

Chemical Upcycling of Commercial Polystyrene via Catalyst-Controlled Photooxidation

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ABSTRACT: Chemical upcycling of polystyrene into targeted small molecules is desirable to reduce plastic pollution. Herein, we report the upcycling of polystyrene to benzoyl products, primarily benzoic acid, using a catalyst-controlled photooxidative degradation method. FeCl_3 undergoes a homolytic cleavage upon irradiation with white light to generate a chlorine radical, abstracting an electron-rich hydrogen atom on the polymer backbone. Under the oxygen-rich environment, high MW polystyrene (>90 kg/mol) degrades down to <1 kg/mol and produces up to 23 mol % benzoyl products. A series of mechanistic studies showed that chlorine radicals promoted the degradation via hydrogen-atom abstraction. Commercial polystyrene degrades efficiently in our method, showing the compatibility of our system with polymer fillers. Finally, we demonstrated the potential of scaling up our approach in a photoflow process to convert gram quantities of PS to benzoic acid.

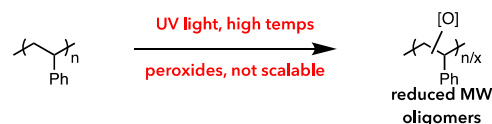
Synthetic chemists and engineers have optimized and streamlined the synthesis of commodity polystyrene (PS) products essential to everyday life. While these robust materials have inspired consumer confidence, the recycling rate is currently less than 1%, and PS products, especially expanded foams, account for approximately a third of the content in landfills in the world.^{1–3} While significant effort is being placed into developing PS alternatives and postfunctionalization,^{4–6} the production costs cannot overcome the financial incentives to continue producing virgin PS.¹ Studies to recycle PS, primarily through pyrolysis and microbial degradation chemically, are an active area of research.^{7–9} An essential requirement of PS waste degradation, however, is a scalable, energy-efficient process that can convert PS into a single product,¹⁰ while being compatible with the several different forms of commercial PS, including solids, expanded foams, copolymers, and polymer fillers.³

Inspired by recent advances in photocatalysis and the opportunities that inexpensive visible light holds in scalable processes,^{11–13} we envisioned a photon-driven, catalyst-controlled oxidative degradation pathway to upcycle commercial PS into benzoic acid and benzoyl derivatives. Irradiation of PS with UV light ($\lambda = 254$ nm) is known to generate radicals on the polymer backbone, which are directly oxidized by ambient atmospheric oxygen to generate peroxy radicals and ultimately lead to cleavage of the polymer chain.^{14–18} To improve the degradation rate, photoinitiators, such as quinones, peroxides, benzophenones, and metal catalysts, have been incorporated to accelerate backbone oxidation, likely via hydrogen-atom transfer (HAT) (Scheme 1A).^{19–22} While these advances have shown promise, conversion of PS into a single product, such as benzoic acid, remains a challenge.²³

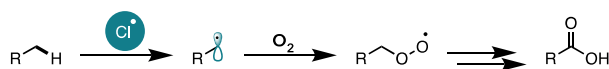
As HAT is a crucial step for photooxidative degradation, we hypothesized that HAT reagents generated by visible light would allow us to avoid using high-energy UV light and allow

Scheme 1. Proposed Upcycling of Polystyrene

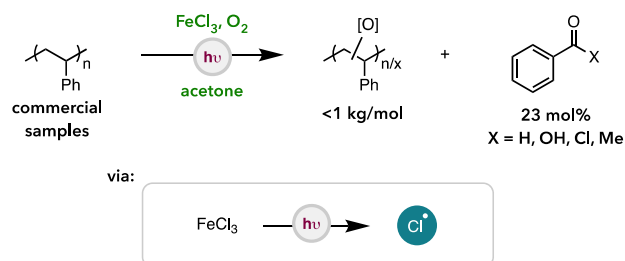
a) Previous photooxidative degradation of polystyrene



b) Chlorine radical for HAT and subsequent oxidative cleavage



c) Chlorine radical generation for oxidative degradation (this work)



more specific control over the abstraction step. Chlorine radicals have seen widespread use as hydrogen atom abstraction agents due to the electrophilic character selectivity for strong, electron-rich C–H bonds ($\Delta H_{\text{diss}}(\text{HCl}) = 103$ kcal/

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mol).²⁴ Given these attributes, we hypothesized that introducing chlorine radical could lead to the abstraction of a benzylic C–H bond from the PS backbone and, upon oxidation, generate peroxy radicals capable of C–C bond cleavage (Scheme 1B). Additionally, unwanted side reactions arising from HAT from solvent can be avoided by employing solvents containing electrophilic C–H bonds, kinetically mismatched from chlorine radical promoted HAT.

While many methods are available for chlorine radical generation, the application to PS waste degradation requires an inexpensive, scalable option using visible light. FeCl₃ and related compounds have been shown as catalysts to generate chlorine radicals under visible light irradiation.^{25,26} Numerous reports have demonstrated efficient HAT from hydrocarbons to promote C–H oxidation or functionalization.^{27,28} We hypothesized that irradiation of PS in the presence of substoichiometric amounts of FeCl₃, in the presence of oxygen, would generate chlorine radicals, and through HAT, promote oxidative degradation of PS under mild conditions and be compatible with polymer waste streams that contain fillers, composite materials, and other polymers (Scheme 1C).

We began our studies by irradiation of PS in the presence of 10 wt % FeCl₃ in acetone, under ambient airflow, with a broad-spectrum white LED lamp. After 20 h, the polymer is converted to PS oligomers ($M_n = 0.8$ kg/mol) with 11 mol % (on a per monomer basis) small-molecule generation, primarily comprised of benzoyl products: benzoic acid, benzaldehyde, benzoyl chloride, and acetophenone (Table 1, entry 1, see the

confirmed that light, FeCl₃, and air are necessary for efficient degradation (entries 2–4). Additionally, when the reaction was conducted under ambient conditions, but in a sealed vial, only 1 mol % benzoyl products are formed, with the mass balance containing modestly degraded polystyrene (entry 5).

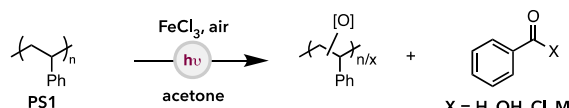
To elucidate the importance of chlorine radical, we compared our method to benzophenone, a known hydrogen abstraction catalyst used in previous PS degradation studies. While some degradation was observed, the amount of benzoyl product formation is significantly diminished, demonstrating the privileged performance of chlorine radical (entry 6). Examining FeCl₃ weight loading showed that using 5 wt % produces less than 9 mol % products, while greater than 10 wt % does not yield improvement (entries 7 and 8, see the Supporting Information for more details). When FeCl₃·6H₂O was used as an alternative, the degradation rate slowed slightly (entry 9). While chloride additives have previously been shown to promote chlorine radical formation and C–H abstraction,³⁰ under our protocol, the addition of LiCl, NaCl, or NH₄Cl did not improve benzoyl product formation (entry 10, see the Supporting Information for the full details). As oxygen is necessary for efficient degradation, we saturated the system with O₂, and under otherwise identical conditions, we observed a much more efficient degradation reaction with 23 mol % products formed in just 20 h (entry 11).

With our optimized conditions in hand, we set to examine the kinetics of polymer degradation and benzoyl product formation (see the Supporting Information for the full experimental details). As high MW PS is not entirely soluble in acetone, we ran identical samples simultaneously, and each sample was removed from the light source at a given time point and analyzed. By the 12 h time point, the total amount of products exceeded 20 mol %. From the 20 h to 48 h time points, the formation of benzoic acid plateaued, indicating that the oxidation of PS oligomers was slowing significantly (Figure 1a).²⁹ Notably, the amount of benzaldehyde increased through 12 h and then decreased over more extended time periods, while benzoic acid increased over time, ultimately becoming the primary product. To confirm that benzaldehyde was converted into benzoic acid, we conducted the experiment in the presence of 10 wt % 4-*tert*-butylbenzaldehyde (Figure 1c). The ¹H NMR data confirmed the quantitative conversion of 4-*tert*-butylbenzaldehyde into 4-*tert*-butylbenzoic acid (~75%), 4-*tert*-butylbenzoyl chloride (~25%), or 4-*tert*-butylbenzene (a trace amount), confirming that under our reaction conditions, benzaldehyde is oxidized to benzoic acid or benzoyl chloride over time. Benzoyl chloride also started diminishing after 12 h, likely via hydrolysis to benzoic acid and regeneration of chloride.

We conducted further mechanistic studies to elucidate the major pathway for backbone oxidation and benzoyl product generation. First, we sought to determine if the oxidized PS backbone could degrade through a Norrish type I cleavage under white light in the absence of FeCl₃. We subjected oxidized polystyrene (dPS1, see the Supporting Information for experimental details) to white light in the absence of FeCl₃ and observed no further degradation (Figure 1b). This result showed that white light is unlikely to promote the Norrish type I cleavage on the oxidized PS. Therefore, these experiments support our hypothesis that HAT via chlorine or oxygen-centered radicals promotes the primary degradation pathway.

On the basis of these data, our proposed mechanism is depicted in Figure 1d. Photogeneration of chlorine radical

Table 1. Optimization of Benzoyl Product Formation



entry ^a	deviation	M_n (kg/mol)	\bar{D}	mol % ^b
1 ^c	none	0.8	1.91	10.9
2 ^d	no light	84	6.41	
3 ^d	no FeCl ₃	87	5.84	
4 ^{e,f}	N ₂	24	6.24	
5 ^{e,f}	no air flow	11	6.03	1.2
6 ^{e,g}	benzophenone (5 wt %)	3.9	1.98	2.3
7 ^e	FeCl ₃ (5 wt %)	1.2	6.06	8.2
8	FeCl ₃ (20 wt %)	1.1	1.71	11.3
9 ^e	FeCl ₃ ·6H ₂ O	1.2	9.10	10.8
10 ^f	LiCl (25 wt %)	0.8	1.55	10.5
11 ^{f,h}	O ₂	0.6	1.31	22.8

^aUsing 20 mg of PS1 and 10 wt % FeCl₃ dissolved in acetone (0.25 mL), irradiated with white LED for 20 h with air cooling and airflow.

^bTotal yield of benzoyl products on a monomer basis; an average of two trials. ^cThree trials were done. ^dA single trial was done. ^eSEC traces were bimodal. ^fPS2 ($M_n = 95$ kg/mol and $\bar{D} = 6.17$) was used. ^gA 390 nm light was used. ^hO₂ balloon.

Supporting Information for product distribution). A trace amount of benzene and chlorobenzene were detected, with the remaining mass balance comprised of oxidized styrene oligomers.²⁹ We also examined other light sources commonly used with FeCl₃ for chlorine radical generation and found that 390 and 427 nm lights provide similar results of polymer degradation, but fewer benzoyl products are obtained (see the Supporting Information for more details). Control experiments

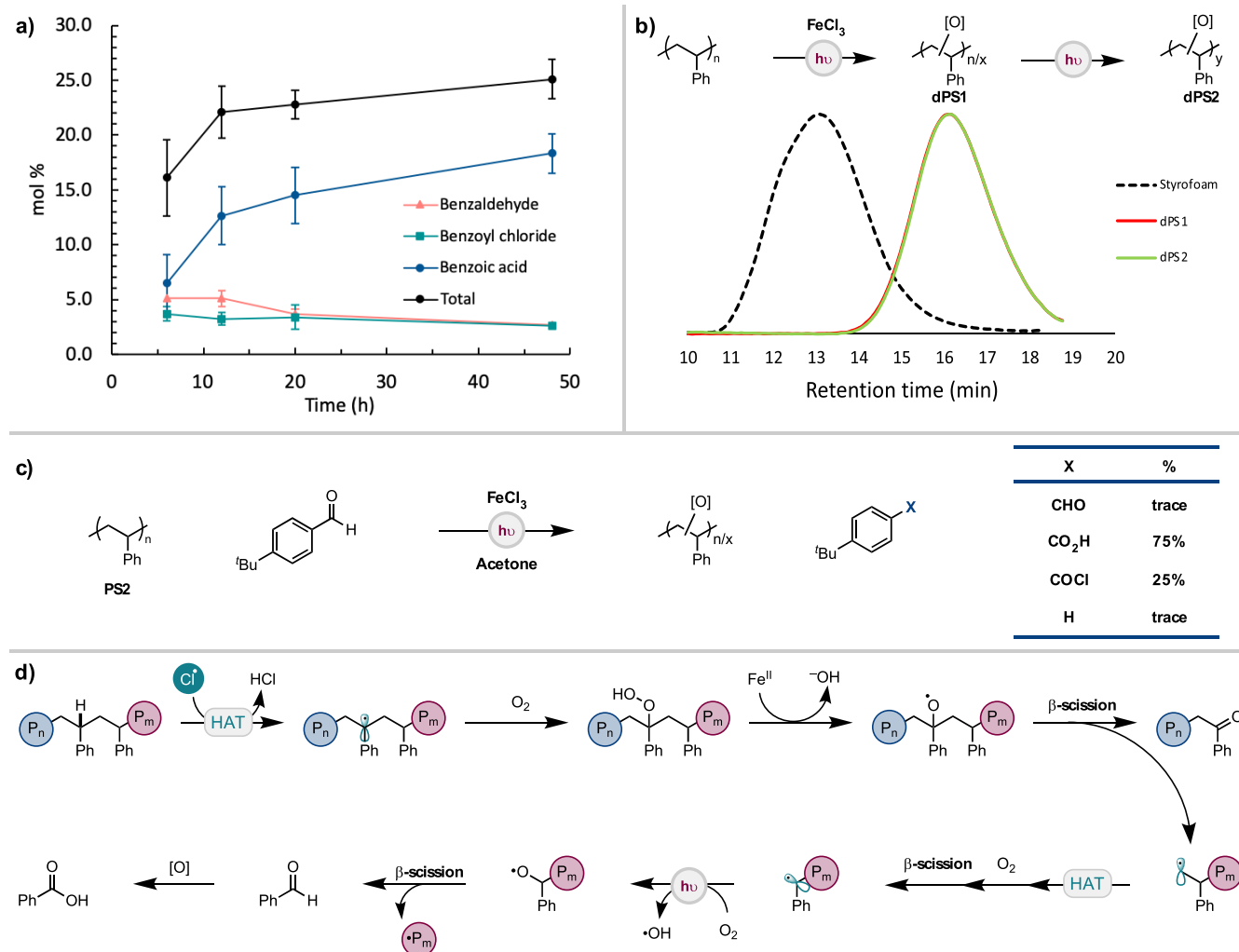


Figure 1. (a) Scatter plot for benzoic acid, benzaldehyde, and benzoyl chloride at each time point for the PS degradation under O_2 . (b) Degradation profile of oxidized PS in the absence of $FeCl_3$. (c) Control experiment to understand the mechanism of small-molecule generation. (d) Proposed mechanism for both chain cleavage and major pathways for benzoyl product generation.

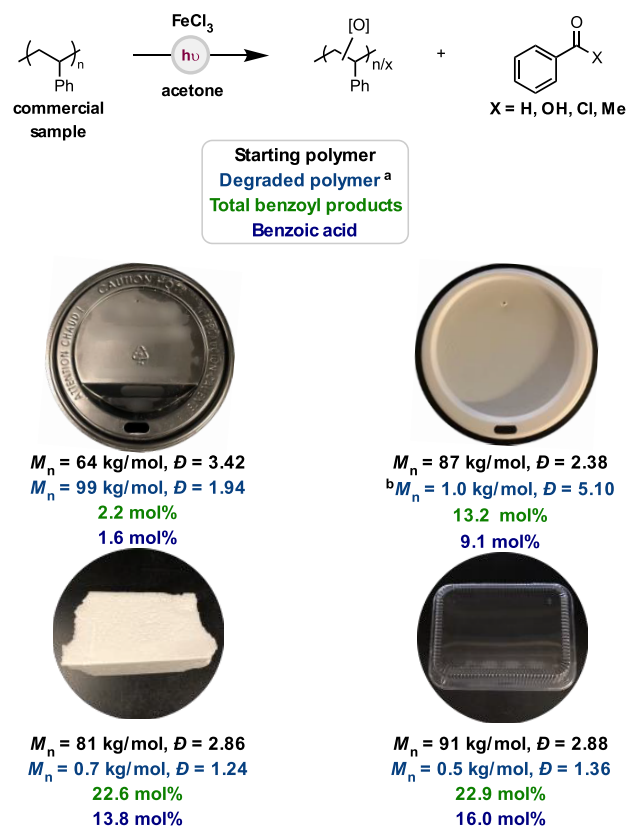
promotes C–H abstraction from the PS backbone to generate a benzylic radical, which upon reaction with oxygen affords a peroxy radical. Hydrogen atom abstraction affords a peroxide, and it is likely that reduction with Fe(II) gives the peroxy radical on the backbone and regenerates Fe(III). β -Scission promotes chain cleavage, leaving a phenyl ketone chain end and a primary radical. Several options exist from this primary radical, ultimately funneling into a benzylic radical on the chain end (see the Supporting Information for a complete discussion of alternatives). Oxidation and β -scission from the resultant oxygen-centered radical affords benzaldehyde and regenerates a primary radical. Oxidation of benzaldehyde to benzoic acid is the ultimate product of the oxidative cleavage process. Evaluation of the total products and oligomers at the end of the reaction suggests some mass loss, likely in the form of formaldehyde or formic acid, indicating that some oxidation of the primary radical may occur (see the Supporting Information for more details).

Given our optimized conditions and mechanistic rationale, we envisioned our mild reaction conditions should be amenable to degradation of commercial PS samples, which may contain additives, such as UV absorbers, radical scavengers, and composite materials, to enhance the

durability.³ Therefore, several PS products, ranging from packaging materials to coffee cup lids, were selected to test the feasibility of our method. We first measured the M_n and dispersities via SEC analysis (Scheme 2) and obtained 1H NMR spectra (see the Supporting Information for more details). As expected, high molecular weights (>60 kg/mol) and broad dispersities (>2.00) were observed for all. The coffee cup lids also contained additional signals in 1H NMR spectra, likely some form of cross-linked polymer or composite materials. All samples were used as obtained without purification.

We observed minimal degradation to PS oligomers when subjecting the black coffee cup lid to our reaction conditions. However, despite the less efficient degradation, we still obtained 2.2 mol % benzoyl products. We also noted a decrease in dispersity and observed insoluble high MW material after the reaction. We hypothesized based on these data that the black dye is inhibiting light penetration, but the smaller PS chains in the sample were still efficiently degraded. Gratifyingly, the white coffee cup lid, Styrofoam, and a clear lid degraded to afford PS oligomers. These results signify that our system could efficiently break down commercial samples of PS, even with additional composite and insoluble material.

Scheme 2. Commercial PS Degradation

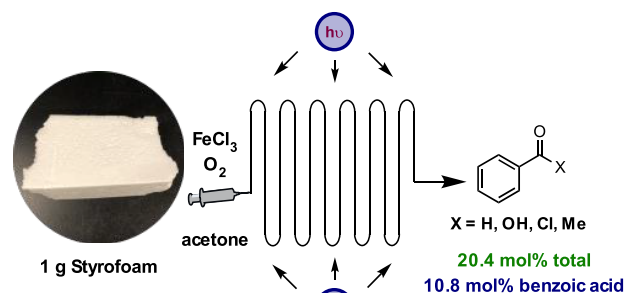


^aUsing 20 mg of commercial PS and 10 wt % $FeCl_3$ dissolved in acetone (0.25 mL), irradiated with white LED for 20 h with air cooling and O_2 balloon (an average of 2 trials). ^bA small, high MW peak was found in SEC analysis.

Additionally, in the case of Styrofoam and the clear lid, we obtained similar levels of benzoyl products, with the formation of benzoic acid in 13.8 and 16.0 mol %, respectively.

Having thus far demonstrated the feasibility of commercial PS degradation under mild conditions to yield benzoyl products, we sought to showcase the scalability of our method. Photochemistry has been developed to proceed on a larger scale, most notably focusing on the transition to photoflow processes, given the inefficiency of batch reactions in photodriven processes.^{12,31} With increasing photonic efficiency and dual-phase gas/liquid flow systems, we envisioned degrading grams of commercial PS in a matter of hours (Scheme 3). Our simple setup comprises two syringe pumps

Scheme 3. Commercial PS Degradation in Flow



and two LED lamps in a 3D printed photoreactor. After some optimization (see the Supporting Information for more details), we found that 1 g of styrofoam ($M_n = 74$ kg/mol) is degraded to oxidized styrene oligomers ($M_n = 0.6$ kg/mol) in just a few hours. Gratifyingly, we also obtained 10.8 mol % benzoic acid, with a total of 20.4 mol % benzoyl products, comparable to our results on a small-batch scale.

We have disclosed a mild and inherently scalable process for chemical upcycling of commercial PS into valuable small-molecule products. Under our mild conditions, high MW PS can be degraded into oligomers and funneled into specific small molecules, like benzoic acid. Furthermore, we have applied the method to several classes of commercial PS, observing highly efficient levels of degradation. Finally, we have demonstrated the scalability of our degradation method on a gram scale through flow chemistry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c01411>.

Experimental details, methods, data, and photographs of experimental setup (PDF)

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Notes

The authors declare no competing financial interest.

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