Electrochemically Initiated Depolymerization of Poly(Methyl Methacrylate)

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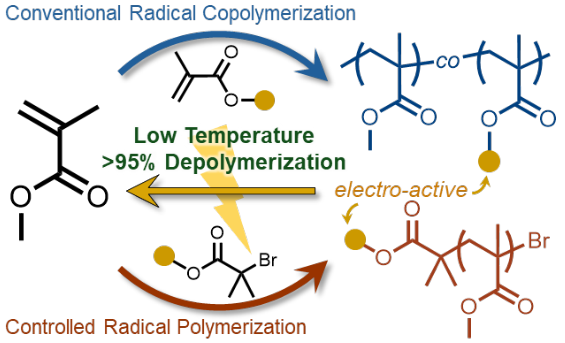

Abstract

Efficient depolymerization of polymers with all-carbon backbones under mild conditions would be valuable in chemically recycling commodity plastics. Poly(methyl methacrylate) (PMMA) is a commodity thermoplastic that is currently depolymerized under temperatures in excess of 400 °C. Herein, we lower the temperatures needed to achieve depolymerization of PMMA by performing radical generation and depropagation with orthogonal stimuli. This first demonstration of electrochemically initiated PMMA depolymerization relies on reduction of phthalimide esters that, upon subsequent decarboxylation, generate polymer-centered radicals. These radicals then spontaneously unzip the polymer back to its monomeric constituents at temperatures as low as 105 °C. We studied the mechanism and efficiency of this transformation as a function of phthalimide ester placement, incorporation density, and polymer molecular weight. We found that chain-end activation is effective for modest molecular weights but suffers diminished efficiency at higher degrees of polymerization. In contrast, pendent-group activation is more effective for depolymerizing higher molecular weight species. Integrating higher molar amounts of phthalimide ester pendants leads to more effective depolymerization, with >95% depolymerization in copolymers with 5 mol% phthalimide ester incorporation. We leveraged this understanding to create a custom electro-distillation apparatus that allowed us to simultaneously electrochemically depolymerize PMMA and directly distill methyl methacrylate in >22% yield, which could ultimately be repolymerized. These findings establish electrochemistry as a versatile and orthogonal stimulus for vinyl polymer depolymerization and provide a foundation for closed-loop electrochemical recycling of widely used plastics.

Keywords: Macromolecular electrolysis, depolymerization, electrochemistry, chemical recycling

Introduction

Macromolecules that can be selectively depolymerized into their monomeric starting materials are of significant interest for subtractive manufacturing, polymer recycling, and transient materials.[1-3] Conventionally, depolymerization is initiated thermochemically. However, triggering depolymerization in this way compromises the thermal and chemical stability that make polymeric materials valuable.[1, 4] This intrinsic tradeoff complicates the design and practical implementation of depolymerizable polymers, particularly in systems that demand robust performance.[5]

Most commodity plastics feature all-carbon backbones, which confer desirable mechanical and thermal properties but also hinder their controlled degradability.[6] Only 10% of plastic waste in the United States is currently recycled, with industrial efforts relying primarily on mechanical recycling that generally yields materials with inferior properties relative to their virgin counterparts.[2, 7] To overcome this limitation, chemical recycling has received increasing attention. This approach aims to revert polymeric materials to their constituent monomers that can be repolymerized into identical or even enhanced materials.[8] While such strategies have proven effective for polymers with heteroatom-containing backbones, translating this approach to vinyl polymers, especially those with all-carbon backbones, remains a significant challenge.[9-11] Developing methods that enable efficient depolymerization and repolymerization of vinyl polymers is therefore essential to close the loop on these widely used materials.

Poly(methyl methacrylate) (PMMA) is a widely used thermoplastic with global production exceeding 4 million tons annually. Its optical clarity, robust mechanical properties, and ease of processability have made it valuable for applications in aperture fabrication, dental implants, and orthopedic cement, among others.[12] However, the same thermal stability that underpins its performance, conferred by its all-carbon backbone, complicates depolymerization to methyl methacrylate (MMA) without significant thermal input or post-polymerization functionalization.[13, 14]

Depolymerization efficiency is governed by the thermodynamic equilibrium between propagation and depropagation.[15] Vinyl polymerizations are generally exothermic and thermodynamically favorable, proceeding spontaneously under standard conditions. However, polymer formation incurs an entropic penalty due to the loss of translational entropy as monomers become incorporated into polymer chains. Because the interplay between enthalpic and entropic contributions is temperature-dependent, there exists a temperature at which the entropic cost surpasses the enthalpic driving force, rendering depolymerization thermodynamically favored. This point is known as the ceiling temperature (T_c), i.e., the temperature above which polymerization becomes unfavorable at a given monomer concentration.[16]

Although elevated temperatures render depolymerization thermodynamically favorable, they must also overcome a significant kinetic barrier, namely, the formation of a reactive site that initiates depropagation. This barrier is particularly pronounced for polymers with all-carbon backbones, where generating depropagating radicals is inherently slow.[17] Recent studies, however, have shown that the inherent chain-end lability of polymers synthesized via reversible-deactivation radical polymerization methods can facilitate chain-end-initiated depolymerization under thermal or photochemical conditions.[15, 17-24] These approaches rely on the activation of pre-installed end groups (e.g., thiocarbonylthio or halogens) to generate chain-end radicals capable of initiating unzipping at dilute concentrations and elevated temperatures.

As an example, Ouchi and coworkers showed that ruthenium-catalyzed reactivation of chlorine-capped PMMA led to 24% depolymerization after 24 h at 100 °C.[20] Additionally, both Gramlich, and Anastasaki reported thermal depolymerization of reversible addition–fragmentation chain transfer (RAFT)-derived polymethacrylates at high dilution (0.1 M and 5 mM repeat unit concentration respectively), achieving 33% and 92% depolymerization, respectively.[19, 22] Notably, these approaches required no exogenous catalysts.

Our group previously reported that photoexcitation of RAFT chain-ends can accelerate solution-phase depolymerization.[15] We also demonstrated that thermally labile phthalimide (Phth) esters incorporated at the α-chain-end enables efficient bulk depolymerization. Interestingly, polymers that had thermally labile groups at both the α (Phth)- and ω (thiocarbonylthio)-chain-ends achieved higher extents of depolymerization than polymers with only one thermally labile chain-end.[17] We have also developed an efficient strategy for pendent-group-triggered depolymerization of PMMA synthesized via conventional radical polymerization, operating at lower temperatures than traditional thermal recycling processes. By incorporating multiple depolymerization triggers per chain, we achieved high (up to 95%) extents of depolymerization, even for PMMA with high molecular weights.[13]

Although these previous reports typically required specialty polymer synthesis, recent studies have shown that commercial PMMA can be retrofitted with either chain-end or pendent active esters to facilitate depolymerizability.[14, 25, 26] However, despite these advances, substantial thermal input (>200 °C) is still required to facilitate depolymerization triggered by phthalimide esters, suggesting an opportunity to develop orthogonal activation strategies.[13, 14, 17, 27, 28]

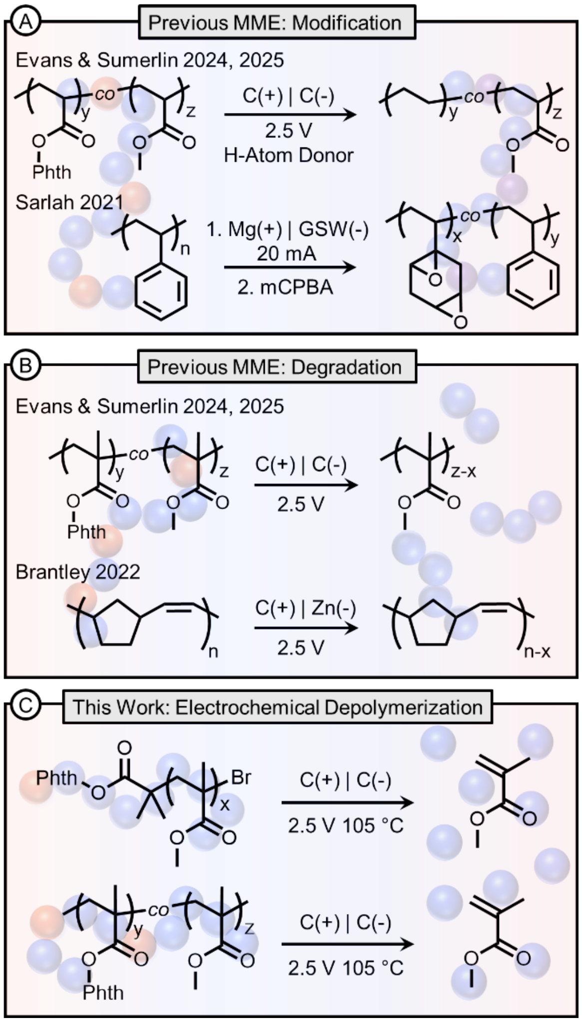

Figure 1. Macromolecular electrolysis (MME) to A) functionalize, B) degrade, and C) depolymerize vinyl polymers. Phth = Phthalimide, GSW = Galvanized Steel Wire, mCPBA = meta-Chloroperoxybenzoic acid

Electrochemical methods offer a scalable, tunable, and energy-efficient stimulus for controlled polymer depolymerization and monomer recovery.[29-34] To date, macromolecular electrolysis (MME) has primarily been explored for either polymer functionalization (**Figure 1A**) or backbone degradation (**Figure 1B**).[35, 36] For example, the Sarlah group reported the electrochemical dearomative reduction of polystyrene and subsequent epoxidation to access materials inaccessible by direct polymerization.[37] Brantley and coworkers demonstrated that all-carbon backbone polymers such as polyalkeneamers could be electrochemically degraded via anodic oxidation and *β*-scission of the olefin-containing backbones.[38] We recently employed a related strategy, using the cathodic reduction of Phth ester pendants to degrade polymethacrylates and functionalize polyacrylates.[29, 39] While these examples highlight the utility of MME for polymer functionalization and degradation, electrochemical depolymerization of polymers with all-carbon backbones has not been previously demonstrated.[36]

We hypothesize that electrochemical activation could initiate the depolymerization of PMMA by targeting either chain-end or pendent Phth esters (**Figure 1C**). This transformation is proposed to proceed via a one-electron reduction of the Phth ester, leading to N–O bond homolysis and formation of a carboxyl radical and Phth anion (**Figure 2**).[29] Subsequent decarboxylation generates a polymer-centered radical that, in the case of polymethacrylates, undergoes β-scission to yield a PMMA macroradical capable of depolymerization.[29, 39, 40]

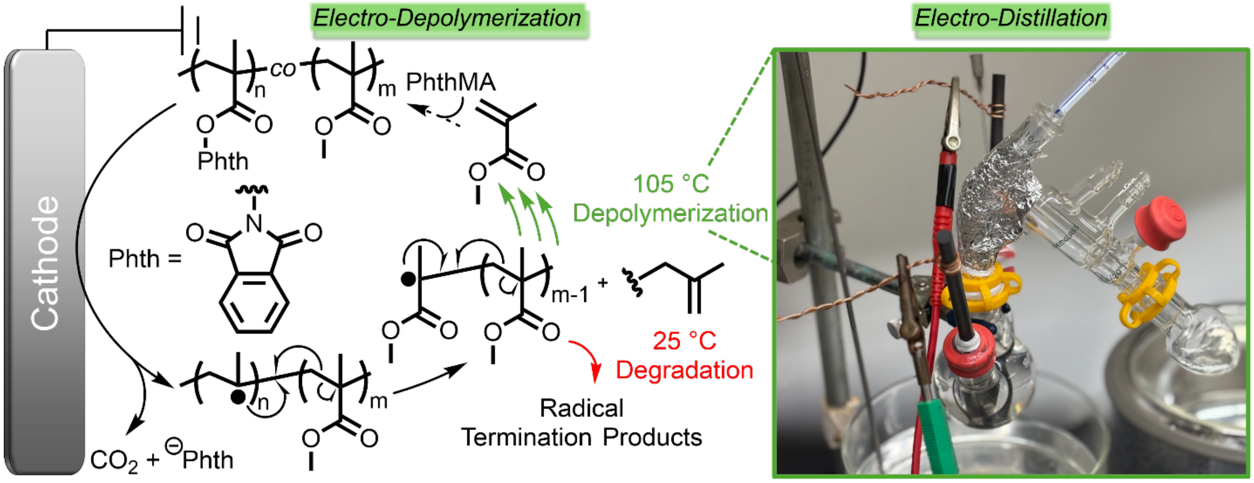

Figure 2. Proposed mechanism of electrochemically triggered depolymerization of Phth-functionalized PMMA via cathodic reduction and custom electro-distillation apparatus enabling electrochemical activation and continuous recovery of volatile MMA.

Herein, we report the electrochemically driven depolymerization of PMMA and subsequent recovery of MMA. Polymers with molecular weights >400 kDa were effectively depolymerized via activation of Phth-ester chain-ends or pendent groups. This approach is amenable to the depolymerization of PMMA synthesized via both conventional and reversible-deactivation radical polymerizations, demonstrating its broad applicability. By employing electrochemistry to activate the N–O bond in Phth ester pendent groups, we depolymerize and collect monomer from high-concentration solutions of polymers produced via conventional radical polymerization at temperatures substantially lower than the >200 °C typically required.[13, 17, 27] These results establish the utility of electrochemistry in depolymerizing all-carbon backbone polymers, providing a route toward improved closed-loop recycling of widely used plastics.

Results and Discussion

To understand the key factors governing electrochemical depolymerization, we began by probing the effect of chain-end activation in Phth-functionalized PMMA. Specifically, we examined how solvent, molecular weight, and trigger location influenced depolymerization efficiency.

As an initial model system, we synthesized a series of Phth ester-terminated PMMA (Phth-PMMA$_X$) via supplemental activator and reducing agent ATRP, spanning number-average molecular weights (M_n) from 10.1 to 97.4 kDa (Figures S4, S6, S8, S10, S12). As an example, electrolysis of Phth-PMMA with M_n = 17.5 kDa (Phth-PMMA$_{175}$, 0.5 mg mL^{-1}) was performed at

105 °C in 0.25 M ^{n}BuBF$_4$/1,4-dioxane using an undivided symmetrical cell with graphite electrodes (Figure S1). A high molecular weight PMMA (M_n = 3100 kDa) internal standard was included to allow for quantification of depolymerization efficiency by size-exclusion chromatography (SEC). Applying a potential of 2.5 V versus open circuit for 24 h led to a 45% decrease in the area of the Phth-PMMA$_{175}$ peak relative to the internal standard, consistent with significant α-chain-end-initiated depolymerization (**Figure 3A, B**).[15, 18, 22] In contrast, omitting the applied potential resulted in only 5% depolymerization (**Figure 3C**), suggesting the electrochemical stimulus was required for depolymerization and that thermal activation of the ω-C–Br bond was minimal. MMA formation was detected after 2 h using ^{1}H NMR spectroscopy (Figure S2, S3) though prolonged electrolysis led to its partial degradation, emphasizing the importance of continuous monomer removal to limit side reactions. To achieve high extents of depolymerization, 24 h was required due to the low density of Phth-end groups in solution, limiting contact with the electrode surface. We suggest that the reaction rate could be increased via the use of higher surface area cathodes, increasing the rate at which redox-active end-groups encounter the electrode and undergo productive electron transfer to initiate depolymerization. Overall, these results confirm that electrochemical activation of Phth end groups can effectively initiate depolymerization of PMMA under mild conditions, with chain-end unzipping accounting for a substantial portion of the polymer breakdown.

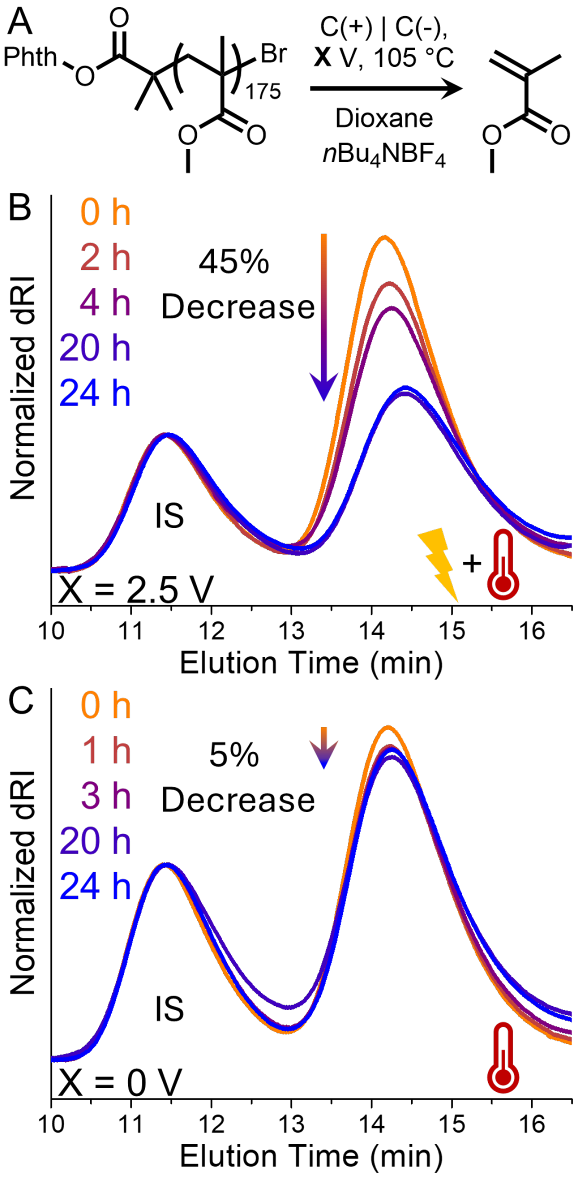

Figure 3. A) Chain-end initiated electrochemical depolymerization of Phth-terminated PMMA. B) SEC timepoints of electrothermal conditions resulting in 45 wt% depolymerization of Phth-PMMA$_{175}$. C) SEC timepoints of a depolymerization control ran without applied potential to the electrodes in the setup that resulted in 5 wt% depolymerization of Phth-PMMA$_{175}$. IS = 3100 kDa PMMA internal standard.

To further understand the parameters that influence chain-end-initiated electrochemical depolymerization, we systematically evaluated both solvent effects and molecular weight dependence. First, we investigated solvents effects under otherwise identical depolymerization conditions (2.5 V, 105 °C, graphite electrodes, 0.25 M ^{n}Bu$_4$NBF$_4$) using Phth-PMMA$_{175}$ as the substrate (**Figure 4A**). Among the solvents investigated, 1,4-dioxane supported the highest extent of depolymerization (45%), followed by *N,N*-dimethylformamide (DMF, 23%), while dimethyl sulfoxide (DMSO, 3%) and 1,2-dichlorobenzene (DCB, 7%) proved significantly less effective (**Figure 4B**). These observations are consistent with other solution-phase depolymerization studies that found ethereal solvents provide high extents of depolymerization due to solvent-generated radicals (Figure S37).[18] Based on these observations, subsequent experiments were conducted in 1,4-dioxane.

Next, we evaluated the impact of polymer molecular weight, reasoning that as chain length increases, the density of electrochemically addressable Phth end-groups decreases. We find that depolymerization efficiency decreased from 49% for polymers of 10.1 kDa to just 5% for polymers of 97.4 kDa (**Figure 4C**). These results indicate that chain-end-initiated depolymerization is strongly influenced by both solvent environment and end-group density, suggesting this approach limits efficiency at higher molecular weights and motivating exploration of alternative initiation mechanisms such as pendent-group activation.

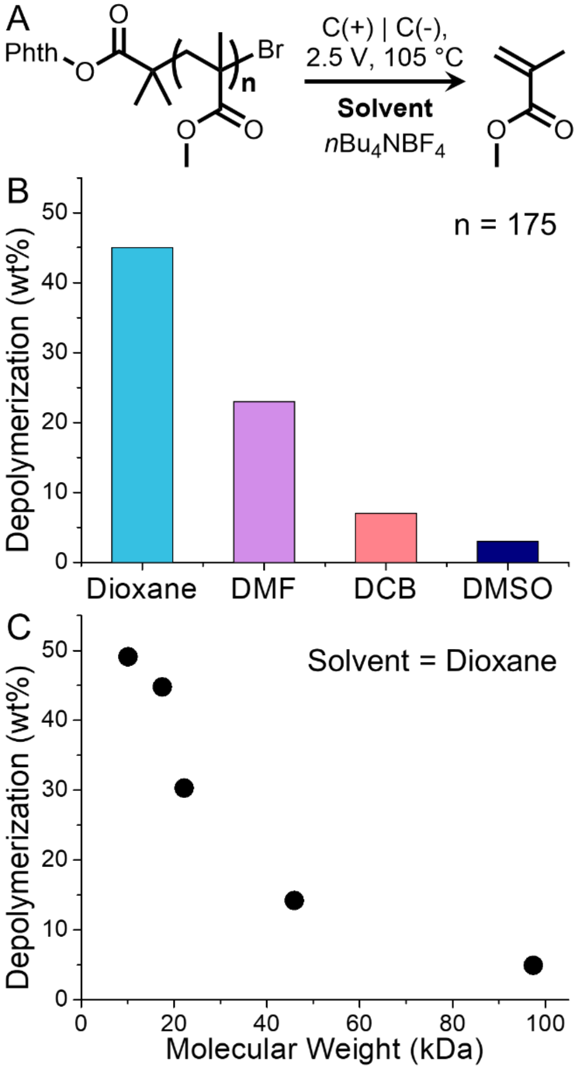

Figure 4. A) Reaction scheme for electro-depolymerization of Phth–PMMA$_x$. B) Effect of solvent on depolymerization efficiency of Phth–PMMA$_{175}$. C) Effect of molecular weight on depolymerization efficiency conducted in 1,4-dioxane.

Given the limitations of chain-end-initiated depolymerization at high molecular weight, we next turned to pendent-group activation as an alternative strategy. We synthesized a statistical copolymer of MMA (99 mol%) and phthalimide methacrylate (PhthMA, 1 mol%) (P(PhthMA$_{0.01}$-*co*-MMA)) with an M_n of 49 kDa (Figure S24). In the absence of applied potential, only 8% depolymerization was observed after 48 h (**Figure 5A, C**). In contrast, applying standard electrochemical depolymerization conditions (0.5 mg mL^{-1} P(PhthMA$_{0.01}$-*co*-MMA), 2.5 V, 105 °C, dioxane, 0.25 M ^{n}Bu$_4$NBF$_4$, 48 h) led to 44% depolymerization, as calculated by the decrease in area of the P(PhthMA$_{0.01}$-*co*-MMA) peak (**Figure 5A, B**). This observed extent of depolymerization was substantially greater than the 14% depolymerization observed under comparable conditions for Phth–PMMA$_{459}$ of similar molecular weight (M_n = 45.9 kDa). The molecular weight of the remaining fragments after depolymerization was found to be 12.1 kDa, which is in close agreement with the theoretical average molecular weight between PhthMA units of 11.2 kDa (Equations S1–S4). This result is consistent with efficient activation of the PhthMA during electrolysis, but the lower observed extent of depolymerization (44% compared to 77% theoretical, Equations S4 and S5) suggests the possibility of termination events after radical generation. These results demonstrate that pendent-group activation enables more efficient electrochemical depolymerization in higher molecular weight PMMA systems where end-group density is low.

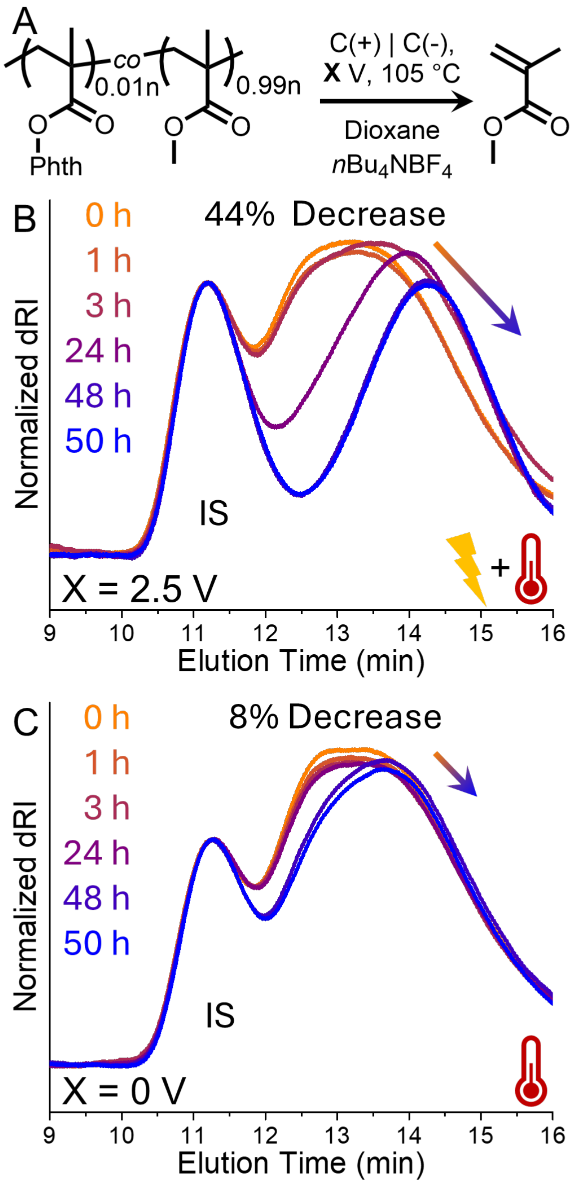

Figure 5. Pendent-group-initiated electrochemical depolymerization of P(PhthMA$_{0.01}$-*co*-MMA). A) SEC timepoints of the electrothermal reaction resulting in 44 wt% depolymerization. B) SEC timepoints of the thermal control resulting in 8 wt% depolymerization. IS = PMMA internal standard.

A key advantage of initiating depolymerization via pendent groups is the ability to increase trigger density, potentially overcoming the inherent limitations that arise when relying on end groups for depolymerization of high molecular weight polymers. To evaluate this, we prepared a series of P(PhthMA$_{0.01}$-*co*-MMA) copolymers with M_n ranging from 49 to 414 kDa (Figures S24, S26, S18, S28, S30) and subjected these polymers to electrochemical depolymerization (0.5 mg mL^{-1} P(PhthMA$_{0.01}$-*co*-MMA), 2.5 V, 105 °C, dioxane, 0.25 M ^{n}Bu$_4$NBF$_4$, 48 h) (**Figure 6A**). We observed a positive correlation between molecular weight and depolymerization efficiency, with the highest molecular weight polymer (M_n = 414 kDa) achieving the highest depolymerization efficiency (68%, **Figure 6B**). This trend contrasts to that observed for chain-end-initiated systems and mirrors behavior previously reported for bulk thermal depolymerization of polymers with pendent triggers.[13] We attribute this enhanced performance at higher molecular weights to the higher number of PhthMA units per chain, which increases the probability of radical generation and results in a greater fraction of each chain that can be depolymerized.

The ability to tune trigger density during synthesis is another advantage of the pendent group depolymerization strategy. We investigated the effect of PhthMA loading by exposing a library of 110 kDa copolymers with various trigger contents (i.e., P(PhthMA$_{0.01}$-*co*-MMA), P(PhthMA$_{0.03}$-*co*-MMA), and P(PhthMA$_{0.05}$-*co*-MMA) (Figure S18, S20, S22)) to identical electrolysis conditions. Depolymerization efficiency had a strong dependence on PhthMA loading. Polymers with 5 mol% PhthMA achieved >95 wt% depolymerization, while those with 3 and 1 mol% reached only 75 wt% and 50 wt% depolymerization, respectively (**Figure 6C**). These findings demonstrate the compositional tunability of pendent-group-initiated depolymerization. When combined with the favorable molecular weight scaling discussed above, this approach provides a model framework for designing depolymerizable polymers tailored to specific processing, application, or recycling requirements.

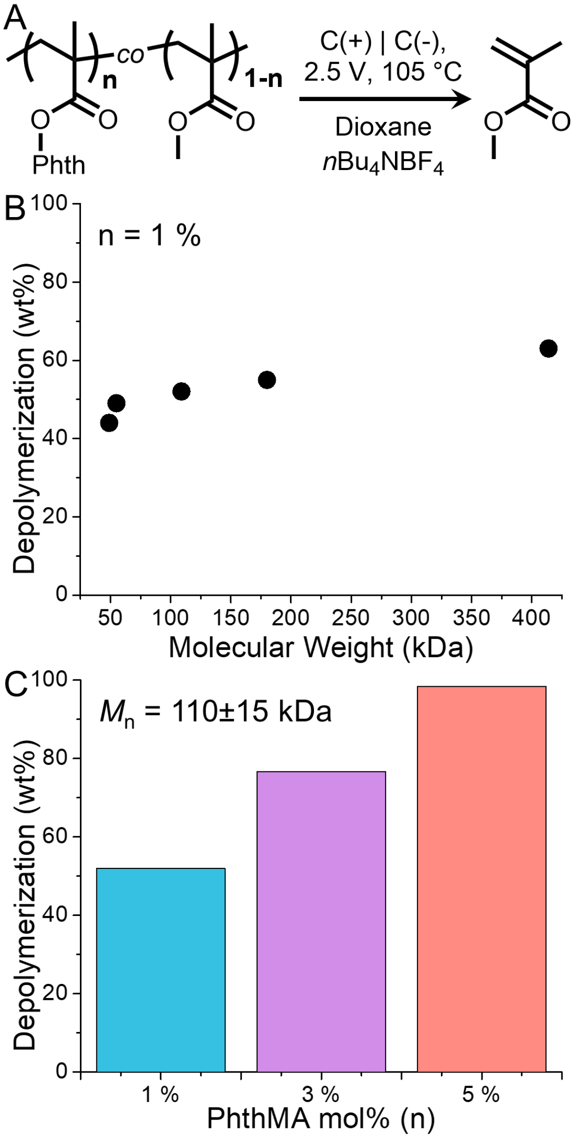

Figure 6: A) Reaction scheme for electro-depolymerization of P(PhthMA-*co*-MMA) at different PhthMA loadings (n) and molecular weights (M_n). B) Effect of molecular weight on depolymerization efficiency of P(PhthMMA$_{0.01}$-*co*-MMA). C) Effect of PhthMA loading on depolymerization efficiency.

To demonstrate the feasibility of closed-loop recycling, we subjected a high-molecular-weight sample of P(PhthMA$_{0.05}$-*co*-MMA) (M_n = 125 kDa) in tetraethylene glycol dimethyl ether (TEGDME, 25 mg mL^{-1} P(PhthMA$_{0.05}$-*co*-MMA)) to electrolysis in a custom electro-distillation apparatus at 2.5 V and 150 °C (see the supporting information for details, Figure S32-34). After 48 h, monomer was recovered in 22% yield (27 mol% MMA) with <5 mol% MMA degradation products in the distillate (Figure S33). The MMA recovered from depolymerization was repolymerized via conventional radical polymerization, yielding polymer with M_n = 4.6 kDa (Figure S35). While distillation efficiency currently limits monomer yield, supported by control experiments with neat MMA (Figure S36), this method validates the central concept that electrochemical depolymerization can enable monomer recovery and reuse from a redox-responsive polymer. These findings represent a promising step forward toward sustainable plastics recovery via electrochemical methods. Future efforts will focus on engineering larger-scale electro-distillation setups that use higher surface area electrodes, such as reticulated vitreous carbon. Additional considerations include improving the seal of the reaction vessel and identifying solvents compatible with high-temperature electrochemistry that improve monomer yield and purity.

Conclusion

This work establishes the first electrochemical strategy for depolymerizing all-carbon backbone polymers, addressing a previous challenge in polymer sustainability. By leveraging phthalimide ester triggers, we achieved efficient depolymerization of PMMA under significantly milder conditions than those required for conventional thermal depolymerization methods. Through systematic evaluation of solvent, trigger density, and polymer architecture, we identified key design parameters governing vinyl polymer depolymerization efficiency.

While end-group-initiated depolymerization was promising for PMMA of relatively modest molecular weight, polymers functionalized with pendent phthalimide esters, accessible via conventional radical polymerization, underwent efficient depolymerization and enabled monomer recovery and repolymerization via a closed-loop process. This demonstration of chemical recycling at high polymer concentrations and moderate temperatures (105–150 °C) effectively expands the scope of sustainable materials chemistry beyond heteroatom-containing systems. These findings position electrochemically initiated depolymerization as a versatile and scalable platform for enabling circularity in vinyl polymers and open new avenues for redox-responsive polymer design, recovery, and reuse.

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Supporting Information

Full experimental details can be found in the supporting information. Information regarding the materials, instrumentation, synthetic procedures, polymerization and depolymerization protocols, and additional characterization, including gel-permeation chromatography and ^{1}H and ^{13}C nuclear magnetic resonance measurements, is presented in the supporting information.

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