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Backbone Degradation of Polymethacrylates via Metal-Free Ambient-Temperature Photoinduced Single-Electron Transfer

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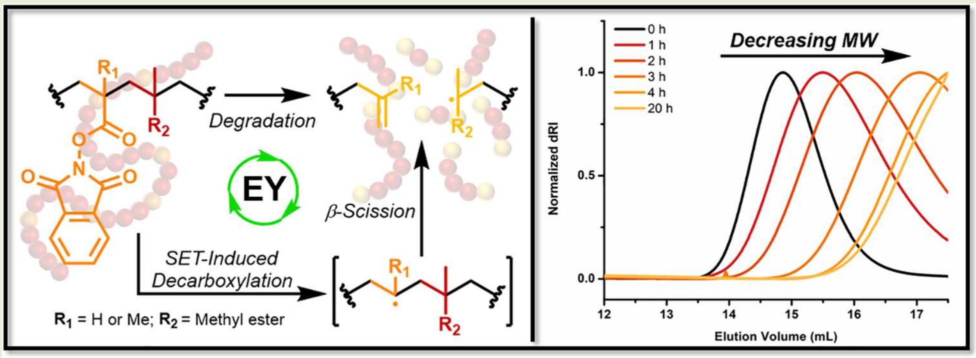

ABSTRACT: Polymeric materials comprised of all-carbon backbones are ubiquitous to modern society due to their low cost, impressive robustness, and unparalleled physical properties. It is well-known that these materials often persist long beyond their intended usage lifetime, resulting in environmental accumulation of plastic waste. A substantial barrier to the breakdown of these polymers is the relative chemical inertness of carbon−carbon bonds within their backbone. Herein, we describe a photocatalytic strategy for cleaving carbon-based polymer backbones. Inclusion of a low mole percent of a redox-active comonomer allows for a dramatic reduction in polymer molecular weight upon exposure to light. The *N*-(acyloxy)phthalimide comonomer, upon reception of an electron from a single-electron transfer (SET) donor, undergoes decarboxylation to yield a backbone-centered radical. Depending on the nature of this backbone radical, as well as the substitution on neighboring monomer repeat units, a *β*-scission pathway is thermodynamically favored, resulting in backbone cleavage. In this way, polymers with an all-carbon backbone may be degraded at ambient temperature under metal-free conditions.

The ubiquity of synthetic polymers in modern society can be attributed largely to their low production cost and robust physical properties. Many high-volume commodity plastics are synthesized via chain growth of alkene-containing monomers (e.g., poly(meth)acrylates, polyolefins, and polystyrene). The exceptional stability of these polymers against erosion or breakdown is due to the relative inertness of the carbon−carbon bonds comprising the polymer backbone. This stability ultimately contributes to the modern challenge of achieving closed-loop plastic recycling, as polymer materials often retain robustness long after their intended usage lifetime.[1−4] Degradation experienced by these vinyl polymers ultimately hinges on molecular weight reduction via backbone fission events facilitated by exogenous, high-energy stimuli (e.g., UV light and high temperature).[5−7] Current strategies to produce degradable vinyl polymers include radical ring-opening polymerization of cyclic ketene acetals, which reduces backbone inertness via inclusion of hydrolyzable ester linkages.[8,9] Beyond this notable exception, backbone cleavage of radical-derived chain-growth polymers is typically limited to fairly severe degradation conditions via free radical mechanisms. A common theme in polymer degradation is radical formation on the polymer backbone followed by bond breaking via *β*-scission.[10−12] Indeed, recent reports by Ouchi et al. outline both partial polymer unzipping and poly(methacrylate) degradation via backbone radical generation using transition metal catalysts at elevated temperatures.[13,14]

There have recently been numerous examples of decarboxylative radical cross-coupling small-molecule reactions utilizing *N*-(acyloxy)phthalimide derivatives as single-electron transfer (SET) acceptors.[15−19] Applying this class of transformation to polymer-based systems seems to be a promising and somewhat untapped avenue to expand the field of post-polymerization modification.[20,21] We and Theato et al. have recently reported

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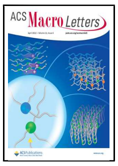

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redox-active monomers containing *N*-(acyloxy)phthalimide (NAP) moieties that possess the ability to function as latent backbone radicals.[21−23] These phthalimide ester compounds are vinyl monomers capable of radical copolymerization and act as SET acceptors. SET from an inexpensive, organic photocatalyst SET donor (Eosin Y, EY)[15,24,25] to the NAP monomer units after incorporation into a polymer triggers the decarboxylative generation of a backbone radical which is then quenched with an H atom donor to afford olefin repeat units. Interestingly, when investigating SET-induced transformations of these phthalimide-ester-containing copolymers, we noticed dramatic reductions in molecular weight for a copolymer of *N*-methacryloxyphthalimide (PhthMA) and methyl methacrylate (MMA), despite other acrylate-based systems retaining their carbon−carbon backbone framework and allowing for quenching of the backbone radical by a hydrogen atom. Intuitively, formation of a backbone radical could allow for three subsequent reaction pathways: β-scission leading to polymer degradation, radical quenching leading to polymer modification, and polymer radical coupling (Figure 1). We reasoned that targeting the β-scission pathway would give rise to polymers that are degradable despite their all-carbon backbones.

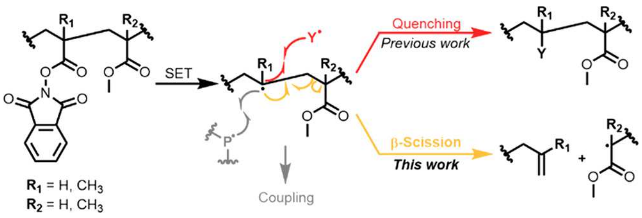


Figure 1. Possible backbone radical fates depending on the presence of radical quenching species and relative radical stabilization of substituents R_1 and R_2.

In this work, we report on vinyl polymers preprogrammed for light-induced, ambient-temperature degradation via inclusion of SET-accepting phthalimide ester-containing repeat units. We find that methacrylate-based polymer backbones are susceptible to polymer degradation, as evidenced by a significant reduction in polymer molecular weight and in accordance with recent findings by Ouchi et al.[13] Low molar incorporation of redox-active NAP monomer units by copolymerization with methacrylates allowed for efficient degradation and molecular weight reduction for vinyl polymers with all-carbon backbones under very mild conditions (i.e., ambient temperature and green light). Furthermore, we were interested in investigating the potential degradation of acrylate- and styrene-based polymers. Application of the photocatalytic system to acrylate-based copolymers in the absence of an H atom donor revealed predominantly polymer coupling with the notable absence of degradation via backbone β-scission. Additionally, SET to copolymers of *N*-acryloxyphthalimide (PhthA) and styrene resulted in a pronounced molecular weight increase in the absence of an H atom donor due to polymer coupling. It was further shown that the increase in molecular weight could be suppressed by increasing the concentration of the radical quencher. Overall, these findings could have significant implications for the future of plastics recycling, as the reported method provides the ability to achieve significant polymer molecular weight reduction under mild conditions with only low inclusion of an NAP comonomer. This work further emphasizes the potential of applying SET-based transformations to polymer systems to facilitate previously unattainable transformations.

PhthA and PhthMA were synthesized to serve as comonomers which act as latent backbone radical sources, providing access to secondary and tertiary radicals, respectively (Figures S1 and S2). Reversible addition−fragmentation chain transfer (RAFT) polymerization[26,27] was then used to prepare the SET-accepting copolymers (Table 1) comprised of MMA and either PhthMA (**1**, **2**) (Figures S3, S4, S10, and S11) or PhthA (**3**) (Figures S5 and S12) as well as methyl acrylate (MA) and PhthA (**4**) (Figures S6 and S13) by using 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDP) as the chain-transfer agent and azobisisobutyronitrile (AIBN) as the thermal initiator at 70 °C (full conditions in the SI). A copolymer containing PhthA and styrene (**5**) (Figures S7 and S14) was likewise synthesized by RAFT, this time using 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) as the chain transfer agent and 1,1′-azobis-(cyclohexanecarbonitrile) (ACHN) as the thermal initiator at 90 °C (full conditions in the SI). The preparation of these polymeric materials via RAFT polymerization, in principle, allows for creation of copolymer materials with advanced architecture and predetermined molecular weight. Furthermore, RAFT polymerization provides control over the polymer molecular weight distribution, with unimodal distributions facilitating the assessment of molecular weight changes following stimulus-induced degradation.

First, the degradation of copolymer **1** was investigated using previously reported conditions for backbone radical generation (Figure 2A). ^{1}H NMR spectroscopic analysis of the starting material and final product revealed a quantitative upfield shift of the phthalimide proton resonances from broad, polymer

Table 1. Redox-Active Copolymers with Molecular Weight Comparison Before and After SET

ID	comonomers	mol % Phth[a]	$M_{n,0}$[b] (g/mol)	$Đ$[c]	$M_{p,0}$[d] (g/mol)	$M_{p,ftheo}$[e] (g/mol)	$M_{p,fobs}$[f] (g/mol)	E_{deg}[g] (%)
1	MMA/PhthMA	9.9	36 300	1.39	55 800	1700	[h]	[h]
2	MMA/PhthMA	1.3	31 000	1.29	38 900	7800	13 000	86
3	MMA/PhthA	1.1	28 300	1.44	43 000	10 600	29 200	71
4	MA/PhthA	1.4	10 500	1.23	12 500	900	[i]	[i]
5	Sty/PhthA	1.9	15 500	1.17	18 100	4300	[i]	[i]

[a] Mole percent of a phthalimide monomer within the copolymer. [b] Number-average molecular weight of the initial polymer. [c] Molar-mass dispersity of initial polymer. [d] Peak molecular weight of initial polymer determined by GPC. [e] Theoretical peak molecular weight following polymer degradation, assuming 100% of phthalimide monomer units, resulted in chain scission events (calculation in the SI). [f] Final observed peak molecular weight following SET. [g] Degradation efficiency calculated using the equation $E_{deg} = (M_{p,0} - M_{p,fobs})/(M_{p,0} - M_{p,ftheo})$. [h] Peak molecular weight and degradation efficiency not determined due to a lack of peak resolution in GPC. [i] Peak molecular weight and degradation efficiency not determined due to lack of polymer degradation and multimodal molecular weight distributions of the postdecarboxylation polymers.

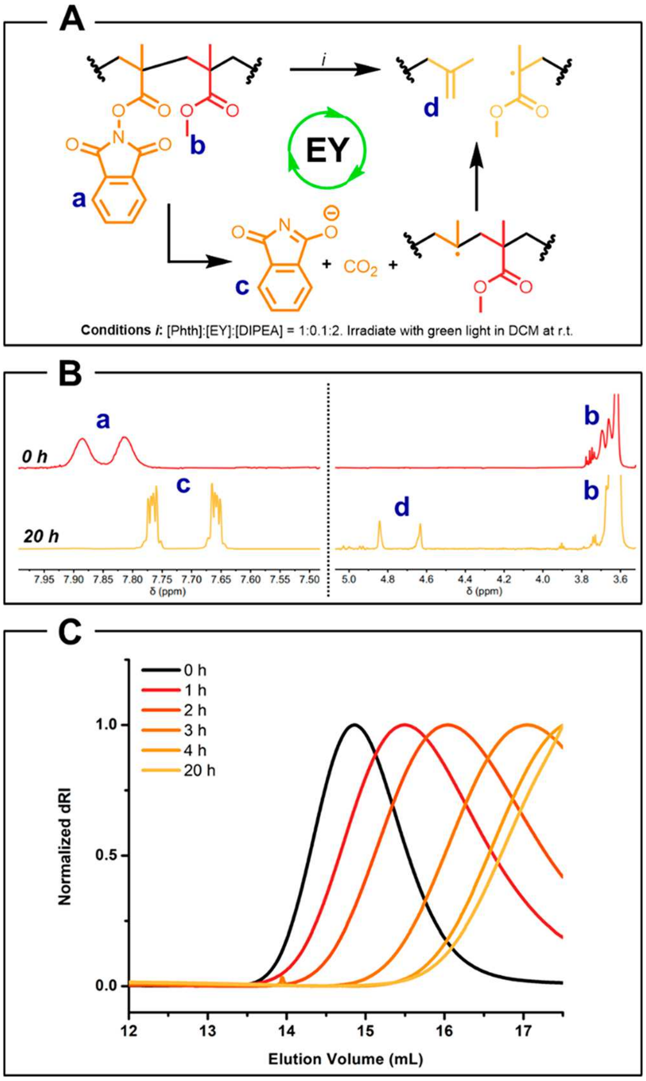


Figure 2. (A) Reaction scheme for poly(methacrylate) degradation using PhthMA as a comonomer. (B) ^{1}H NMR spectra before (top) and after (bottom) polymer degradation. (C) GPC traces at reaction time points revealing a decrease in polymer molecular weight.

peaks to sharp, small-molecule peaks with higher shielding due to detachment from the electron-withdrawing ester (Figures 2B and S17). Additionally, the emergence of alkenyl proton peaks in the ^{1}H NMR spectrum of the product was observed, which is strong evidence of polymer backbone cleavage via β-scission, leading to unsaturated isobutenyl chain ends. As evidenced by gel permeation chromatography (GPC) (Figure 2C), a dramatic reduction in polymer molecular weight was achieved in only a few hours. Control studies utilizing copolymer **2** and a PMMA homopolymer synthesized via RAFT (Figures S9 and S16; conditions in SI) confirmed the necessity for each reaction component (phthalimide ester, EY, DIPEA, and green light), as no degradation occurred without all components (Figures S27 and S28).

Quantifying the reduction in molecular weight following SET-induced degradation was complicated, as the resulting polymer was too low in molecular weight, resulting in a lack of resolution between the polymer peak and solvent peak in the GPC elugram. Thus, we applied the same reaction conditions to an analogous polymer with lower PhthMA incorporation (**2**), with the hope of breaking the copolymer down into segments large enough to observe in GPC. Gratifyingly, once again vinyl protons appeared in the ^{1}H NMR spectrum of the product (Figure S18), and a significant decrease in polymer molecular weight was observed (Figure 3B). In this case the product of the reaction was large enough to assess on GPC. By comparing the $M_{\mathrm{p,fobs}}$ of the polymer to the $M_{\mathrm{p,ftheo}}$ assuming 100% of NAP monomer units would produce a scission event, the degradation efficiency (E_{deg})[13] was calculated to be 86% (Table 1, equations in SI). The molar-mass dispersity increase following degradation is attributed to the statistical incorporation of PhthMA monomer units. While the average chain had 4.0 PhthMA monomers, the amount of PhthMA per chain would vary, resulting in variability in the amount of chain-scission points. Additionally, we synthesized P(PhthMA-*co*-MMA) via conventional radical polymerization (Figures S8 and S15; conditions in SI) and exposed it to decarboxylating conditions, which revealed polymer degradation via ^{1}H NMR spectroscopy and GPC (Figures S22 and S29). Overall, through SET-induced backbone radical generation, efficient degradation of polymethacrylates was achieved using a metal-free system at ambient temperature using green light as the stimulus.

Next, we sought to explore other comonomer combinations to determine if other copolymers could be made degradable through inclusion of either PhthA or PhthMA as a comonomer. Keeping in mind that the prevalence of β-scission would be impacted by the stability of the nascent backbone radical and the stability of the post-scission radical, we synthesized a copolymer using comonomers MMA and PhthA, reasoning that a secondary backbone radical would be likely to undergo β-scission to create a resonance-stabilized tertiary methacryloyl radical. Following application of the standard reaction conditions to copolymer **3**, we once again observed both significant molecular weight reduction by GPC and new vinyl peaks in the ^{1}H NMR spectrum of the product (Figures 3C and S19). The E_{deg}, however, was lower in this case (71%) than in the PhthMA-MMA system (Table 1). We reason that the lower efficiency may be due to either the higher reactivity of the backbone radical to be quenched by a hydrogen atom from *N*,*N*-diisopropylethylamine (DIPEA) or potentially a lower steric strain and reduced stability of the resulting less highly substituted unsaturated chain end. We next investigated a copolymer with an all-acrylate backbone containing PhthA and MA (**4**). Following SET to copolymer **4**, complete decarboxylation was revealed by ^{1}H NMR spectroscopy (Figure S20). However, instead of polymer degradation, an increase in molecular weight due to polymer coupling was observed (Figure 3D). In this case, the rate of β-scission was slow compared to the rate of coupling. In previous work it was shown that production of a backbone radical in copolymer **4** in the presence of an H atom donor yielded ethylene/acrylate copolymers,[21−23] meaning that polymer coupling can be suppressed through the addition of a radical quenching species.

Finally, we wanted to investigate the potential for degradation of a styrene-based copolymer. We used PhthA as a comonomer, expecting that a secondary backbone radical would be most likely to undergo scission to create a secondary benzylic radical. As evidenced by ^{1}H NMR spectroscopy, complete decarboxylation occurred upon application of the standard reaction conditions (Figure S21), but, unexpectedly, a dramatic increase in molecular weight was observed via GPC (Figure S23). To investigate the topology of the resulting polymer, we used GPC to compare log(molar mass) with

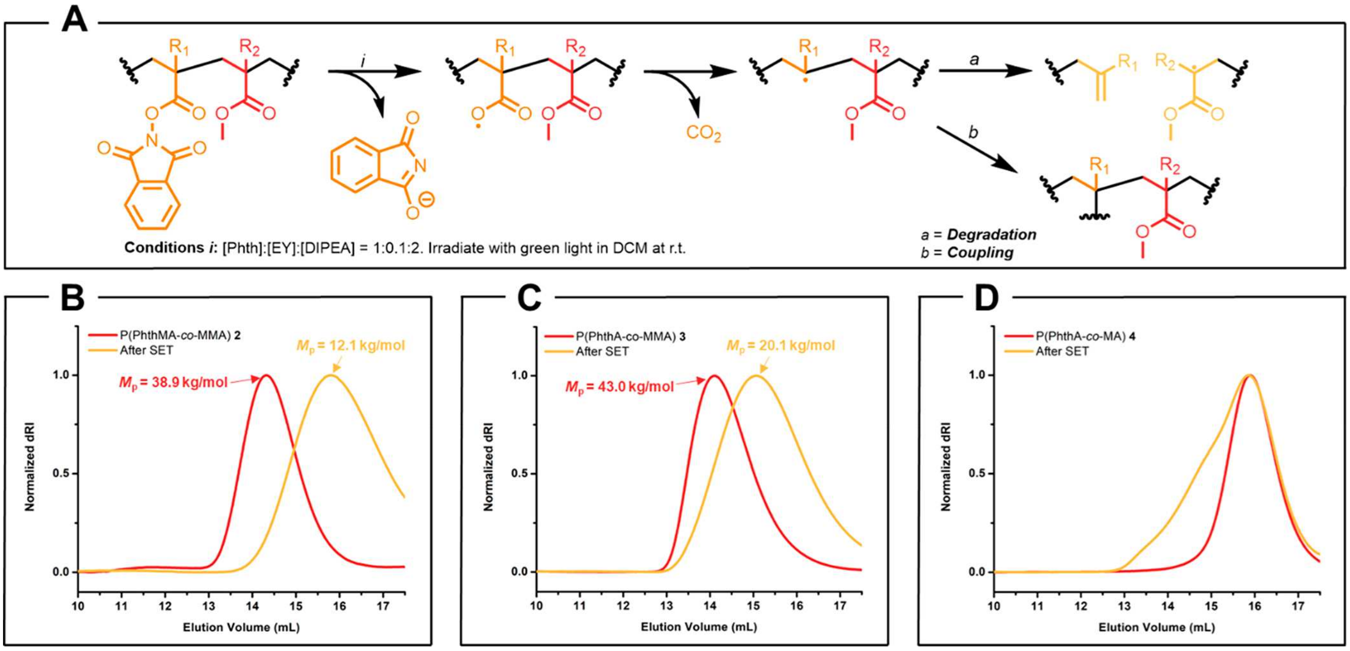


Figure 3. (A) Reaction scheme for SET to polymers containing redox-active phthalimide ester pendants in the absence of a radical quenching species displaying two potential reaction pathways: degradation and coupling. (B) GPC traces before and after SET to a copolymer **2**, revealing polymer degradation. (C) GPC traces before and after SET to copolymer **3**, revealing polymer degradation. (D) GPC traces before and after SET to copolymer **4**, revealing polymer coupling.

elution volume for the post-SET high MW polystyrene and compared it to a linear polystyrene standard of a similar molecular weight (Figure S26). The product eluted as a higher molar mass polymer at the same elution volume as the linear polystyrene analog, which seems to support the formation of a nonlinear morphology.[28,29] The observed coupling was similar to that observed with copolymer **4**; however the observed molecular weight increase was significantly more pronounced. Since the only difference between the systems (**4** and **5**) is the backbone comonomer (MA vs styrene), styrene must play some part in increasing the prevalence of coupling. It is plausible that an unstable nascent secondary backbone radical will initiate either intra- or intermolecular H atom abstraction from the benzylic position of a styrene repeat unit,[12,30] producing a stable tertiary benzylic radical which is long-lived enough to couple to other polymer chains. To elucidate the mechanism of this transformation and test the backbone coupling hypothesis, we performed additional trials using varying amounts of the H atom donor, tributyltin hydride (Bu_3SnH), to observe whether increasing the concentration of radical quencher would lead to suppression of coupling. Indeed, upon an increase in H-donor concentration, the product GPC trace began to approach that of the starting polymer (Figure S23). ^{1}H NMR spectroscopy confirmed that complete decarboxylation had taken place (Figures S24 and S25), which implies that any backbone radical was quickly quenched by an H atom rather than undergoing coupling. Additionally, the log(molar mass) was plotted against elution volume and compared with that of a polystyrene standard of similar molecular weight. Different from the case without an H donor, the product polymer eluted with similar or lower molar mass at the same elution volume as the standard, consistent with a linear morphology (Figure S26). As with copolymer **4**, in this system it seems the rate of β-scission (k_β) is low, while radical quenching can be favored over polymer coupling through the addition of a radical quenching species. While the stability of a benzylic radical is much higher than that of a secondary alkyl radical, k_β was still low in this system as compared to the high k_β in a similar methacrylate-based system. This is reminiscent of a phenomenon present in RAFT polymerization in which a chain extension of polystyrene with MMA leads to poor control over the molecular weight distribution due to preferential fragmentation of the RAFT intermediate radical toward the better methacryloyl radical leaving group.[31] Altogether, these results seem to suggest that radical stabilities are not the only important variables to consider when predicting the fate of a polymer backbone-centered radical. Ultimately, increasing the H donor concentration to favor only radical quenching in copolymer **5** is a noteworthy achievement because, although the polymer did not degrade, statistical radical copolymers of styrene and ethylene were created.

In light of these and previous findings, we propose a mechanism for SET-induced decarboxylative radical generation that yields a polymer backbone-centered radical (Figure 4).[15] In this mechanism, EY is excited by green light to EY*, which is reduced by DIPEA and subsequently acts as an SET donor, transferring an electron to a phthalimide ester moiety. This triggers decarboxylation of the phthalimide ester, yielding phthalimide, CO_2, and a backbone radical. The path followed once the backbone radical is generated is dependent on factors such as the stability of the backbone radical, the stability of a post-scission radical, steric effects of neighboring units, and the presence of a radical quenching species. The combination of these effects allows for three pathways: (1) backbone radical quenching, (2) polymer degradation via backbone scission, and (3) polymer coupling. Overall, the investigated methacrylate-based, redox-active copolymers underwent degradation when exposed to decarboxylating conditions, while polymer coupling or quenching predominated for the acrylate- and styrene-

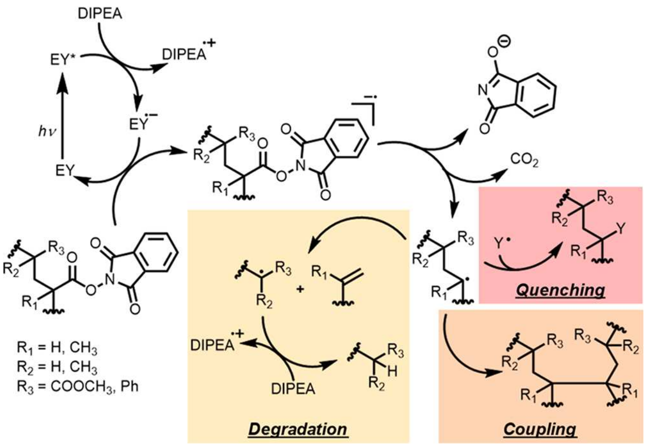
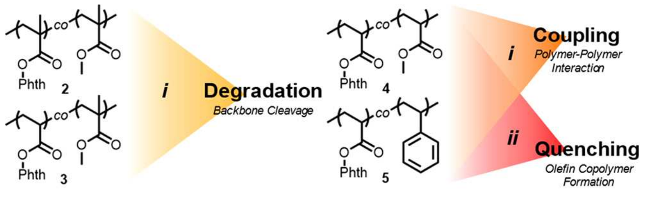


Figure 4. Proposed mechanism for SET-induced decarboxylative backbone generation in polymers highlighting the three potential fates of the backbone radical: quenching, degradation, and coupling.

based, redox-active copolymers, depending on the presence of an H donor (Figure 5).



Conditions *i*: [Phth]:[EY]:[DIPEA] = 1:0.1:2; DCM, r.t., green light. *ii*: Same as *i* with addition of H donor.

Figure 5. Summary of reported fates of phthalimide-ester-containing copolymers following SET-induced decarboxylative backbone radical generation.

In conclusion, we have reported an SET-induced decarboxylation approach to polymer degradation. A dramatic reduction in polymer molecular weight was observed under metal-free conditions at ambient temperature using low-energy green light as a stimulus with ca. 1 mol % of redox-active comonomer. This approach may have significant implications for the future of degradable vinyl polymers and plastics recycling. Furthermore, polymer coupling via the backbone radical as well as backbone radical quenching to produce ethylene/styrene radical copolymers are reported. Overall, SET leading to polymer backbone radical generation is a rapidly growing area of research, and these findings provide the framework for further exploration into new routes and methods for material upcycling, post-polymerization modification, and polymer degradation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.2c00091.

> Materials, instrumentation, methods, ^{1}H NMR spectra for all compounds, and GPC elugrams for all polymers (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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