages, and the metal complex is covalently attached to each chain end until chemically cleaved at the end of the polymerization.

Pyrylium and acridinium salts (**3a** − **c**, Figure 2) have been identified as good candidates for facilitating photo-oxidation.[9b]

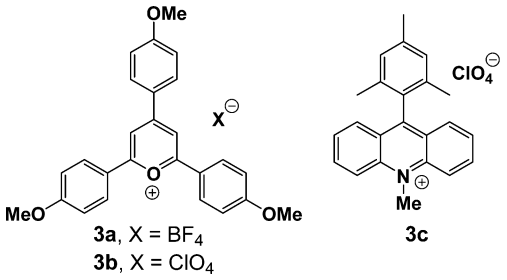


Figure 2. Photoredox mediators used in this study.

These mediators are capable of facilitating electron transfer when in the photoexcited state and were expected to be good oxidizers for the vinyl ether initiators (**2**). Whereas the initiators **2a**−**c** display oxidation potentials in the range of 1.43 to 1.30 V vs SCE,[6] the oxidizing power of excited state pyrylium and acridinium cations have been calculated to be 1.74 and 2.06 V vs SCE, respectively.[11,12] To explore the photoredox initiation of ROMP, we used an initial monomer concentration of ca. 1.9 M in CH_2Cl_2, with a monomer to initiator (**1**:**2a**) molar ratio of ca. 100:1. Using a blue LED light source (λ = 450−480 nm) in the presence of **3**, the best yields were obtained from the pyrylium tetrafluoroborate salt **3a**. In general, **3b** gave lower yields than **3a**, and **3c** failed to produce any detectable PNB.

The structure of the PNB was confirmed by ^{1}H NMR analysis in comparison with an authentic sample prepared via traditional ROMP using the Grubbs first-generation initiator (see Supporting Information). The glass transition temperature (T_g) of samples prepared by either traditional or photoredox mediated ROMP were also found to be consistent with one another. Specifically, the T_g of PNB prepared by Ru-mediated ROMP (M_n = 49.5 kDa) was found to be 53.3 °C, versus 49.5 °C for a sample prepared by photoredox initiation (M_n = 43.9 kDa).

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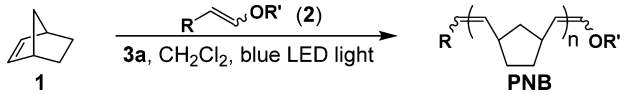
Table 1. Polymerization Results and GPC Data for Photoredox Mediated ROMP



entry	initiator	1:2:3[a]	$[1]_0$ (M)[b]	conversion (%)[c]	time (min)	$M_{n,\,theo}$ [kDa]	$M_{n,\,exp}$ [kDa]	Đ
1	**2a**	97:1:0.03	1.9	88 (73)	30	8.0	15.1	1.7
2	**2b**	97:1:0.03	1.9	92 (80)	30	8.4	14.9	1.6
3	**2c**	106:1:0.03	2.0	87 (67)	30	9.0	15.8	1.6
4	**2c**	104:1:0.10	1.9	80 (76)	150	7.8	13.5	1.4
5	**2c**	104:1:0.25	1.9	90 (73)	120	8.9	19.2	1.6
6	**2c**	48:1:0.03	1.8	95 (78)	60	4.3	8.1	1.4
7	**2c**	57:1:0.03	1.2	93 (58)	120	5.0	11.5	1.4
8	**2c**	491:1:0.03	5.3	51 (25)	120	23.6	22.2	1.5
9	**2c**	494:1:0.03	1.8	72 (50)	60	33.4	43.9	1.5
10	**2c**	1000:1:0.03	1.9	61 (47)	120	57.4	60.2	1.6
11[d]	**2c**	103:1:0.03	1.9	53 (29)	2580	5.0	7.2	1.3
12[e]	**2c**	102:1:0.03	1.9	88 (53)	90	8.5	15.5	1.4

[a]Initial molar ratio of **1**, **2**, and **3**. [b]Initial concentration of **1**. [c]Conversion of **1**, as determined by ^{1}H NMR analysis; isolated yields after precipitation given in parentheses. [d]Reaction mixture exposed only to ambient light from fume hood. [e]Reaction mixture exposed to blue LED light with half of the bulbs blocked out. $M_{n,\,theo}$ is theoretical number-average molecular weight calculated from initial **1**:**2** ratio and % conversion of **1**. $M_{n,\,exp}$ is experimental number-average molecular weight, calculated from a weight-average molecular weight determined by GPC using multiangle laser light scattering (MALLS). Dispersities (Đ) determined by GPC analysis.

Each initiator (**2**) gave PNB in good yield via the photoredox method (Table 1, entries 1−3). Whereas **2a** provides a distinguishable NMR handle (see Supporting Information), the majority of the polymerizations were conducted with **2c** simply due to commercial availability of this initiator. The amount of photoredox mediator **3a** that was required for successful polymerization was found to be quite low. Specifically, we observed consistent M_n values and % conversions when using mediator to initiator ratios (**3a**:**2**) of 0.03 to 0.25 (Table 1, entries 3−5). A higher loading of mediator did manifest some bimodality in the GPC traces, with high MW shoulders appearing with increasing amounts of mediator. We speculate that this may be due to the increased concentration of active chain ends and therefore greater extent of chain−chain coupling. Additionally, the complexity of reversible chain end deactivation/reactivation is likely influenced by the amount of mediator.

Varying the initial monomer to initiator ratio provided some degree of control over the final M_n (entries 3, 6−10). We observed a consistent correlation between the theoretical and experimental M_n values, with experimental values generally being greater than expected for the given monomer to initiator ratios and % conversions. Dispersities were found to vary between 1.3 and 1.7 across different experiments and remained fairly consistent during the course of each polymerization. We also found that the initial monomer concentration could be varied, with even very high (5.3 M) concentrations giving successful polymerizations (entry 8). This suggests that bulk polymerization using liquid monomers may be possible in the future with this approach.

Importantly, the initiator, mediator, and light source were each found to be required for the polymerization. In the absence of blue LED light, but with exposure to ambient lighting from the fume hood, we observed slow conversion to give PNB (Table 1, entry 11). Similarly, using blue LED light with half of the bulbs blocked out also gave PNB at an expected longer reaction time (entry 12). It is noteworthy that the reduced light intensity in each case gave lower Đ in comparison with other experiments, although the extent and origin of this trend are not yet clear. In the complete absence of light, no PNB was observed.

During the course of the polymerization, we observed a gradual increase in M_n with increasing conversion of monomer, consistent with the chain growth nature of ROMP (Figure 3).

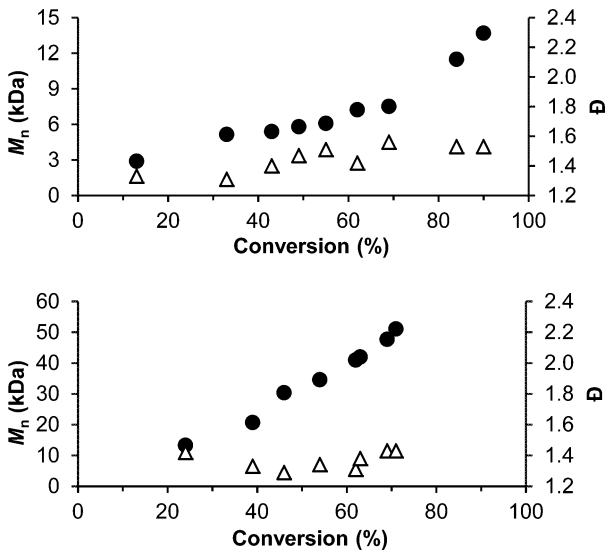


Figure 3. Plot of M_n (●) and Đ (△) vs % conversion of monomer using initial **1**:**2c** of (top) 100:1 and (bottom) 500:1.

Although there was a positive correlation, the linearity was not as precise as traditional "living" ROMP using, for example, Grubbs third-generation initiator.[1c,13] This could be ascribed to the relative rates of initiation and propagation in the photoredox method, or any number of early termination events.

Mechanistically, we envision oxidation of the vinyl ether via electron transfer to the excited pyrylium cation to give the vinyl ether radical cation (e.g., **A** → **B**, Scheme 3). Notably, the propagating radical cation chain end likely forms a dynamic redox couple with the reduced pyrylium species. The reversibility would manifest an ability for the radical cation chain end to be reduced to terminate polymerization, and then oxidize and reinitiate upon exposure to light. We investigated this temporal

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control by monitoring the polymerization with intermittent exposure to blue LED light. As shown in Figure 4, polymerization

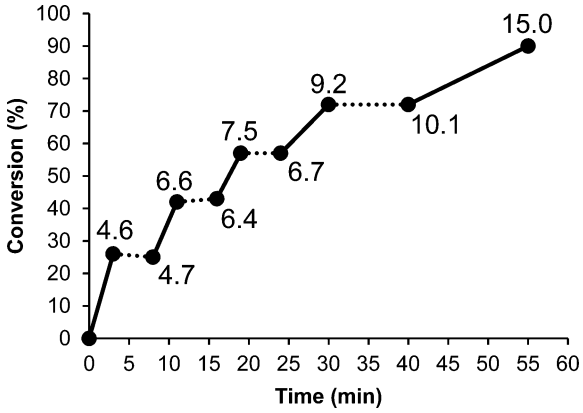

Figure 4. Plot of % conversion of monomer vs time. Solid lines indicate periods of exposure to blue LED light. Dotted lines indicate periods in the dark. Data point labels indicate M_n values (kDa). Initial conditions: **1**:**2a** = 100:1, $[\mathbf{1}]_0$ = 1.9 M.

ceased in the dark and was reinitiated upon exposure to blue light. Specifically, we observed little to no further conversion of monomer in the dark as determined by ^{1}H NMR spectroscopy and no significant changes in M_n as judged by GPC analysis. This suggested to us that the pyrylium cation and vinyl ether form a dynamic redox couple and that the radical cation chain end undergoes oxidation−reduction cycles during the polymerization. Furthermore, the correlation between % conversion and increasing M_n during the alternating light/dark cycles is consistent with chain end activation/deactivation cycles, as opposed to photomediated initiation of new polymer chains upon re-exposure to light.

In summary, we have developed the first protocol for achieving metal-free ROMP. The approach utilizes one-electron oxidation of electron-rich vinyl ethers to initiate the process, which can be achieved either electrochemically or via photoredox processes. A photoredox approach enabled high yields of polymerization in short reaction times under mild conditions. This demonstration may lead to a complementary approach to synthesizing ROMP polymers via a metal-free protocol, with potential to offer unique synthetic control over end group functionality. The success of the photoredox mediation may also provide new opportunities for spatiotemporal control over production of ROMP-based polymers and materials.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, representative cyclic voltammograms, and characterization of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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