Selective Electrocatalytic Degradation of Ether-Containing Polymers

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Abstract: Leveraging electrochemistry to degrade robust polymeric materials has the potential to impact society's growing issue of plastic waste. Herein, we develop an electrocatalytic oxidative degradation of polyethers and poly(vinyl ethers) via electrochemically mediated hydrogen atom transfer (HAT) followed by oxidative polymer degradation promoted by molecular oxygen. We investigated the selectivity and efficiency of this method, finding our conditions to be highly selective for polymers with hydridic, electron-rich C–H bonds. We leveraged this reactivity to degrade polyethers and poly(vinyl ethers) in the presence of polymethacrylates and polyacrylates with complete selectivity. Furthermore, this method made polyacrylates degradable by incorporation of ether units into the polymer backbone. We quantified degradation products, identifying up to 36 mol% of defined oxidation products, including acetic acid, formic acid, and acetaldehyde, and we extended this method to degrade a polyether-based polyurethane in a green solvent. This work demonstrates a facile, electrochemically-driven route to degrade polymers containing ether functionalities.

Plastic disposal and pollution continue to increase annually, with 11 billion metric tons of plastic projected to accumulate in the environment by 2025.[1,2] To address the economic and environmental concerns of this trend, implementation of a circular polymer economy is of great importance.[3,4] Mechanical reprocessing is currently the most utilized form of plastics recycling. However, this method often affords lower-value materials with diminished properties. Thus, developing new strategies to chemically deconstruct and repurpose polymers—especially those not previously known to degrade readily—is an area of significant research interest.[5–18] Photodegradation has emerged as a promising strategy for polymer upcycling.[19–25] For example, the Stache group and several others have recently reported the photooxidative degradation of polystyrene to benzoic acid through a hydrogen atom transfer (HAT) mechanism.[26–33] Knowles and co-workers have also developed light-driven depolymerizations of hydroxylated polymers through proton–coupled electron transfer (PCET).[34,35] However, while photochemical methods have gained much attention for plastic valorization, the use of electrochemistry to drive polymer degradation is far less explored.

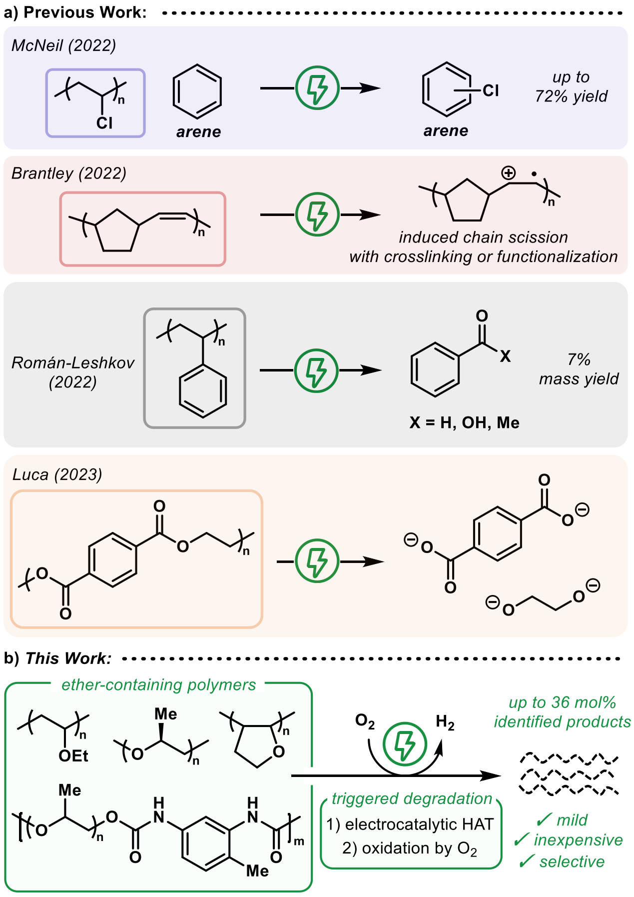


Figure 1. a) Previous electrochemical strategies to degrade polymers b) this work developing an electrochemically-driven oxidative degradation of ether-containing polymers.

Electrochemistry is currently undergoing a resurgence in organic and polymer synthesis due to its mild, scalable, and efficient nature.[36–44] Many methods have been developed to generate reactive species electrochemically;[45–50] however, these methods typically focus on bond-forming transformations as opposed to bond-breaking reactions,[51] with only a few reports of electrochemical methods for polymer upcycling or degradation (Figure 1a). In 2022, McNeil and co-workers reported electrochemical dechlorination of poly(vinyl chloride), where generated chlorine radicals were used to synthesize value-added chloroarenes.[52] Brantley and co-workers reported a direct oxidation of olefin-containing polymers, which was used to induce chain scission events—albeit with significant crosslinking—or backbone functionalization reactions.[53] In 2021, Sarlah and co-workers developed an electrochemical dearomatization of polystyrene.[54] More recently, Román-Leshkov and co-workers explored the efficacy of electrochemically formed phthalimido-*N*-oxyl (PINO) radicals to activate benzylic C–H bonds in small molecules—reporting a combination of oxidation and C–C bond scission events, with promising initial results applying this strategy toward polystyrene degradation.[55] Earlier this year, Luca and co-workers reported an electroreductive degradation of poly(ethylene terephthalate),[56] and Ackermann and co-workers developed a mangana-electrocatalytic azidation of polystyrene, polyethylene, and polypropylene with up to 7 mol% functionalization.[57] Among these early examples of electrochemical polymer degradation and upcycling, other inspiring work includes that by Stephenson, Stahl, and others to depolymerize lignin using oxidative C–H activation strategies.[58–61]

Our group recently reported a strong, biorenewable thermoplastic—poly(2,3-dihydrofuran) (PDHF)—which was synthesized via cationic polymerization of a cyclic vinyl ether.[62] We demonstrated an accelerated oxidative degradation of PDHF by a proposed HAT mechanism; however, these initial conditions required stoichiometric amounts of a strong oxidant. Inspired by recent advances in electrocatalysis, we envisaged leveraging electrochemistry to target the activated, electron-rich C–H bonds in ether-containing polymers to develop a catalytic approach for a mild and selective oxidative degradation using molecular oxygen (Figure 1b). Herein, we demonstrate that catalytic amounts of *N*-hydroxyphthalimide (NHPI) in the presence of pyridine, acetic acid, oxygen, and a constant electrochemical current were highly effective for oxidative degradation of ether-containing polymers. Furthermore, we achieved temporal control by an electrochemical stimulus, and we demonstrated excellent selectivity of this method for polymers with hydridic, electron-rich C–H bonds. Analysis of the degradation products revealed the formation of oxidized small molecules, such as acetic acid, formic acid, and acetaldehyde. This electrocatalytic degradation strategy provides a mild, inexpensive, and efficient route to degrade ether-containing polymers with activated C–H bonds selectively.

Our initial studies began by surveying the ability of various electrochemical mediators to oxidatively degrade poly(ethyl vinyl ether) (PEVE) that had an initial number-average molecular weight (M_n) of 15 kg/mol. In our effort to develop a practical degradation method, we avoided the use of platinum-group electrodes or highly specialized glassware at the outset. To an undivided electrochemical cell open to air and fit with a reticulated vitreous carbon (RVC) anode and a steel cathode, we added PEVE, dichloromethane (DCM), tetrabutylammonium tetrafluoroborate (TBABF$_4$), acetic acid, and one of the following mediators: 1,4-diazabicyclo[2.2.2]octane (DABCO), *N*-methylmorpholine *N*-oxide (NMO), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), hydroxybenzotriazole (HOBt), benzanilide, quinuclidine, or *N*-hydroxyphthalimide (NHPI) (Figure 2). We selected the above mediators due to their propensity for electrochemical oxidation (Figures S74-S83), which could generate nitrogen- or oxygen-centered radicals for C–H bond abstraction.[45,49] Furthermore, cyclic voltammetry studies showed protic mediators to be more electrochemically active in the presence of a weak base; therefore, we also added pyridine in reactions with benzanilide, HOBt, and NHPI. We applied a constant current of 0.5 mA and monitored the M_n over time using gel permeation chromatography (GPC). In the presence of NHPI, we observed a significant decrease in M_n from 15 kg/mol to 1.5 kg/mol after 2 hours and a linear increase in M_n^{-1} vs. time, indicating a chain scission mechanism (Figures 2 and S22). In contrast, electrolysis with quinuclidine resulted in a smaller decrease in M_n from 15 kg/mol to 9.8 kg/mol after 2 hours, and we observed no change in M_n with DABCO, NMO, TEMPO, HOBt, or benzanilide mediators. These results demonstrate that

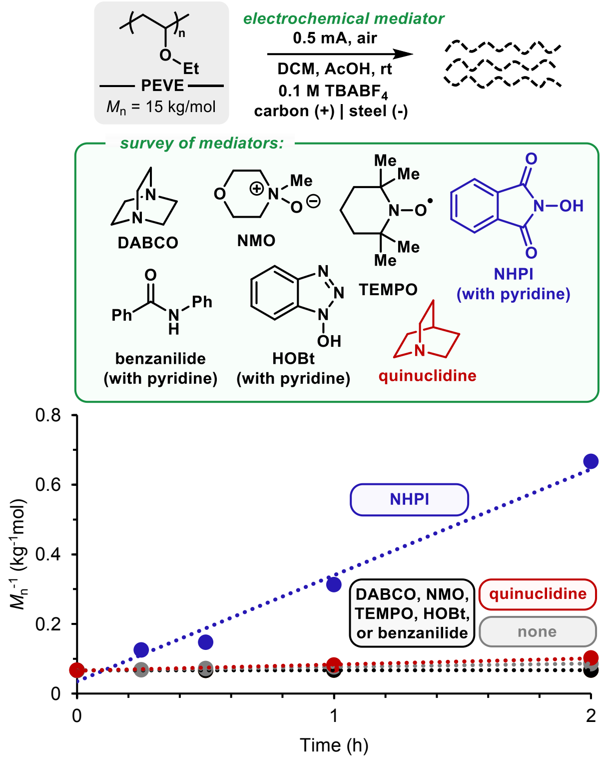
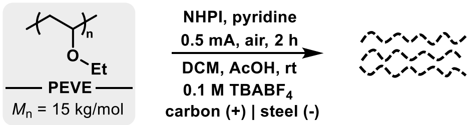


Figure 2. Reaction scheme used to survey different electrochemical mediators for the degradation of poly(ethyl vinyl ether) (PEVE) (above), and plot of M_n^{-1} vs. time for degradations with various mediators (below).

Table 1. Optimization of PEVE degradation rate.



Entry	Deviation	M_n (kg/mol)[a]	M_n^f/M_n^i (%)
1	none	1.5	10
2	no NHPI	12	80
3	no pyridine	3.1	21
4	no acetic acid	2.8	19
5	argon atmosphere	14	93
6	oxygen atmosphere	1.1	7.3

[a] Determined by gel permeation chromatography in reference to polystyrene standards.

the identity of the electrochemical mediator is pivotal for efficient polymer degradation.

To further interrogate the electrochemical degradation of PEVE using NHPI, we conducted control experiments by removing each component from the reaction. Without NHPI, we observed less efficient degradation of PEVE with only a slight decrease in M_n from 15 kg/mol to 12 kg/mol after 2 hours (Figure 2, Table 1, entry 2). Likewise, we also observed less efficient degradation without pyridine or acetic acid (Table 1, entries 3 and 4). These results support that NHPI as an electrochemical mediator—deprotonated by a weak base and aided by an acid additive—is most effective for polymer degradation. Upon saturating the electrochemical cell with argon, almost no degradation was observed after 2 hours (Table 1, entry 5, Figure S23); however, using an oxygen atmosphere resulted in an accelerated degradation rate (Table 1, entry 6, Figure S23), supporting that molecular oxygen plays a critical role in this degradation. In addition, we substituted other components, such

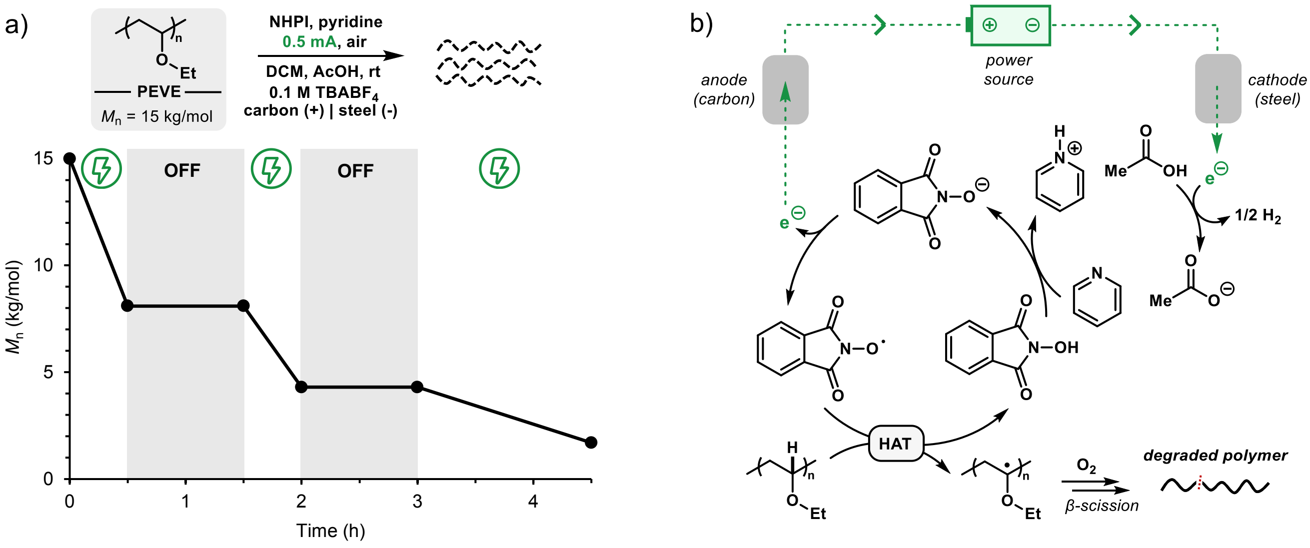


Figure 3. a) Plot of M_n vs. time illustrating temporal control over PEVE degradation using the presence or absence of current to turn the degradation on or off, respectively, and b) proposed catalytic cycle of the NHPI-mediated degradation of PEVE.

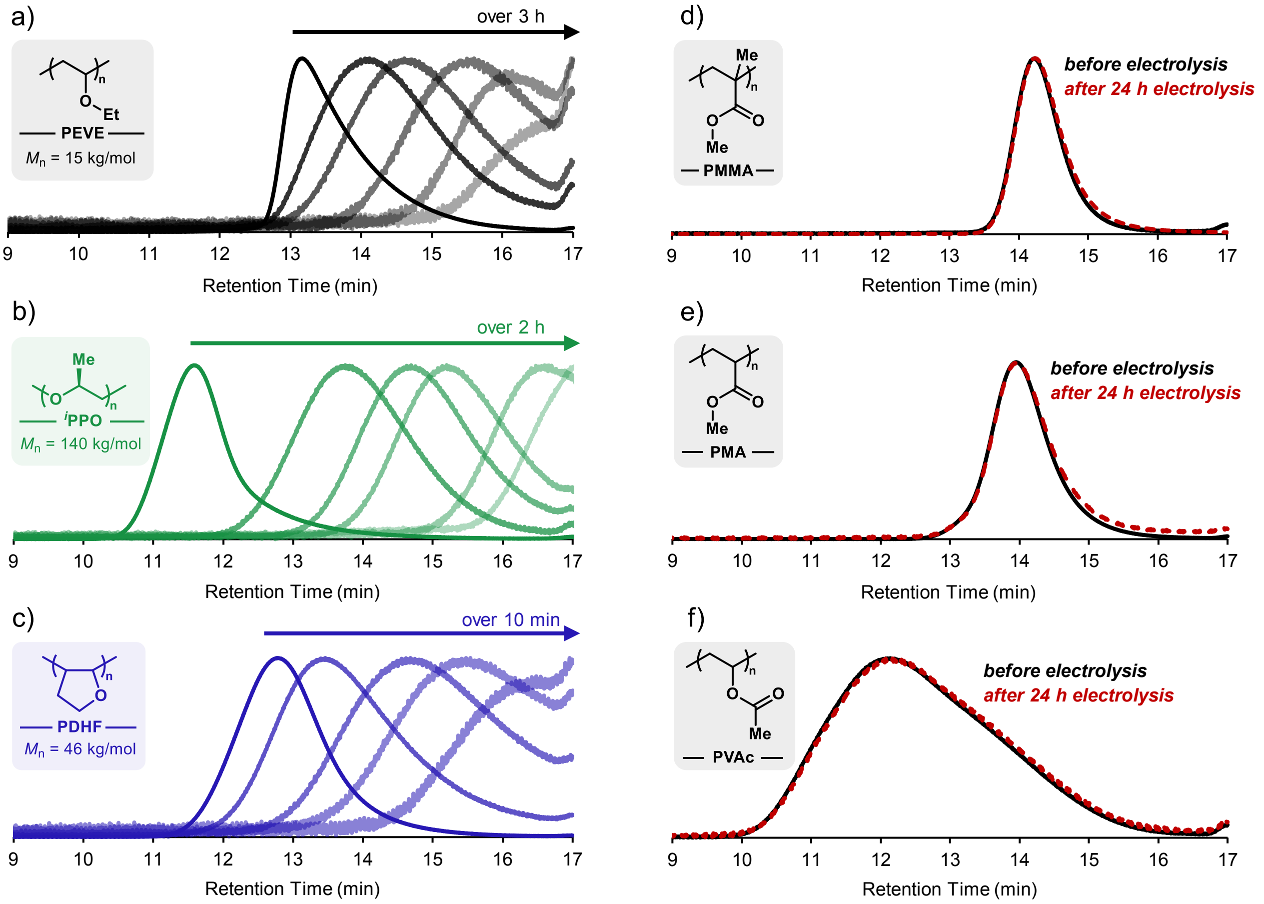


Figure 4. a) Corresponding GPC traces for degradations of a) PEVE, b) ^{i}PPO, and c) PDHF, showing efficient chain scission over time, and d) PMMA, e) PMA, and f) PVAc, showing no polymer degradation after 24 hours of electrolysis.

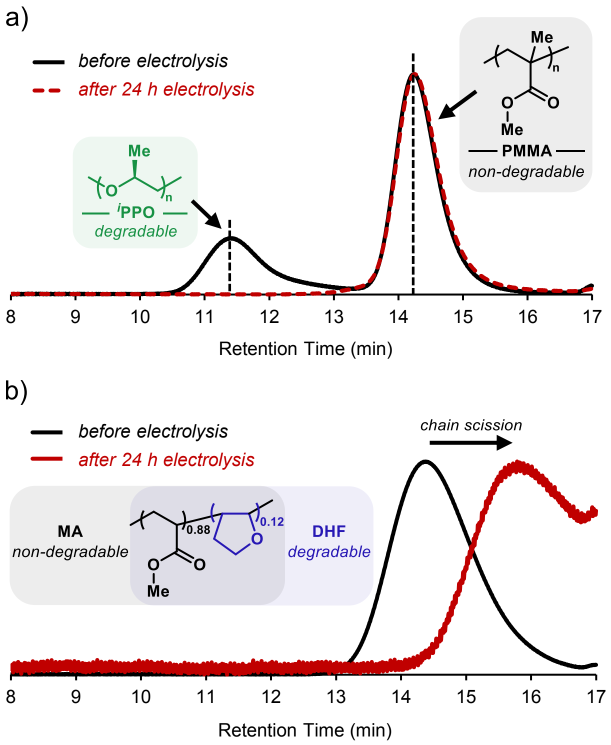


Figure 5. Corresponding GPC traces for degradations of a) ^{i}PPO in the presence of PMMA, showing selective degradation of ^{i}PPO, and b) a poly(MA-*co*-DHF) copolymer, showing evidence of chain scission.

as the electrolyte salt, cathode material, and acid additive, which all resulted in equivalent or less efficient degradation of PEVE (Table S1). Finally, in the absence of current, we observed no polymer degradation.

We next examined the ability of this system to provide temporal control over polymer degradation. Applying 0.5 mA of constant current for 30 minutes resulted in a decrease in M_n from 15 kg/mol to 8.1 kg/mol (Figure 3a, Figure S24). We then switched the current off for 1 hour, during which time we observed no change in M_n. Cycling between subsequent on, off, and on periods decreased M_n to 4.3 kg/mol and 1.7 kg/mol during the on periods, respectively, with no change in M_n during the off period. This result demonstrates that a constant electrochemical stimulus is needed for polymer degradation. Based on this result, our control experiments which show the necessity of each component, and literature precedent,[32,45,55] we propose that NHPI is deprotonated by pyridine and oxidized at the anode to form a phthalimide-*N*-oxyl radical, which can subsequently abstract a hydrogen atom from an electron-rich C–H bond on the PEVE backbone (Figure 3b). The resulting carbon-centered radical is then quenched by molecular oxygen, which leads to the *β*-scission of an adjacent C–C bond (Figures S69, S71, and S73) and a decrease in M_n. We hypothesize that the presence of acetic acid supplies protons to the cathode for reduction to molecular hydrogen, completing the electrochemical circuit.

To expand the scope of this electrochemical degradation strategy, we sought to apply our conditions to other poly(vinyl ethers) and polyethers. In particular, we were interested in PDHF and isotactic poly(propylene oxide) (^{i}PPO), which Coates and co-workers synthesized in 2020 by an enantioselective epoxide polymerization.[63,64] PDHF and ^{i}PPO represent strong thermoplastics with ultimate tensile strengths similar to polycarbonate and nylon-6,6, respectively.[62,64] Subjecting either PEVE, ^{i}PPO, or PDHF to our electrolytic conditions resulted in efficient degradations with monomodal shifts to lower molecular weights (Figure 4a-c). These results show that this electrochemical method can be generally applied to polymers containing ether functionalities. Furthermore, due to the unfavorable polarity matching between electrophilic radicals with electron-deficient C–H bonds,[65] we reasoned that this method would not degrade polymers containing only electron-deficient C–H bonds. To test this hypothesis, we subjected poly(methyl methacrylate) (PMMA), poly(methyl acrylate) (PMA), or poly(vinyl acetate) (PVAc) to our electrolytic conditions for 24 hours (Figures 4d-f). We observed no polymer degradation in each case, confirming high selectivity for polymers containing hydridic, electron-rich C–H bonds.

Methods to selectively degrade one polymer in the presence of others are highly desirable, particularly for targeted plastics upcycling and recycling strategies. To further explore the chemoselectivity of our system, we blended a sample of ^{i}PPO (degradable) with PMMA (non-degradable), resulting in a bimodal GPC trace (Figure 5a). After applying our electrolytic conditions to this blended sample for 24 hours, the GPC trace showed only

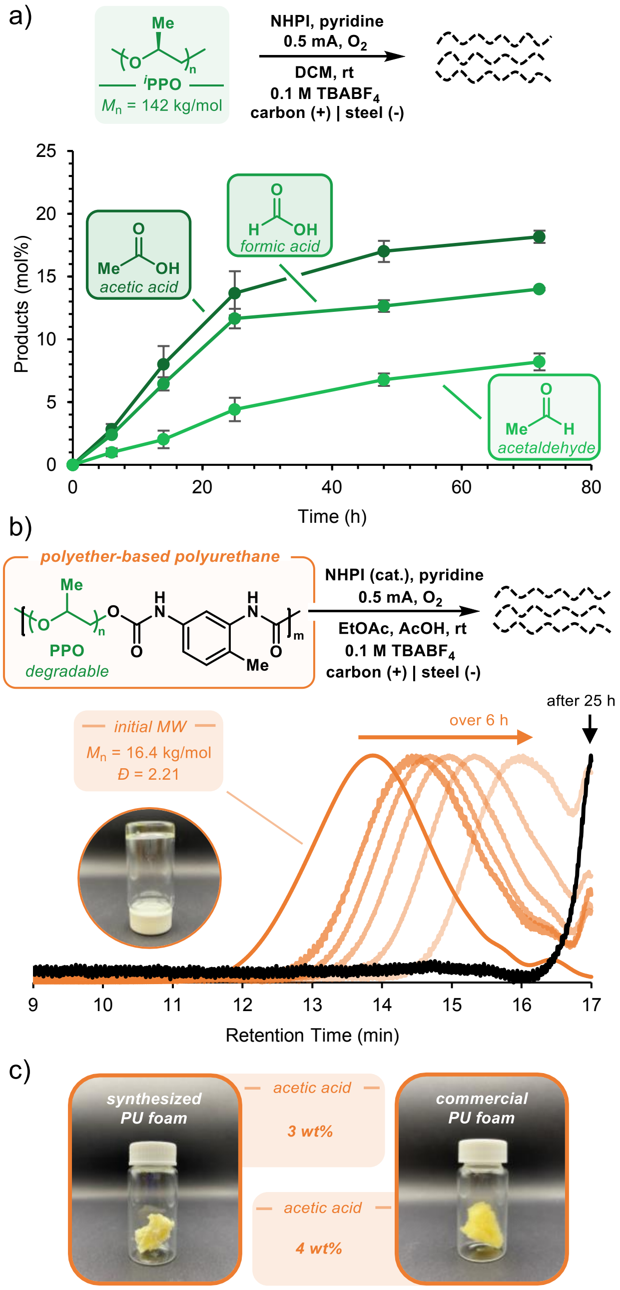


Figure 6. a) Plot of the degradation products produced (mol% with respect to the polymer repeat unit) vs. time in the electrochemical degradation of ^{i}PPO, b) electrocatalytic degradation of a polyether-based PU in ethyl acetate solvent, and c) quantified acetic acid products from the electrochemical degradation of a synthesized and commercial PU foam.

a monomodal distribution corresponding to the original PMMA sample. We observed similar results when degrading PDHF in the presence of PMA (Figure S26). Together, these results indicate that our electrochemical method can selectively degrade ether-containing polymers, even in the presence of PMMA or PMA.

Furthermore, we sought to incorporate ether groups into a traditionally non-degradable polymer to make it degradable by our system. PMA is an ideal candidate for this strategy, as PMA is a regularly used polymer that is not easily degraded.[17,25,66] Vinyl ethers are known to incorporate in the radical polymerization of acrylates; thus, we used a radical RAFT polymerization to prepare a sample of PMA with approximately 12 mol% incorporation of DHF (Figure 5b, Figure S11). Subjecting this copolymer to our electrochemical conditions decreased M_n from 6.5 kg/mol to 1.8 kg/mol after 24 hours (Figure S27). In contrast, the PMA homopolymer did not degrade under these conditions. These results demonstrate this electrochemical method as an enabling strategy for rendering polymers degradable by incorporation of ether units.

To further investigate this oxidative degradation, we used ^{1}H NMR to analyze the degradation products. We identified the major degradation product of PEVE to be acetic acid (36 mol%, with respect to the monomer repeat unit) and those of ^{i}PPO to be a mixture of acetic acid (14 mol%), formic acid (12 mol%), and acetaldehyde (4 mol%) after 25 hours of electrolysis. When looking at the relative amounts of degradation products generated over time from ^{i}PPO (Figure 6a), we observed a linear increase of acetic acid, formic acid, and acetaldehyde during the first 25 hours. After this time, the generation of degradation products gradually stabilized. We next sought to lower the amount of NHPI and observe the effect on product generation. After reducing the NHPI loading to 0.2 equivalents relative to the ^{i}PPO repeat unit, we observed similar amounts of acetic acid (14 mol%), formic acid (13 mol%), and acetaldehyde (4 mol%) after 25 hours of electrolysis, supporting that this degradation is catalytic in NHPI (Figure S52).

To demonstrate the utility of this method, we applied this electrocatalytic degradation to a polyether-based polyurethane (PU). PUs constitute an estimated 5-8 wt% of global polymer production with a significant fraction made from polyether polyols for the creation of flexible foams.[67,68] Although Dichtel and co-workers recently developed a promising method to reprocess PUs using carbamate exchange catalysis,[69–71] PUs are not currently recycled, which has been attributed to the high temperatures required for PU glycolysis.[72,73] We synthesized a polyether-based PU and subjected it to our electrochemical conditions using catalytic NHPI (20 mol%) and ethyl acetate (EtOAc) as a greener solvent alternative to DCM. Aliquots taken over 6 hours revealed a shift in M_n to low molecular weights, providing evidence of efficient degradation. After 25 hours, the M_n was below the detectable limit by GPC. While the use of EtOAc precluded the quantification of degradation products by ^{1}H NMR, running the reaction in DCM showed equivalent levels of acetic acid (13 mol%), formic acid (10 mol%), and acetaldehyde (4 mol%) compared to the degradation of ^{i}PPO at 25 hours (Figure S56). In addition, we subjected a synthesized PU foam and a commercial PU foam to our electrochemical conditions (Figure 6c, Figures S57 and S58), resulting in acetic acid degradation products (3 wt% or 4 wt%, respectively). We hypothesize that this degradation can be used with complementary methods for PU waste valorization, such as biological funneling[13] or the enzymatic hydrolysis of low molecular weight carbamates developed by Bornscheuer and co-workers.[74] Overall, these results demonstrate a green, inexpensive, and mild route to degrade polyether-based PUs.

In summary, we have developed an electrocatalytic oxidative degradation of polyethers and poly(vinyl ethers) and studied its mechanism, selectivity, and efficiency. PEVE, ^{i}PPO, and PDHF all degraded under our electrolytic conditions, while polymers containing electron-poor C–H bonds remained completely intact. Importantly, we leveraged this selectivity to degrade ^{i}PPO or PDHF in the presence of PMMA or PMA, respectively, and we rendered PMA degradable by incorporating ether units into the polymer backbone. Finally, we quantified the relative amounts of oxidized products, and demonstrated this strategy for the catalytic degradation of a polyether-based PU in a green solvent. We anticipate that this mild, inexpensive, and selective method will serve as an enabling technology for the design and degradation of high-performance polymers, with potential applications in chemoselective etching, post-polymerization functionalization, chemical upcycling, and tandem biodegradation strategies.

Supporting Information

The authors have cited additional references within the Supporting Information.[32,62,64,75–87]

The data that support the findings of this study are openly available in eCommons at https://doi.org/10.7298/e8d7-bh51

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Notes

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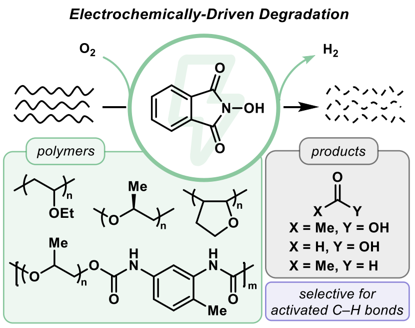

Electrochemically mediated hydrogen atom transfer (HAT) followed by oxidative polymer degradation promoted by molecular oxygen provides an electrocatalytic oxidative degradation of polymers with activated C–H bonds, such as polyethers, poly(vinyl ethers), and polyether-based polyurethanes. A study of the mechanism, selectivity, and efficiency of this method led to the identification of oxidized small-molecule degradation products.

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