ACS POLYMERS Au
AN OPEN ACCESS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Decarboxylation-Triggered Polymer Deconstruction

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Cite This: https://doi.org/10.1021/acspolymersau.5c00146

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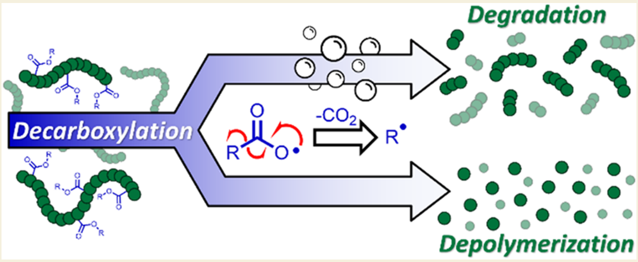
ABSTRACT: Decarboxylation is an emerging strategy to remediate plastic waste. Herein, we discuss recent advances that leverage activated ester or carboxylic acid decarboxylation to deconstruct polymers. Specifically, we address state-of-the-art strategies that rely on thermolytic, photolytic, or electrolytic stimuli to induce decarboxylation. Throughout, we highlight the key advances of each report and provide our insight on future directions for the field. We anticipate that continued developments in the field will lead to strategies for the controlled deconstruction of versatile polymeric materials.



KEYWORDS: *depolymerization, decarboxylation, sustainability, chemical recycling, upcycling, photochemistry, electrochemistry*

INTRODUCTION

Many synthetic polymers have all-carbon backbones that are resistant to deconstruction. This stability supports their widespread use in demanding applications, but hinders their breakdown in natural and engineered environments.[1−3] As a result, environmental plastic accumulation is a global concern and a focal polymer science challenge. In response, there has been growing interest in developing strategies to systematically degrade macromolecules, depolymerize polymers back to their constituent monomers,[4−10] or convert them into small molecules with repurposed functionality.[11−23]

Approaches for cleaving all-carbon polymer backbones often rely on harsh conditions, such as high temperatures, strong oxidants, or metal-based catalysts.[24−30] As a result, milder deconstruction methods are being actively explored.[10] Polymers that incorporate carboxylic acid or ester functionalities in the backbone or as pendent groups are particularly attractive because these moieties offer strategic handles for initiating deconstruction via radical decarboxylation.

Radical decarboxylation releases CO_2, typically from esters or carboxylic acids (Figure 1A). This process generates a carbon-centered radical that can couple with a wide variety of functional groups, ranging from simple hydrogen atoms to complex functional moieties, or undergo a subsequent intramolecular C−C bond cleavage (e.g., β-fragmentation). One of the earliest examples of decarboxylative functionalization was reported by Kolbe in 1849, where electrochemical oxidation of aliphatic carboxylic acids yielded alkyl dimers (Figure 1B).[31] Since Kolbe's discovery, numerous strategies have been developed to harness decarboxylation for chemical transformations.[32−43] More recently, this chemistry has been explored as a strategy for postpolymerization modification (Figure 1C). Herein, we summarize recent advances and identify future directions in the specific area of polymer deconstruction mediated by decarboxylation. Readers interested in the decarboxylative postpolymerization modification of polymers are referred to recent reports on this topic.[44−48]

POLYMER DEGRADATION

We define polymer degradation as any process that fragments the polymer backbone without necessarily regenerating the parent monomer(s). Many of the reports discussed in this section stem from the initial discovery by Oda and co-workers that *N*-hydroxyphthalimide (NHPI) esters can be used as a latent source of radicals generated via photochemical reductive decarboxylation.[49,50] This approach is mechanistically divergent from Kolbe or Hofer-Moest reactions that rely on oxidation of a carboxylate anion to generate carboxyl radicals and typically require basic conditions and high overpotentials. NHPI esters are directly reduced to carboxyl radicals under milder conditions, providing a more user-friendly platform to perform decarboxylative transformations. Since Oda's discovery, a number of groups recognized the potential of leveraging this transformation to generate backbone radicals on polymers via pendent-group decarboxylation. Initial efforts with NHPI esters were primarily devoted to functionalizing polymeric

Received: September 29, 2025
Revised: November 13, 2025
Accepted: November 14, 2025

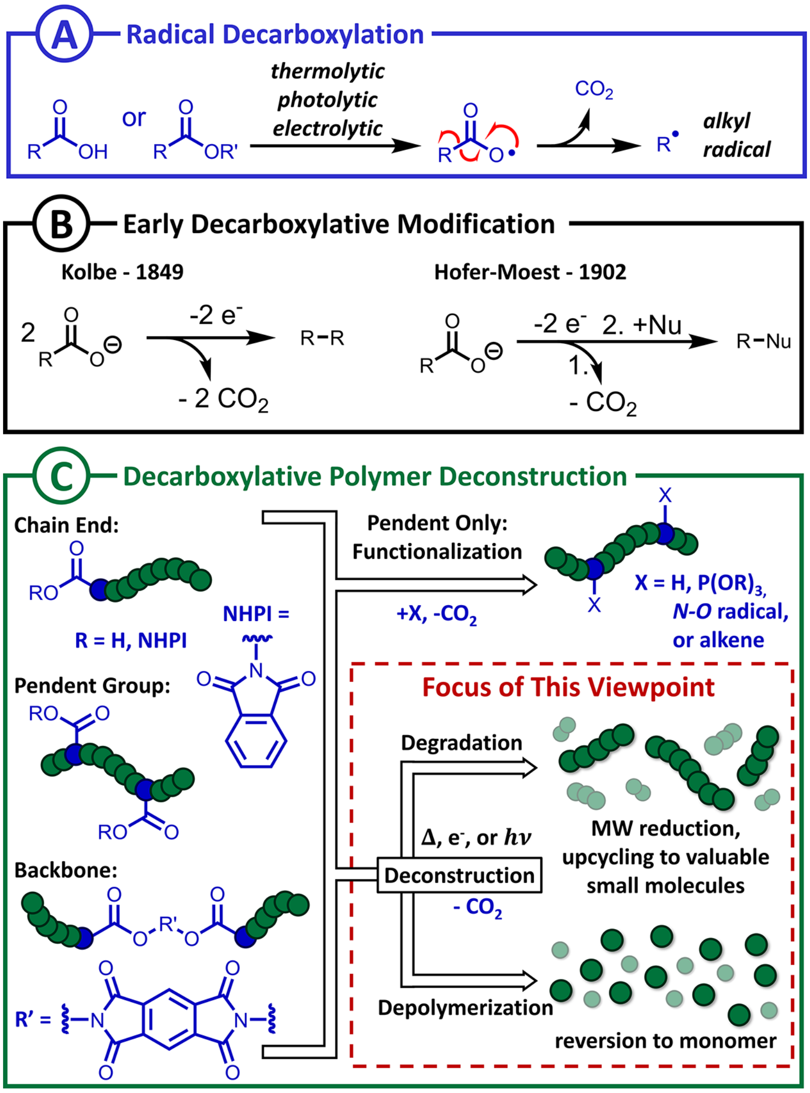


Figure 1. (A) Mechanism of the radical decarboxylation of carboxylic acids or activated esters. (B) Early examples of decarboxylation used to couple (left) or modify (right) small molecules. (C) Ways polymers bearing carboxylic acid or *N*-hydroxyphthalimide (NHPI) ester triggers can be modified or deconstructed via thermolytic, electrolytic, or photochemical decarboxylation.

substrates by trapping the intermediate radicals after photochemical, ruthenium-catalyzed pendent-group decarboxylation.[51−54] However, when poly(methyl methacrylate-*co*-*N*-(methacryloxy)phthalimide methacrylate) (P(MMA-*co*-PhthMA)) was used as the substrate, a significant reduction in the molecular weight (MW) of the polymer was observed (Figure 2).[55]

Exploring this observation in more detail, Sumerlin and coworkers developed a metal-free photocatalytic strategy to degrade polymethacrylates triggered by pendent-group decarboxylation (Figure 2).[55] In this approach, *N*,*N*-diisopropylethylamine (DIPEA) reductively quenched a photoexcited organocatalyst, Eosin Y (EY), generating an aminium radical cation and an EY radical anion. The EY radical anion subsequently reduced the pendent NHPI esters in P(MMA-*co*-PhthMA), leading to N−O bond cleavage and carboxyl radical generation. Finally, radical decarboxylation furnished a backbone-centered tertiary radical that underwent *β*-scission, causing polymer degradation. Using a 36.3 kg mol^{-1} sample of P(MMA-*co*-PhthMA) containing 10 mol % of PhthMA, photocatalytic degradation was complete within 20 h.

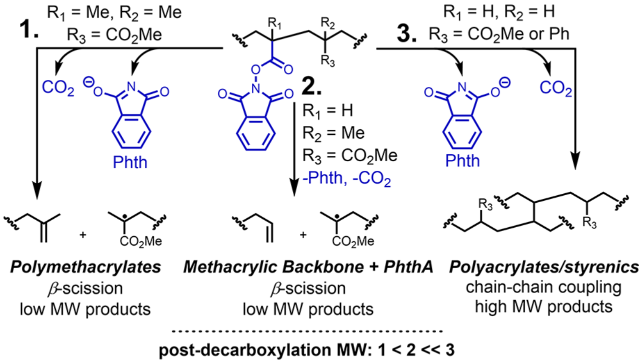


Figure 2. Decarboxylative degradation of poly(methyl methacrylate) (PMMA) copolymers under reductive photoredox conditions (left, center). Poly(methyl acrylate) (PMA) and polystyrene (PSt) copolymers with pendent NHPI esters underwent chain−chain coupling instead of *β*-scission (right). In each case, Eosin Y (EY) was used as a photocatalyst and *N*,*N*-diisopropylethylamine (DIPEA) as a sacrificial reductant under green light irradiation.

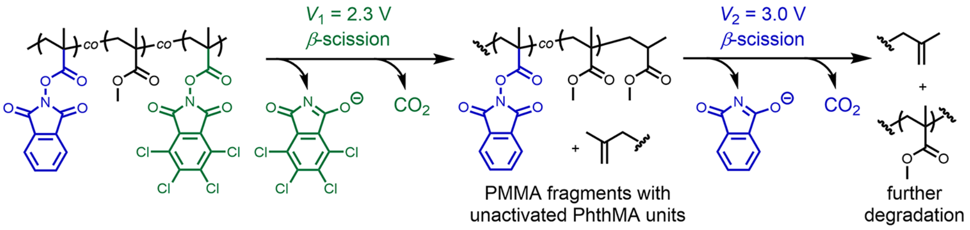


Figure 3. Redox-selective macromolecular electrolysis of phthalimide (Phth) ester containing copolymers, where Phth and tetrachlorophthalimide esters can be decarboxylated at different voltages, resulting in two independent β-scission events.

Replacing PhthMA with *N*-(acryloxy)phthalimide acrylate (PhthA) resulted in higher-MW degradation products. These results were attributed to increased side reactions when generating secondary backbone radicals. When copolymers of PhthA and methyl acrylate (MA) or styrene (St) were subjected to these reaction conditions, complete decarboxylation was observed without reduction in the MW of the polymers. Instead, higher-MW products were observed, consistent with chain−chain coupling between macroradicals. These observations indicate that the efficiency of decarboxylation-triggered deconstruction is governed by the relative kinetics of β-scission versus competing radical reactions, including hydrogen atom abstraction and termination. Secondary radicals formed from acrylate and styrene backbones are less prone to undergo β-scission than tertiary radicals derived from methacrylates. While termination or abstraction events tend to dominate under conditions of high radical concentration, increasing viscosity, lowering instantaneous radical flux, or employing higher temperatures can potentially shift the balance toward unimolecular β-scission. Ultimately, this report established decarboxylation as an effective strategy for polymer degradation, provided that β-scission occurs faster than competing radical processes such as chain−chain coupling or hydrogen atom abstraction. These results also emphasize that establishing structure−reactivity relationships for polymer degradation is critical for the de novo design of next-generation, inherently degradable materials.

While photocatalytic methods for pendent-group decarboxylation are highly effective for polymer degradation, there are inherent limitations associated with light-driven processes. Issues such as limited scalability, light penetration, and narrow control over redox potentials have motivated interest in alternative strategies for activating NHPI esters under milder, more-selective conditions such as macromolecular electrolysis. Like photoredox catalysis, electrochemical reduction operates via single-electron transfer processes that can initiate NHPI ester cleavage and subsequent decarboxylation.[56−59] However, electrochemistry offers practical advantages in that it is inherently scalable and allows precise control over redox potentials simply by adjusting the applied voltage. Moreover, the ability to externally control the reaction kinetics may prove useful in more advanced uses of decarboxylative chemistry (e.g. subtractive manufacturing).

With these features in mind, Hughes et al. recently reported the electrochemical decarboxylative degradation of P(MMA-*co*-PhthMA).[60] Upon electrolysis at 2.5 V (unreferenced cell potential), the pendent NHPI esters were reduced, with decarboxylative degradation being hypothesized to occur via the same mechanism described above for the EY-catalyzed system. Later work by Gilchrist et al. demonstrated that incorporating *N*-(methacryloxy)tetrachlorophthalimide methacrylate (TCPhthMA) as a comonomer in terpolymers with PhthMA and MMA enabled the chemoselective electrolysis of these copolymers by exploiting differences in reduction potential to sequentially electrolyze each phthalimide ester (Figure 3).[61] Specifically, a P(MMA-*co*-PhthMA-*co*-TCPhthMA) terpolymer containing 2 mol % of each phthalimide-containing monomer was electrolyzed in a two-electrode configuration at 2.3 V for 24 h. At this applied voltage, the first electrolysis step selectively targeted the thermodynamically easier-to-reduce TCPhthMA repeat units, resulting in a decrease in molecular weight due to β-scission and the disappearance of the UV absorbance band of the TCPhthMA moieties at 342 nm. The potential was subsequently raised to 3.0 V for 30 h to target the PhthMA repeat units. Further degradation of the polymer via reductive decarboxylation and subsequent β-scission of the polymer backbone was observed. Notably, this strategy also worked to selectively functionalize polyacrylates containing both phthalimide and tetrachlorophthalimide repeat units. Overall, electrolysis is a highly tunable stimulus for the decarboxylative degradation of polymers and provides an orthogonal route to activate NHPI esters relative to more conventional stimuli, such as heat and light.

Substantial efforts have been devoted to advancing methods for recycling polymethacrylate materials, either by depolymerization or by initiating midchain scission through the generation of backbone radicals.[8,55,62−79] By contrast, the deconstruction of polyacrylates has seen far less development.[80] Currently, the most widely employed strategy for creating degradable polyacrylates involves the copolymerization of acrylate monomers with specialized cyclic comonomers via radical ring-opening polymerization.[81−83] While this approach is a useful strategy of periodically incorporating degradable heteroatom moieties that facilitate degradation, most monomers susceptible to radical ring-opening must be synthesized, and difference in relative reactivity with acrylate comonomers can lead to compositional drift or gradient architectures that may compromise efficient degradation. Recent advances using α-lipoic acid as a commercially available, degradable comonomer have begun to address these challenges.[84−87] Nonetheless, challenges persist in achieving efficient degradation. For example, systems using α-lipoic acid as the degradable comonomer typically rely on activating the disulfide linkage in α-lipoic acid homo dyads, meaning that copolymer sequence and composition have a dramatic impact on degradation.

Decarboxylation of polyacrylates offers a viable alternative for deconstruction, though slow fragmentation of the acrylate backbone generally requires an additional step to impart degradability. Seidel, Sumerlin, and co-workers introduced a two-step, one-pot strategy, where polyacrylates underwent dehydrodecarboxylation, and subsequent oxidative degradation of the resulting backbone C═C bonds led to efficient

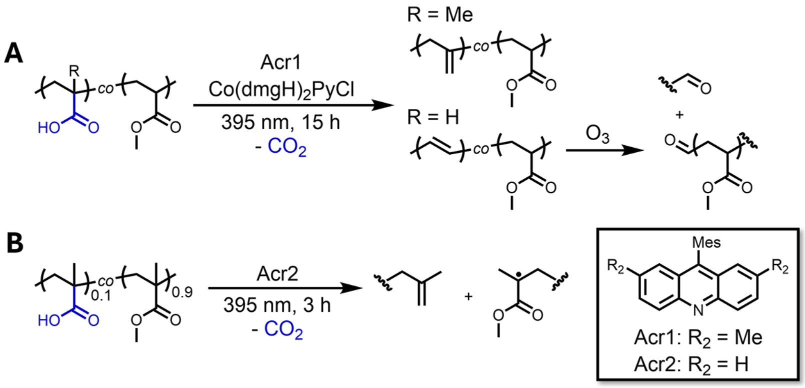


Figure 4. (A) Poly(MMA-*co*-methacrylic acid) (P(MMA-*co*-MAA)) degradation via photochemical decarboxylation with an acridine catalyst under UV light. (B) PMA copolymer dehydrodecarboxylation; P(MA-*co*-acrylic acid) (R = H) dehydrodecarboxylation afforded backbone unsaturations that were used to degrade the polymer via ozonolysis. Co(dmgH)$_2$PyCl = Chloro(pyridine)cobaloxime.

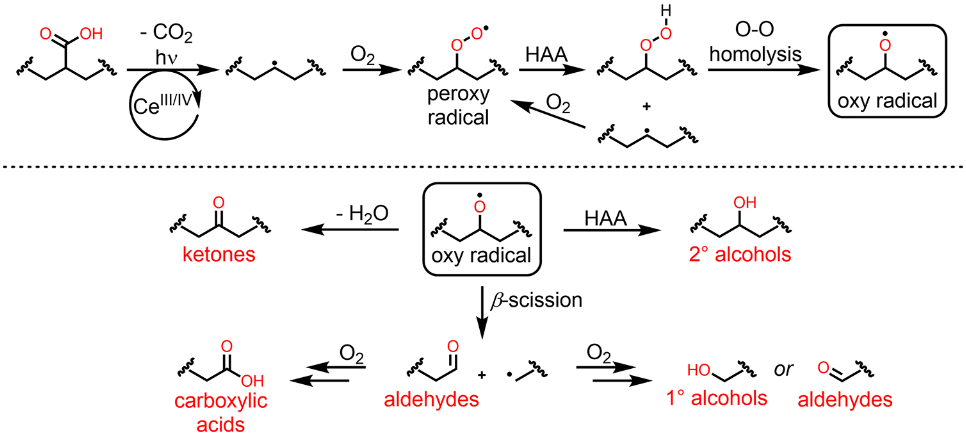


Figure 5. Simplified degradation mechanism of carboxylate-functionalized polyethylene via sequential ball-milling with $CeCl_3 \cdot 7H_2O$ and photolytic decarboxylation, resulting in small-molecule degradation products such as alcohols, aldehydes, ketones, and carboxylic acids. HAA = hydrogen atom abstraction.

degradation (Figure 4A).[88] This work built off of an earlier report, from the same laboratories, that showed MMA-*co*-methacrylic acid copolymers are degradable under visible light irradiation in the presence of an acridine photocatalyst (Figure 4B).[62] First, the authors established that the carboxylic acids present in copolymers of MA and acrylic acid (AA) can be converted into alkenes using an acridine photocatalyst and cobaloxime cocatalyst. Under optimized conditions, 74% of pendent carboxylic acids were dehydrodecarboxylated into alkenes. Subjecting these polymers to ozonolysis resulted in degradation of the backbone. Because no purification of the decarboxylated polymer was necessary before successful ozonolysis, a one-pot process was also feasible, allowing ozonolysis to be conducted sequentially in the same reaction vessel to result in polymer degradation. This strategy was also used to successfully degrade copolymers of AA with *tert*-butyl acrylate, *N,N*-dimethylacrylamide, or St, demonstrating its generality. A subsequent study found that degradation of decarboxylated P(MA-*co*-AA) could be achieved using nitroarenes under violet light irradiation.[89] This approach avoids using toxic ozone gas and the generation of potentially explosive ozonide intermediates. Instead, polymer degradation is hypothesized to occur via the fragmentation of a 1,3,2-dioxazolidine intermediate. These studies demonstrate that decarboxylation can be used to generate degradable handles throughout a polymer chain when directly triggering polymer degradation with decarboxylation is not possible.

While most decarboxylative degradation strategies to date have focused on relatively polar polymers such as (meth)acrylates and solution-based chemistry, recent work has extended this concept to nonpolar, polyolefin materials in the bulk polymer state. These efforts demonstrated that decarboxylation can serve as a direct trigger for backbone cleavage as well as an entry point to radical chain processes that amplify the extent of degradation. Along these lines, Nozaki, Takahashi, and co-workers used pendent carboxylic acids as triggers to degrade polyethylene (PE)-like materials (Figure 5).[90] In this study, 8.3 kg mol^{-1} PE bearing pendent carboxylic acids was ball-milled in the presence of a $CeCl_3$ hydrate for 1 h. The resulting polymer (6.5 kg mol^{-1}) was then irradiated with 430 nm light in the solid state for 4 d at 80 °C, which resulted in low-MW fragments. The authors proposed O_2 oxidized Ce(III) to Ce(IV), which then coordinated to the pendent carboxylate groups. Photoexcitation of this cerium-carboxylate complex led to electron transfer and ultimately reductive decarboxylation, resulting in a secondary backbone radical and regeneration of Ce(III). Control experiments indicated that the backbone radical was trapped by O_2, yielding a reactive, pendent peroxy radical that could initiate a chain reaction by abstracting a hydrogen atom from a polymer backbone. The resulting hydroperoxide underwent O−O bond homolysis, yielding a pendent oxy radical. The oxy radical could undergo several reaction pathways, all generating oxidized byproducts. Hydrogen atom transfer to a hydroxyl radical yielded an equivalent of water and ketone. Alternatively, hydrogen atom abstraction from the backbone resulted in the generation of secondary alcohols and propagated the chain reaction by generating a backbone-centered radical. Finally, *β*-scission resulted in polymer degradation and formation of aldehydes and primary alkyl radicals. Aerobic oxidation of these byproducts led to the generation of carboxylic acids and primary alcohols, respectively. Importantly, these results suggest one decarboxylation event can cause more than one C−C bond scission event along the polymer backbone, demonstrating a substoichiometric (relative to repeat unit) amount of trigger can result in near-stoichiometric polymer degradation. Additionally, the generation of oxidized byproducts suggests this method may be amenable to upcycle PE waste into valuable small-molecule feedstocks.

Despite the key advances in the examples highlighted above, many of the polymer degradation strategies exploited so far are limited by a lack of control over the degradation products. In many instances, the products are oligomeric fragments of the parent polymer that would still need to be purified, remediated downstream, or upcycled into valuable small molecules. Developing new strategies to selectively degrade polymeric materials into useful chemical building blocks remains an important goal. Such strategies would enable the recapture and reuse of polymer-derived small molecules to prepare fuels, agrochemicals, pharmaceuticals, or other valuable feedstocks. Another promising route to chemical building block recovery is depolymerization, a mechanistically distinct process that favors monomer regeneration over the formation of ill-defined oligomeric fragments.

DEPOLYMERIZATION

Chemical recycling to monomer via depolymerization is a powerful strategy for a circular plastics economy. Unlike random chain scission, depolymerization of vinyl polymers proceeds through an unzipping mechanism that can regenerate the original monomers. However, this process requires conditions that favor depropagation over propagation.

Vinyl polymerizations are generally exothermic and thermodynamically favorable, allowing polymers to form spontaneously under standard conditions.[91] However, polymerization incurs an entropic penalty due to the reduction in entropy as monomers are incorporated into the growing chain.[91] Because the interplay between enthalpy and entropy is temperature dependent, there is a threshold at which the entropic cost surpasses the enthalpic benefit, making depolymerization the more favorable process.[92,93] This threshold is known as the ceiling temperature (T_c), which represents the temperature above which depolymerization becomes thermodynamically favorable at a given set of conditions.[92,93] Therefore, heating a polymer that contains an active end group above its T_c shifts the equilibrium toward monomer formation. This thermodynamic equilibrium can also be expressed in terms of the equilibrium monomer concentration ($[M]_{eq}$), i.e., the concentration at which the polymerization and depolymerization reaction rates are equal at a given temperature.[93,94] When a polymer with an active chain end is heated above its T_c, it will depolymerize until $[M]_{eq}$ is reached, assuming that no irreversible termination events occur. However, even when depolymerization is thermodynamically favored, it may still be hindered by high kinetic barriers to active end-group formation. To this end, decarboxylation can be used to lower the temperature necessary to generate active radicals needed for depropagation, decreasing the energy input required to achieve depolymerization.

Propagation and depropagation are inherently related by the principle of microscopic reversibility, where generating active chain-ends can lead to either process depending on the reaction conditions. The chain-ends inherent to reversible-deactivation radical polymerization (RDRP) conveniently lower the kinetic barrier to radical generation, so under conditions that favor depropagation ($T > T_c$, $[M] < [M]_{eq}$), these polymers will undergo depolymerization. This concept was first demonstrated by Gramlich and co-workers via depolymerization of polymethacrylates at 70 °C in dilute ([repeat unit] ≅ 100 mM) 1,4-dioxane solutions.[95] This discovery changed how we approach end-group activation of RDRP-generated polymers, by using the reactivated radicals to undergo depolymerization instead of polymerization.

Subsequent developments have led to many examples of polymethacrylate depolymerization being carried out at high dilution and often employing catalysts to accelerate radical generation.[8,63−79] Bulk depolymerization strategies are more compatible with industrial recycling workflows and reduce the energy and material costs associated with solvent use.[96−100] In these cases, it is usually necessary to remove the generated monomer from the reaction (e.g., via distillation) to remain below $[M]_{eq}$ throughout the depolymerization process. Notably, some of these solvent-free approaches leverage decarboxylation as a means to initiate backbone radical formation and drive depolymerization. For example, Sumerlin and co-workers recently reported that installing NHPI esters at the *α*-chain-end of PMMA enabled triggered PMMA depolymerization (42% extent of depolymerization) via low-temperature (220 °C) decarboxylation under solvent- and catalyst-free conditions (Figure 6A).[97] Polymers that contained thermally labile groups at both the *α*- and *ω*-chain-ends achieved even higher degrees of depolymerization (up to 92%).

Matyjaszewski and co-workers were able to leverage a similar phenomenon to initiate depolymerization from four sites on PMMA by placing a ditopic NHPI (pyromellitic) ester in the center of telechelic PMMA chains.[100] Homolytic N−O bond

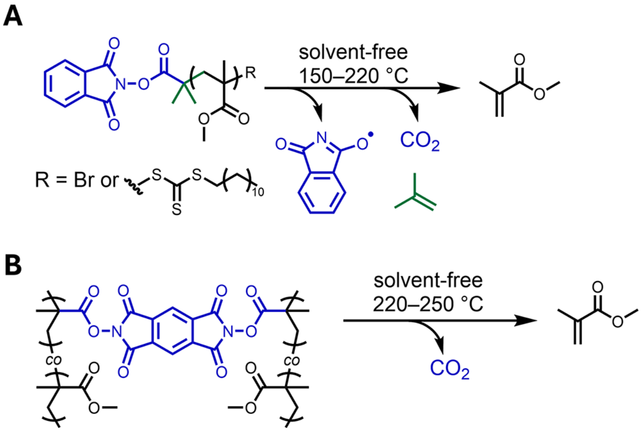


Figure 6. Catalyst-free, bulk depolymerization of (A) PMMA bearing *α*-end NHPI esters and either bromine or trithiocarbonate (TTC) *ω*-ends and (B) PMMA network synthesized with a pyromellitic cross-linker.

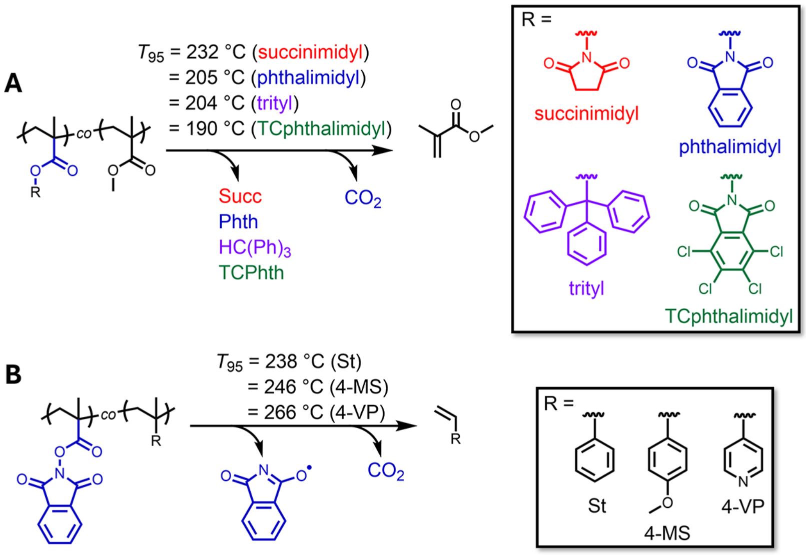


Figure 7. (A) Depolymerization of P(MMA-*co*-succinimide methacrylate) (P(MMA-*co*-SMA), P(MMA-*co*-PhthMA), P(MMA-*co*-trityl methacrylate) (P(MMA-*co*-TrMA)), and P(MMA-*co*-tetrachlorophthalimide methacrylate) (P(MMA-*co*-TCPhthMA)) copolymers affording tunable onsets of depolymerization depending on the chosen thermolytic trigger; Succ = succinimidyl radical leaving group. (B) Depolymerization of P(St-*co*-PhthMA), P(4-vinylpyridine-*co*-PhthMA) (P(4-VP-*co*-PhthMA)), and P(4-methoxystyrene-*co*-PhthMA) (P(4-MS-*co*-PhthMA)), demonstrating selective onsets of depolymerization depending on which styrenic monomer is used.

thermolysis and radical decarboxylation occurred in both directions along the polymer chain, leading to more-efficient depolymerization at higher molecular weights. Incorporating pyromellitic diesters as cross-links in a polymer network was a viable strategy to depolymerize thermoset materials (Figure 6B). While these reports demonstrated that decarboxylation from chain-end or midchain triggers is an effective strategy to initiate depolymerization, their reliance on polymers prepared by RDRP and the need for specifically incorporated initiator-derived triggers limit broader applicability.

Postpolymerization installation of depolymerization triggers expands the utility of these methods beyond specially prepared samples to existing commercial samples. To this end, Young et al. developed a strategy to install NHPI ester chain ends on PMMA prepared by conventional radical polymerization.[101] Mechanochemical chain-scission of PMMA in the presence of PhthMA monomer resulted in macroradicals that were trapped with PhthMA units. The resulting polymers contained short runs of NHPI ester units at their ends and were susceptible to subsequent low-temperature depolymerization under bulk, catalyst-free conditions.

Chain-end and midchain decarboxylation strategies offer effective ways to initiate depolymerization, but their efficiency is constrained by the limited number and distribution of reactive sites along the polymer backbone. As the molecular weight of the polymer increases, the probability of complete depolymerization decreases due to a higher likelihood of irreversible radical termination, competing side reactions such as hydrogen atom abstraction, and the simple statistical dilution of reactive ends in bulkier samples. As an alternative to chain-end-triggered depropagation, labile pendent groups can be used as decarboxylative triggers for depolymerization. By incorporating multiple triggers along the polymer backbone, this approach enables new radicals to be generated even after potential termination events, reducing the impact of side reactions that would otherwise halt depropagation. Moreover, by removing the reliance on specific end groups needed to initiate depolymerization, this approach is more amenable to polymers prepared by more common synthetic approaches like conventional radical polymerization.

To this end, the depolymerization of polymethacrylates containing various activated-ester pendent groups was recently reported.[98] By using pendent TCPhth, NHPI, or *N*-hydroxysuccinimide esters, the onset temperature of PMMA depolymerization was tunable from 190 to 232 °C (Figure 7A). This approach also resulted in high degrees of depolymerization regardless of the MW of the polymer. Separately, Kohsaka and co-workers reported that copolymers of trityl methacrylate (TrMA) and MMA undergo decarboxylation-induced depolymerization at 270 °C under vacuum (95% MMA recovered).[102] On a 10 g scale, 81% of MMA was recovered, indicating pendent-group activation is a scalable strategy for polymethacrylate depolymerization.

The overwhelming majority of reports of decarboxylation-induced degradation or depolymerization have involved polymethacrylates because the β-scission of methylacryoyl radicals readily outcompetes other radical processes like chain−chain coupling or hydrogen atom abstraction. Conversely, these processes are more competitive with β-scission from acroyl or styryl radicals. Despite this, pendent-group activation has also been expanded as a strategy to deconstruct polystyrenics (Figure 7B).[103] Specifically, copolymers of PhthMA and St, 4-methoxystyrene, or 4-vinylpyridine all achieved >50% depolymerization when thermolyzed at 238, 246, or 266 °C, respectively. These results suggest the pendent-group approach to triggering decarboxylation is an efficient strategy to achieve high degrees of depolymerization for various monomer classes.

The strategies described above rely on incorporating decarboxylation-sensitive groups during polymer synthesis, which limits their applicability to postconsumer or existing materials that lack such functionalities. Additionally, some triggers may undergo slow, premature decomposition over time. To overcome these limitations, postpolymerization

https://doi.org/10.1021/acspolymersau.5c00146

modification can be leveraged to retrofit commercial polymers with decarboxylation triggers (Figure 8).[102,104] By partially hydrolyzing PMMA and then esterifying the small fraction of resulting methacrylic acid residues with the decarboxylation trigger (trityl chloride or NHPI), high extents of depolymerization can be achieved. Interestingly, depolymerization remains efficient for commercial samples of PMMA, despite these materials containing small amounts of acrylate comonomers and additives specifically included to suppress depolymerization. Ironically, the presence of acryloyl units could be advantageous for postpolymerization trigger installation methodologies that rely on sequential hydrolysis-esterification, since these units are expected to be even more reactive than their methacryloyl neighbors.

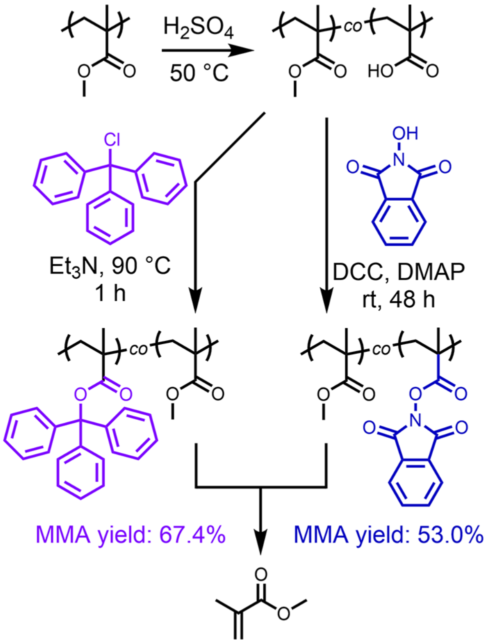


Figure 8. Postpolymerization pendent-group modification of partially hydrolyzed, commercial PMMA (P(MMA-*co*-MAA)) with either trityl chloride (left) or NHPI (right) to give P(MMA-*co*-TrMA) or P(MMA-*co*-PhthMA), respectively. These PMMA copolymers retrofit with decarboxylation triggers could then be reverted to monomer in high yields. DCC = *N*,*N*′-dicyclohexylcarbodiimide; DMAP = 4-dimethylaminopyridine.

Postpolymerization approaches are particularly important because they offer a route to address commodity polymers that are already in circulation and create the possibility of transforming otherwise persistent plastics into depolymerizable materials. Building on this foundation, future efforts could explore a broader palette of decarboxylation triggers that respond to thermal, photochemical, redox, or electrochemical stimuli, with an emphasis on strategies that maximize atom efficiency and minimize waste. Expanding the chemistry in this way would provide additional means of controlling depolymerization while enabling selective activation under milder conditions to increase compatibility with diverse polymer backbones and real-world processing environments.

PERSPECTIVE AND OUTLOOK

Decarboxylation is a powerful strategy for the triggered deconstruction of macromolecules. The broader challenge is to translate these elegant laboratory demonstrations into strategies that can be realistically applied to existing plastic waste streams and industrially relevant settings. Despite significant progress, most approaches rely on specialty comonomers or require RDRP methods to achieve efficient deconstruction. There is a clear need for new generalizable triggers that can initiate radical-mediated polymer deconstruction without such constraints. One promising direction is the development of postpolymerization modification techniques that enable efficient and selective installation of decarboxylation handles. In addition, nearly all efforts in this area have focused on (meth)acrylic polymers, limiting the broader applicability of the approach. Expanding decarboxylative approaches to other classes of polymers is essential if this chemistry is to serve a meaningful role in addressing the global plastic pollution crisis.

To date, most studies have leveraged thermal stimuli to initiate decarboxylation focused deconstruction or depolymerization. This approach is particularly useful due to the ability to scale these reactions to the scales needed for commodity polymer deconstruction. However, opportunities exist to explore the ability to implement orthogonal activation strategies (e.g., photochemical, electrochemical) to further expand the utility of this chemistry. Developing scalable photochemical and electrochemical processes will also necessitate closer integration of polymer chemistry with materials engineering, reactor design, and energy sciences to ensure that these approaches are viable beyond the bench scale.

Moreover, while decarboxylation has proven effective for generating radicals that drive polymer backbone scission, future efforts should also focus on discovering new chemical transformations that enable radical formation at chain ends or internal positions without necessarily relying on carboxylic acid derivatives. Ideally, these chemistries will work with triggers inherently present in commodity materials, for example, those that facilitate hydrogen atom abstraction from polymer backbones,[8,105] or with triggers that can be installed simultaneously during material deconstruction.

The development of such chemistries will be critical for extending triggered deconstruction to commodity polymers and mixed-waste streams. Moreover, recent research has demonstrated that the utility of deconstruction can extend beyond sustainable plastics to enable the generation of porous materials through the selective depolymerization of microphase-separated block copolymer materials.[106] It is reasonable to assume that other deconstruction methods described in this Viewpoint may also prove useful for advanced materials synthesis. Collectively, progress in this area will depend on interdisciplinary collaboration, the establishment of shared benchmarks for evaluating depolymerization efficiency under practical conditions,[107] and an openness to coupling decarboxylation with other deconstruction mechanisms. By setting these priorities, the community can accelerate the transition of decarboxylation from an emerging concept to a central tool in sustainable polymer chemistry.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Research was primarily supported as part of the Center for Plastics Innovation (CPI), an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), under award #DE-SC0021166. Support was also provided by the Defense Advanced Research Projects Agency (DARPA) under Award Number HR00112430352. The views, opinions, and/or findings expressed are those of the authors and should not be interpreted as representing the official views or policies of the Department of Defense or the U.S. Government. M.E.L. was supported by the Department of Defense (DoD) through the National Defense Science & Engineering Graduate (NDSEG) Fellowship Program.

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