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Communication

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Electrochemically Controlled Cationic Polymerization of Vinyl Ethers

Brian M. Peterson, Song Lin,* and Brett P. Fors*

Cornell University, Ithaca, New York 14853, United States

Supporting Information Placeholder

ABSTRACT: Control of polymer initiation, propagation and termination is important in the development of complex polymer structures and advanced materials. Typically, this has been achieved chemically, electrochemically, photochemically, or mechanochemically. Electrochemical control has been demonstrated in radical polymerizations; however, regulation of a cationic polymerization has yet to be achieved. Through the reversible oxidation of a polymer chain end with an electrochemical mediator, temporal control over polymer chain growth in cationic polymerizations was realized. By subjecting a stable organic nitroxyl radical mediator and chain transfer agent to an oxidizing current, control over polymer molecular weight and dispersity is demonstrated and excellent chain end fidelity allows for the synthesis of block copolymers.

Recently there has been a significant push to develop polymerizations where polymer chain growth is controlled by a chemical,[1] electrochemical,[2] photochemical,[3] or mechanochemical[4] stimulus. The spatiotemporal control offered by these stimuli give an additional means to precisely regulate polymer structure and, hence, function.[5] Of these stimuli, electrochemistry offers unique advantages because both applied voltage and current can be modified and monitored throughout the polymerization process.[6] Taking advantage of this, Matyjaszewski developed an electrochemically mediated atom transfer radical polymerization (eATRP),[7] which has proved powerful in a number of applications.[8] More recently, Matyjaszewski[9] and Yan[10] independently reported electrochemically mediated reversible addition fragmentation chain transfer processes (eRAFT). However, to date, electrochemical mediation of controlled polymerizations has been restricted to radical mechanisms and its implementation in other polymerization types remains a challenge.[1,2] In this study, we address this challenge and disclose a controlled cationic polymerization where chain growth is electrochemically regulated.

Recently, our group developed a cationic polymerization of vinyl ethers that was controlled by light.[11] By selectively oxidizing a dithiocarbamate polymer chain end with an appropriate photoredox catalyst, we were able to reversibly form a propagating carbocation that participated in a controlled cationic RAFT process.[11,12] In an analogous strategy, we hypothesized that we could reversibly form the carbocation in this process with electrical potential instead of light, which would give a system where chain growth would be regulated electrochemically (Figure 1).

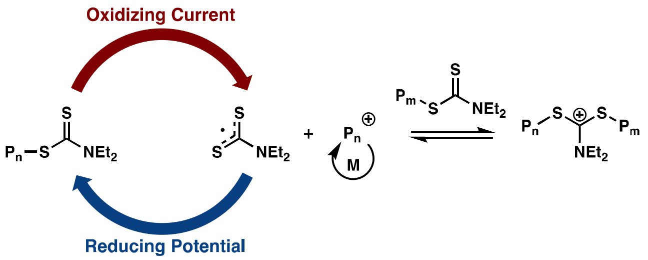


Figure 1: Proposed electrochemically mediated cationic polymerization of vinyl ethers.

Our group has previously shown that upon photochemical oxidation of a dithiocarbamate chain transfer agent (CTA), **1**, mesolytic cleavage occurs to generate an oxocarbenium ion and a stabilized dithiocarbamate radical.[11c] Cyclic voltammetry (CV) of **1** showed that an irreversible oxidation was occurring, suggesting that a similar oxidation followed by mesolytic cleavage process could be occurring at the electrode surface (Figure 2a). To test our hypothesis that this oxidation/mesolytic cleavage at the anode would give rise to cationic polymerization, we looked at the polymerization of isobutyl vinyl ether (IBVE) in a divided electrochemical cell with reticulated vitreous carbon (RVC) electrodes. Encouragingly, when a constant potential of 325 mV (vs Fc^+/Fc) was

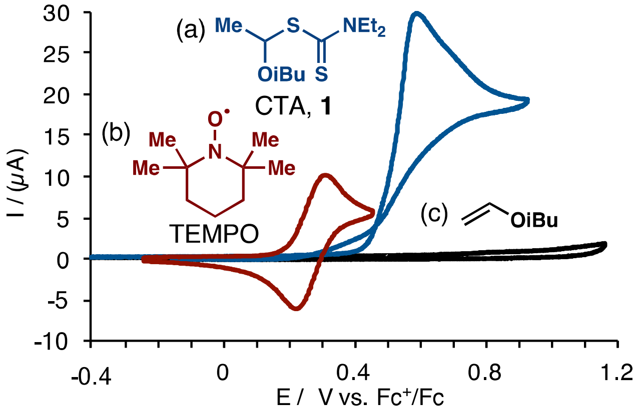
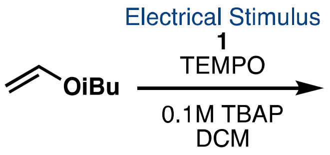


Figure 2: CV of (a) 1 X 10^{-3} M isobutoxy-*N,N*-diethyl dithiocarbamate, (b) 5 X 10^{-4} M (2,2,6,6-tetramethyylpiperidin-1-yl)oxyl (TEMPO), and (c)1 X 10^{-3} M isobutyl vinyl ether in 0.1 M tetrabutylammonium perchlorate in dichloromethane at 20 mVs^{-1}.

applied to a solution of IBVE, **1**, and tetrabutylammonium perchlorate (Bu_4NClO_4) in dichloromethane, cationic polymerization did occur (Table 1, entry 1). However, the polymers resulting from this direct electrolysis of the CTA exhibited broad dispersities (*Đ*) with bimodal molecular weight distributions (see supporting information, Figure S7).

Table 1: Development of IBVE polymerization mediated by the electrooxidation TEMPO.



Entry[a]	Stimuli	[M]:[**1**]:[TEMPO]	$M_{n,Theo}$[b] (kg/mol)	$M_{n,Exp}$ (kg/mol)	*Đ*
1[c]	325 mV	100:1:0	10.3	10.9	1.97
2[c]	325 mV	100:1:1	8.3	8.4	1.23
3[c]	325 mV	100:1:0.1	9.9	7.1	1.50
4[c]	325 mV	100:1:50	9.9	6.6	1.39
5[c]	325 mV	100:0:1	–	27.9	2.93
6	1 mA	100:2:1	5.0	6.8	1.07
7	1 mA	100:1.5:1.5	6.9	8.8	1.09
8	1 mA	100:1:1	10.4	10.1	1.15
9	0.1 mA	100:0.25:0.25	28.8	22.5	1.33
10[d]	1 mA	100:1:1	9.5	8.1	1.45
11[e]	1 mA	100:1:1	9.9	10.7	1.20

[a] [IBVE] = 3.84 M (in DCM), V_{tot}= 5 mL, [Bu_4NClO_4] = 0.1 M, RVC Anode, Ag Reference, RVC Cathode (Divided cell). [b] $M_{n,Theo}$ = [M]/[CTA] × MW_M × Conversion + MW_{CTA}. [c] Potential vs Fc^+/Fc. [d] Electrolyte = [Bu_4NPF_6] = 0.1 M. [e] Electrolyte = [Bu_4NBF_4] = 0.1 M

We reasoned that the observed uncontrolled polymerization could be attributed to polymer plating on the electrode as a result of the irreversible oxidation of the CTA.[9] To circumvent this issue, we envisaged that the use of a mediator capable of reversible electron transfer at the electrode and homogenous oxidation of the CTA would provide controlled polymerization.[13] Indeed, the addition of TEMPO (Figure 2b), which fit the criteria for the mediator, to the reaction mixture resulted in a 8.4 kg/mol polymer with a *Đ* of 1.23 (Table 1, entry 2).[14] Importantly, excellent agreement between theoretical and experimental molar masses was observed, demonstrating that we have a controlled cationic polymerization that is electrochemically mediated. Approximately 1 equivalent of TEMPO with respect to CTA was found to be optimal for these polymerizations, with deviations to higher or lower concentrations leading to a loss in control over the molecular weight (Table 1, entries 2 vs 3-4). As a control experiment and in further support of our mechanistic hypothesis, elimination of the RAFT equilibrium by removal of the CTA led to uncontrolled polymerization (Table 1, entry 5).

Upon further investigation, we found that higher conversion of the monomer could be obtained under galvanostatic conditions, wherein the potential is allowed to drift in unison with $E_{1/2}$ of the TEMPO redox couple as the concentration of $TEMPO^+$ increases.[15] Delivering an anodic current (1 mA) resulted in controlled polymerizations that could be run to full conversion (Table 1, entries 6–9).[16] Interestingly, switching the electrolyte to tetrabutylammonium hexafluorophosphate or tetrabutylammonium tetrafluoroborate resulted in slightly broader *Đ*s (Table 1, entries 10,11).[17]

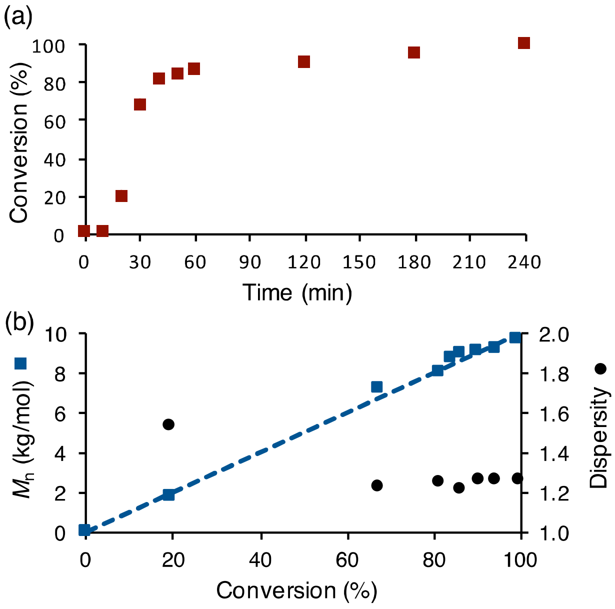


Figure 3: (a) Conversion of isobutyl vinyl ether with time. (b) Relationship between M_n and conversion.

Under optimal galvanostatic conditions, monitoring the reaction conversion as a function of time revealed a short induction period followed by fast polymerization with full conversion being reached within 3 hours (Figure 3a). Additionally, M_n increased linearly and *Đ* decreased with conversion, characteristic of a controlled chain growth mechanism (Figure 3b).

To demonstrate temporal control over polymer chain growth, a reaction mixture of IBVE, CTA, and TEMPO was subjected to 1 mA anodic current for twenty minutes. Subsequently, the electrode was set to (-)875 mV vs Fc/Fc^+ for 30 minutes; we reasoned that this potential should reduce the dithiocarbamate radical (or disulfide) to the corresponding anion, which would cap propagating oxocarbenium ions.[18] Indeed, switching to a reducing potential stopped polymer chain growth with little to no background reaction observed.

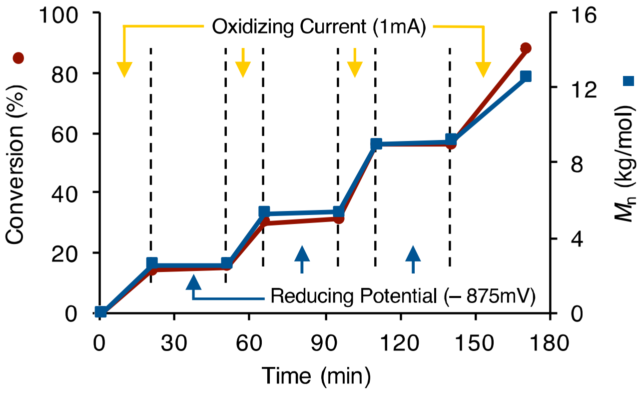


Figure 4: Temporal control of polymer chain growth with intermittent oxidizing current and reducing potential.

Reinitiation was then achieved by again applying the oxidizing current for 15 minutes. This process was successfully repeated multiple times, with polymerization only occurring when an oxidizing current was applied (Figure 4). These data demonstrated that we have excellent electrochemical control over polymer chain growth and the reactions can be reversibly initiated or terminated by switching the direction of current flow in the cell.

Table 2: Polymerization of vinyl ether and stryl monomers.

Entry[a]	Monomer	$M_{n,Theo}$[b] (kg/mol)	$M_{n,Exp}$ (kg/mol)	Đ
1	*n*BuVE	9.9	9.7	1.32
2	*n*PrVE	10.2	8.1	1.11
3	EVE	10.4	9.7	1.14
4	Cl-EVE	10.3	11.3	1.12
5[c]	*p*-OMe-Styrene	10.2	9.2	1.33

[a] [M] = 42% in DCM v/v, V_{tot} = 6 mL, [Bu_4NClO_4] = 0.1 M, RVC Anode, Ag Reference, RVC Cathode (Divided), Reaction time = 4 h. [b] $M_{n,Theo}$ = [M]/[CTA] × MW_M × Conversion + MW_{CTA}. [c] Applied current = 2 mA.

To explore the scope of our electrochemical polymerization protocol, we surveyed an array of vinyl ethers. *n*-Butyl vinyl ether (*n*BuVE), *n*-propyl vinyl ether (*n*PrVE), ethyl vinyl ether (EVE), and 2-chloroethyl vinyl ether (Cl-EVE) all underwent polymerization under the optimized galvonostatic conditions (Table 2). The resulting polymers showed good agreement between theoretical and experimental molecular weights, along with narrow Đs. Notably, 4-methoxystyrene was polymerized under slightly more demanding conditions (2 mA), constituting an improvement upon the photocontrolled polymerizations we previously reported, which did not promote polymerizations of styryl monomers.[11a,19] Although the resulting polymer has slightly broader dispersities when compared to the vinyl ethers, this preliminary finding highlights the versatility of this electrochemically mediated polymerization.

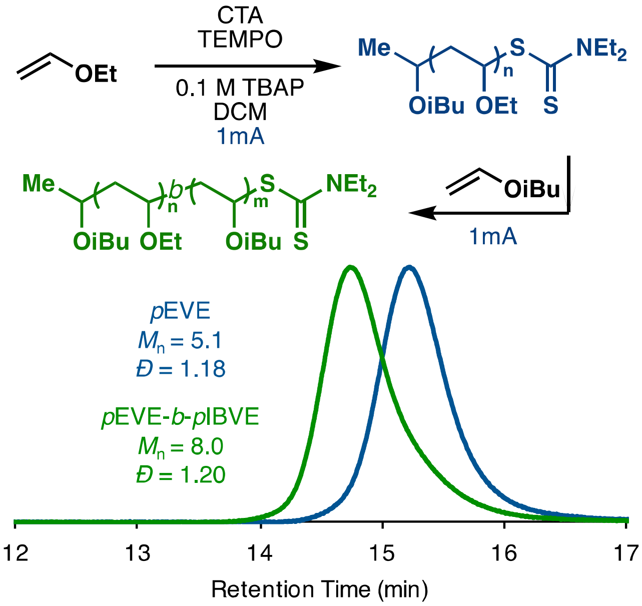


Figure 5: Synthesis and GPC traces of poly(ethyl vinyl ether) and poly(ethyl vinyl ether-*block*-isobutyl vinyl ether.

To further probe chain end fidelity delivered by this method we successfully chain extended a macroinitiator. A 5.1 kg/mol poly(EVE) was first synthesized under the optimized conditions, to which, IBVE was added to the anodic chamber and an oxidizing current was resumed. A clear shift to higher molar masses was observed to give a 8.0 kg/mol poly(EVE-*b*-IBVE) with narrow dispersity (Figure 5).

To further understand the role of TEMPO in these reactions, we found that when an oxidizing potential (325 mV vs Fc^+/Fc) was applied to a solution of the CTA and TEMPO, tetraethylthiuram disulfide was observed as a result of the dimerization of **II**, a byproduct of oxidatively cleaved CTA. Based on this result and our polymerization data above, we propose that the oxidized TEMPO cation undergoes an attack by the CTA to form a stabilized cationic intermediate **I** (Figure 6).[20] Fragmentation of the cation gives the dithiocarbamate radical **II** and the oxocarbenium ion that participates in the RAFT process, as well as regenerates TEMPO; together, this two step process completes an innersphere electron transfer. We hypothesize that when the current in the electrochemical cell is reversed, dithiocarbamate radical **II** or its dimeric form gets reduced to the anion and caps the propagating cation.[18] This recapping step gives efficient electrochemical control over polymer chain growth.

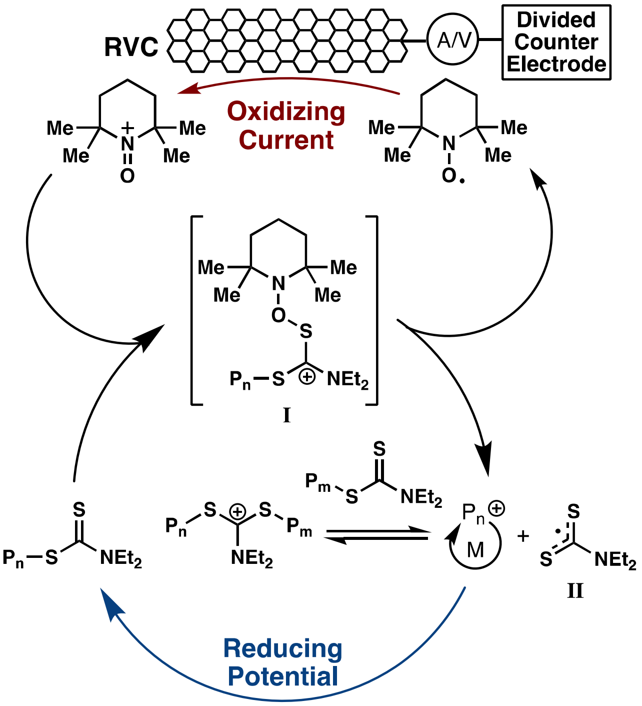


Figure 6: Proposed catalytic cycle of the TEMPO mediated polymerization of vinyl ethers.

In summary, we have developed an electrochemically mediated cationic polymerization, which offers excellent temporal control over polymer growth. A variety of poly(vinyl ethers) with narrow dispersities and predictable M_n values were obtained and the ability to polymerize less activated monomers was demonstrated. High chain end fidelity allows for the synthesis of block copolymers, while reversible electrochemical activation/deactivation of chain ends allows precise temporal control of chain growth. This new electrochemical handle for controlling cationic polymer growth should allow for the synthesis of complex polymer architectures, and provide a template for future electrochemically controlled polymerizations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

> General experimental considerations, experimental procedures, and additional supporting data (PDF)

AUTHOR INFORMATION

Corresponding Author

*bpf46@cornell.edu
*songlin@cornell.edu

Notes

The authors declare no competing financial interest.

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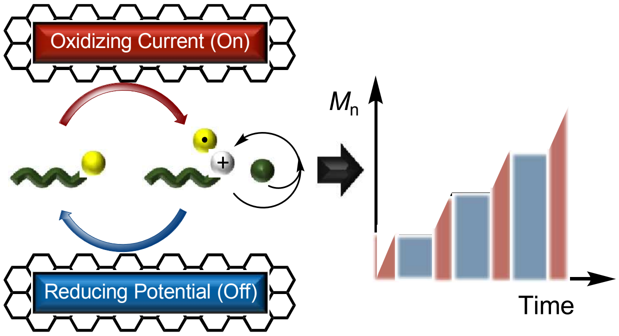

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