Photochemical Upcycling/Modification of Polystyrene-based Plastic Waste

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Abstract: The escalating accumulation of plastic waste in landfills and marine environments has become a pressing concern to society. Among all plastic-based waste, polystyrenes are widely utilized as a commodity plastic and present very low recyclability. To improve this scenario, photocatalysis has recently become one of the viable techniques which can be performed under mild conditions. In this concise review, we have highlighted recent advancements in the valorization of polystyrene-based plastic waste by mainly focusing on the selective functionalization of the C–H bonds. This strategy clearly holds strong promise for the sustainable and efficient conversion of polystyrene-based waste and contributes to the reduction of waste and resource conservation.

Keywords: Homogeneous · Photocatalysis · Polystyrene · Upcycling

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1. Introduction

Plastics are highly versatile and are ideal materials for packaging, as adhesives, foams, fibers and many more.[1,2] Consequently, their extensive use has led to remarkable surge in production and is making them ubiquitous in all aspects of the society.[3] It is estimated that the global accumulation of plastics will reach close to 600 million metric tons by 2050.[4] Despite their widespread use, a significant issue arises due to the lack of their recyclability. As a result, approximately 400 million metric tons of plastics are discarded annually.[5] Alarmingly, only <10% of plastic waste is recycled so far, with the recycling rate of polystyrene is as low as 1% (Fig 1a).[6] This situation certainly calls for urgent action to develop sustainable methods to valorize plastic-based waste to mitigate the environmental impact of plastic-based waste accumulation.

Currently, mechanical processing is the only strategy for the recycling of plastic-based waste on the industrial-scale by which one can convert plastic-based waste into useful materials with the same inherent characteristics (primary recycling) or can produce products (secondary recycling) with diminished quality. This is considered as a typically loop-closed and downcycling model. In terms of energy value, the plastic-based wastes are comparable to crude oil which renders itself a desirable material for the energy production.[7] Although incineration of waste is a useful approach for generating heat and electricity and reducing landfill buildup, it also releases hazardous substances and is associated with low energy recovery efficiency.[8] To address all these limitations, chemical recycling emerges as a promising alternative for producing high-quality monomers and/or value-added chemicals.
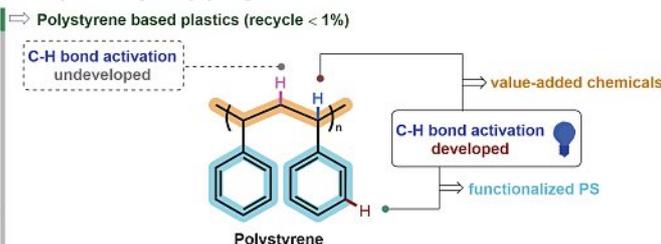

Fig 1. a) The end life of plastic waste. b) The photocatalyzed upcycling of PS.

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This approach is often referred as an upcycling model which provides sufficient economic incentives.[9,10] Among the existing chemical upcycling strategies, a photochemical process under benign conditions by utilizing photocatalysts and light has gained remarkable attention for the development of a sustainable method to transform plastic-based waste into valuable chemicals or building blocks.[11–18]

In this context, we should mention that the field of homogeneous photocatalysis has experienced significant growth and development in recent years in this field. The upcycling strategy has primarily focused on the selective activation of C–H bonds in polystyrenes, specifically, researchers have targeted the iterative aromatic C–H bond, benzylic tertiary C–H bond, and secondary C–H bond present in polystyrenes (PS, Fig 1b).[19] In fact, remarkable progress has been achieved for the selective activation of aromatic C–H bonds, leading to the formation of functionalized polystyrenes. Additionally, the selective activation of benzylic C–H bonds resulted in the generation of aromatic products. In this review, our objective is to provide a comprehensive summary of the recent advancements in homogeneous photochemical upcycling strategies which are designed to address the challenges posed by polystyrene-based plastic wastes. Additionally, we will delve into the underlying mechanisms behind these strategies to offer a clear understanding of the upcycling process.

2. Photocatalyzed Postpolymerization Modification (PPM) of Polystyrene

Post-polymerization modification (PPM) represents a straightforward approach to obtain valuable polymers by introducing functional groups into the polymer structure.[20,21] This process diversifies the physical properties of polymers, enhances their versatility and utility in further applications. Numerous endeavors such as alkylation,[22–24] acylation,[25–28] halogenation,[29–32] perfluoroalkylation,[33] sulfonation,[34,35] and alkyl lithium metalation or super- base metalation[36–40] have been utilized for the functionalization of the aromatic C–H bonds in PS under metal-catalyzed conditions. However, the field of photocatalytic PPM still remains largely underdeveloped but offers significant potential for the further advancement.

In this context, the group of Leibfarth reported successful examples of photocatalytic PPM strategy for polystyrenes (Scheme 1). In 2019, Leibfarth and co-workers described a controlled trifluoromethylation of polystyrene by using $Ru(bpy)_3Cl_2$ as the photocatalyst along with pyridine *N*-oxide and trifluoroacetic anhydride (TFAA) in DCM under the irradiation of 420 nm blue light at room temperature.[41] The extent of C–H bond trifluoromethylation was finely tuned by adjusting the equivalents of TFAA and pyridine *N*-oxide. For example, the utilization of 0.5 equivalent of pyridine *N*-oxide and 0.55 equivalent of TFAA resulted in approximately 19% of the desired trifluoromethylated products. Conversely, employing higher quantity of reagents, approximately 5.0 equivalents of pyridine *N*-oxide and 5.5 equivalents of TFAA, a significantly higher yield of the desired product (71%) was achieved. Importantly, this strategy was extended to substituted polystyrene; for instance, when 2.0 equivalents of pyridine N-oxide and 2.2 equivalents of TFAA were used, independent trifluoromethylation yields of 63% and 23% were achieved for poly(4-methylstyrene) and poly(4-tert-butylstyrene), respectively.

In 2020, the same group further developed fluoroalkylation by using phenazine as the photocatalyst.[42] However, the metal-free system exhibited lower reactivity compared to $Ru(bpy)_3Cl_2$. In the presence of 5.0 equivalents of pyridine *N*-oxide and 5.5 equivalents of TFAA, the yield of the trifluoromethylation product was 33%. The author proposed a mechanistic pathway for the functionalization process, wherein either $Ru(bpy)_3Cl_2$ or phenazine was raised to the excited state under irradiation by a 420 nm light source.
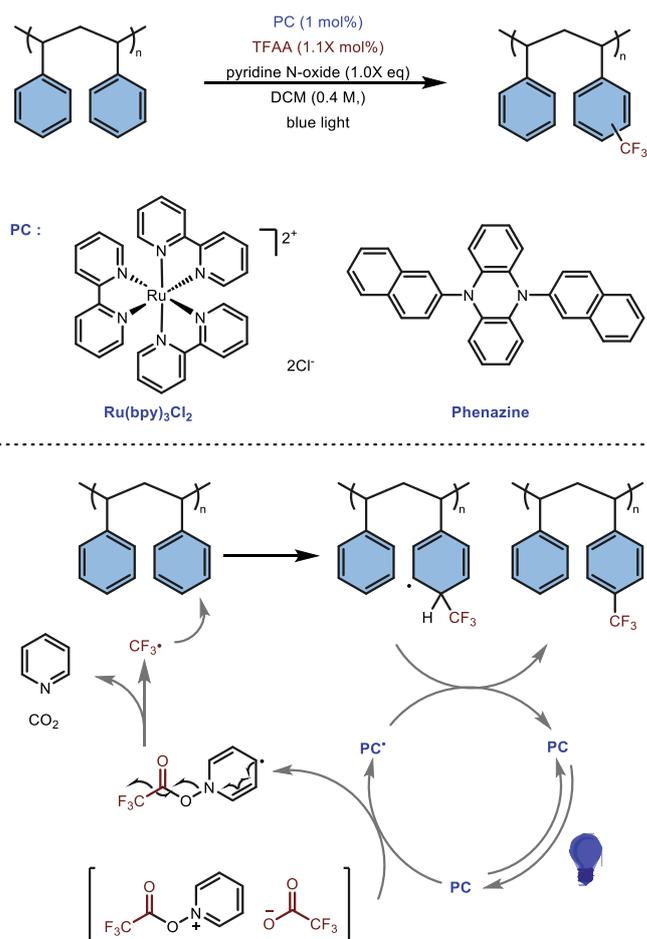
Scheme 1. Photocatalysis PPM of PS.

Subsequently, pyridine *N*-oxide reacted with TFAA, leading to the formation of an adduct that functioned as an oxidant. This adduct accepted an electron from the excited state of the photocatalyst, resulting in the generation of a CF_3 radical along with the release of pyridine and CO_2. The CF_3 radical then engaged in an attack on the aromatic ring in polystyrene to create an intermediate species. This intermediate species subsequently donated an electron to the photocatalyst radical cation, followed by the protonation, culminating in the formation of the trifluoromethylation product and ultimately completing the photocatalytic cycle.

3. Photocatalyzed Upcycling of Polystyrene

The photocatalyzed upcycling strategies of polystyrene-based plastic wastes aim to selectively generate high-quality monomer subunits or value-added chemical feedstocks by offering a potential reduction in reliance on fossil fuel-based resources.[43–46] However, a major challenge arises from the presence of substantial activation barriers (ranging from 83 to 323 kJmol^{-1}),[47] resulting from the inert covalent bonds and limited reactive functional groups in the polymer backbone.

In recent years, this field has witnessed significant progresses through the application of hydrogen atom transfer (HAT) strategies. Various research groups have developed noteworthy HAT-based methodologies, demonstrating improved efficiency and selectivity for the upcycling of polystyrenes. These advancements hold strong promise for furthering the field of photocatalyzed upcycling by unlocking the valuable potential of polystyrene-based waste for the sustainable synthesis of chemicals and resource management.
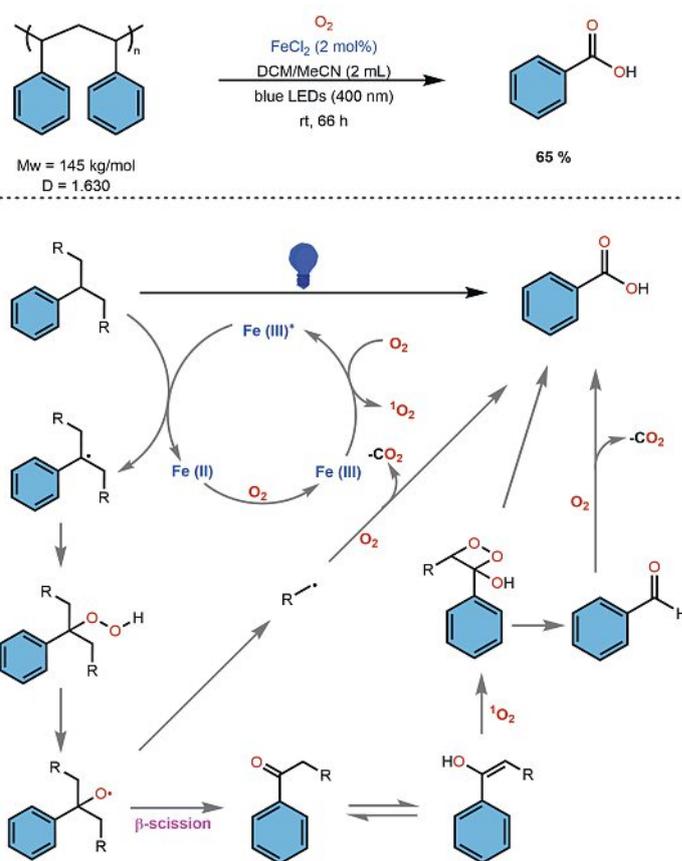
3.1 *Metal-catalyzed Upcycling of Polystyrene*

In 2021, the Zeng group observed that alkyl aromatics underwent photoinduced oxidation in the presence of molecular oxygen (Scheme 2).[48] This oxidation process was subsequently utilized for the targeted degradation of polystyrene into benzoic acid. The experimental protocol employed $FeCl_3$ as an economical catalyst and TBACl as a source of Cl radicals while Cl_3CCH_2OH served as an additive under the irradiation of 390 nm light in the presence of O_2. The primary focus of the study was to explore the compatibility of simple alkyl aromatics under optimal conditions. However, only one instance of the degradation of polystyrene (with M_n = 229.3 kg/mol and D = 1.630) was presented in this study and this degradation resulted in a 67% yield of benzoic acid.
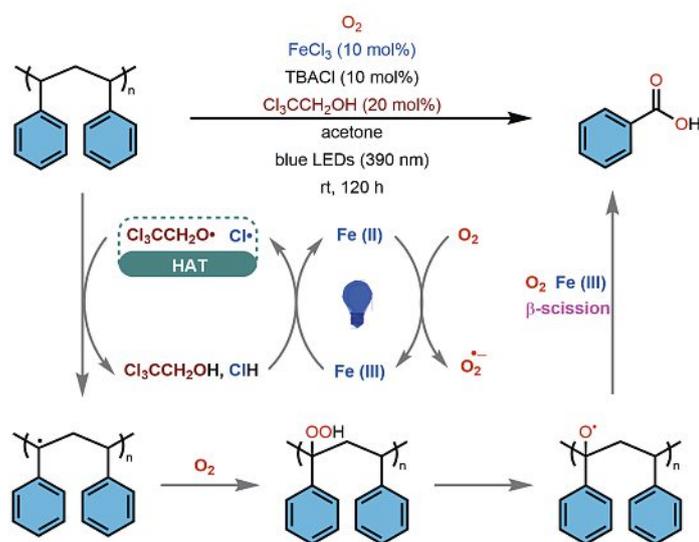
Scheme 2. $FeCl_3$ catalyzed upcycling of PS.

This report also proposed the reaction mechanism based on the results of radical scavenging reactions and the time course reaction of 4-fluorotoluene which was monitored by using ^{19}F NMR. During the monitoring of the reaction, intermediate species such as hydroperoxide, benzyl alcohol, and fluorobenzaldehyde were independently detected. Based on these findings, authors suggested that Cl_3CCH_2OH and TBACl reacted with $FeCl_3$ to generate the corresponding alkoxy and Cl radical, and Fe(II) species *via* a ligand-to-metal charge transfer (LMCT) process which was facilitated by the light. Both of these radicals were capable of abstracting a hydrogen atom from the benzylic position of alkyl aromatics, resulting in the formation of a carbon-centered radical. This radical then reacted with O_2, followed by hydrogen atom transfer (HAT) and oxygen transfer steps, ultimately yielding an oxygen-centered radical. Subsequently, the oxygen-centered radical underwent β-scission to produce benzoic acid as a final product in the presence of Fe(III) and light. Simultaneously, the generated Fe(II) species underwent a single electron transfer (SET) process to regenerate Fe(III) and $O_2^{\bullet-}$. This highly reactive oxygen species plays a critical role in the oxidation of the corresponding intermediates.

Later, Hu *et al.* developed a degradation method for PS-based plastic waste by utilizing $FeCl_2$ as a photocatalyst, O_2 or air as the oxidant, 400 nm blue LEDs as the light source, and the primary product of this degradation process was benzoic acid in 65% yield (Scheme 3).[49] Under the optimal reaction conditions, real life plastic-based waste materials such as PS foam and PS-cups exhibited the formation of benzoic acid with yields of 65% and 67% respectively.
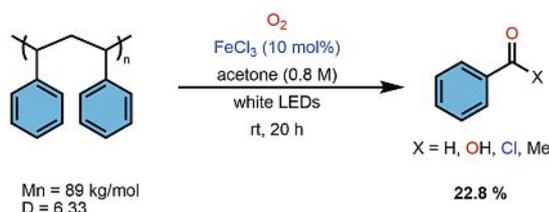

Scheme 3. $FeCl_2$ catalyzed upcycling of PS.

Furthermore, the degradation of PS-based copolymers including styrene-allyl alcohol copolymer resulted in a 56% yield of benzoic acid, poly(styrene-co-acrylonitrile) yielded 33% of benzoic acid, ABS produced 31% of benzoic acid, and styrene-maleic anhydride copolymer generated benzoic acid with 44% yield. Moreover, the combination of polystyrene and iron salt facilitated the degradation of PS-based plastics under ambient conditions. The authors assessed the degradation capability of a PS and $FeCl_2$ mixture under ambient conditions exposed to air. The results revealed that $FeCl_2$ was able to degrade the PS-based waste by reducing its molecular weight from 129 kg/mol to 91 kg/mol over a period of 12 days. The experiments were carried out by using natural sunlight with an average day length of 13 hours. This approach presented a promising strategy for the conversion of plastic waste into valuable chemicals.

The authors illustrated a comprehensive mechanism for this transformation, which was different from the mechanism proposed by Zeng *et al.* They demonstrated that Fe(II) was oxidized to Fe(III) in the presence of O_2 and served as the active photocatalyst. The excited state of Fe(III*) (E [Fe(III*)/Fe (II)] = 2.98 V vs. SCE in MeCN) selectively oxidized the benzylic C–H bond and generated the corresponding benzylic C-centered radical which subsequently reacted with O_2 to yield the O-centered radical. Subsequently, the O-centered radical underwent a β-scission to form the crucial intermediate ketone. The enol form of the ketone participated in a reaction with $^1O_2$ which resulted in the formation of a four-membered ring, a characteristic intermediate in the oxidation of styrene-type alkenes. With the opening of the four-member ring, the formation of benzoic acid occurred, accompanied by the generation of benzaldehyde. Finally, benzaldehyde underwent further oxidation to yield the final product.

In 2022, Stache *et al.* conducted a study that was very similar to the previous report by investigating a system which employed $FeCl_3$ as the catalyst in a highly concentrated solution (0.8 M) of

acetone (Scheme 4).[50] The reaction was carried out under the irradiation of white LED light for 20 hours, resulting in a 22.8% yield of the benzoyl product. Notably, they also compared the white LED light with light at 390 nm and 427 nm and observed that white LED light was a superior light for the degradation of polystyrene. The authors also conducted a detailed analysis of the kinetics for the degradation of polystyrene to benzaldehyde, benzoyl chloride, and acetophenone to gain insights into the reaction process and mechanism. However, it was found that the system was not sufficiently robust to handle real-life polystyrene waste such as a black coffee cup lid which yielded only 2.2 mol% of benzoyl products. To address the scalability concern, the authors introduced a flow system. When 1 g of styrofoam was introduced into the flow system, rapid degradation occurred, reducing the molecular weight of styrofoam from Mn = 74 kg/mol to Mn = 0.6 kg/mol after a few hours. This degradation was accompanied by the generation of 20.4% benzoyl products including 10.8% benzoic acid.
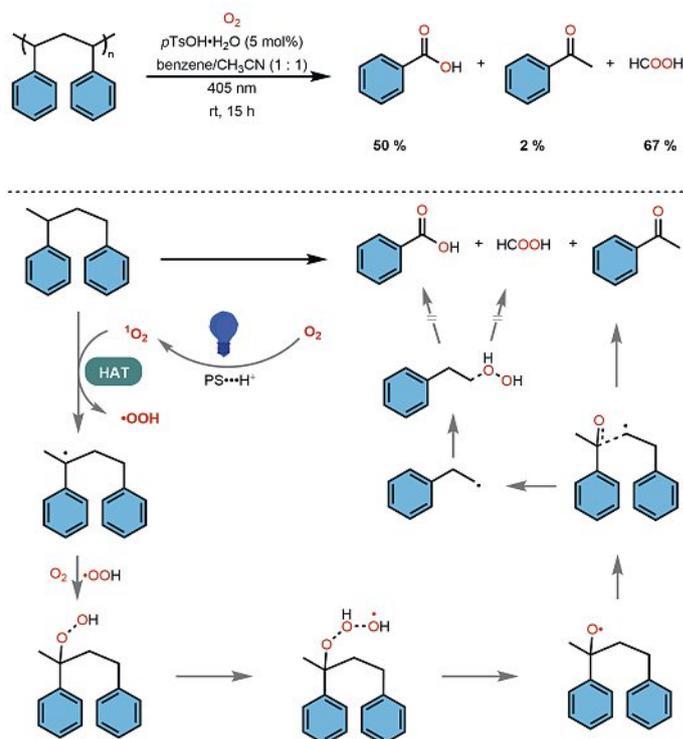

Scheme 4. FeCl₃ catalyzed upcycling of PS with white LEDs.

3.2 Photocatalyzed Upcycling of Polystyrene in Metal-free System

In 2022, the groups of Xiao and Qi presented a highly effective and mild photo-acid-enabled degradation method for polystyrene for the production of a mixture of value-added chemicals (Scheme 5).[51] The reaction system described in their report allowed the upcycling of 1.0 mmol of polystyrene to generate formic acid (67%), benzoic acid (50%), and benzophenone (2%). However, by employing 5 mol% of pTsOH·H$_2$O as the catalyst under the irradiation of 405 nm violet-blue light, a remarkably shorter reaction time of 15 hours was required to achieve a similar yield. The researchers also examined six different types of post-consumer polystyrene-based wastes (PS cup lid, yogurt container, PS packaging waste, PS foam, PS food box, and weighing boat waste) to achieve excellent yields of the products: formic acid (58–64%), benzoic acid (40–48%), and benzophenone (2–3%). An important feature of this system was easy scalability by using a flow system to allow potential industrial applications and to reduce further environmental impact.

Of particular interest, the authors proposed a compelling mechanism by integrating experimental findings with computational calculations. In this proposed mechanism, singlet oxygen played a crucial role during the degradation process of polystyrene. The singlet oxygen was formed from molecular oxygen (O$_2$) by utilizing the *in situ* generated [PS···H⁺] adduct which acted as a photosensitizer under the irradiation of light. The singlet oxygen exhibited the ability to abstract a hydrogen atom from the benzylic position of the PS backbone, leading to the formation of a tertiary C-centered radical and a hydroperoxyl radical. These radicals then combined to produce a peroxide compound which served as stable active intermediates for the subsequent cleavage of C–C bonds. The hydroxyl radical subsequently substituted the peroxide compound to form a doublet transition state that further generated an O-centered radical. This radical facilitated the cleavage of C–C bonds through β-scission which resulted in the production of acetophenone and an alkyl radical. The alkyl
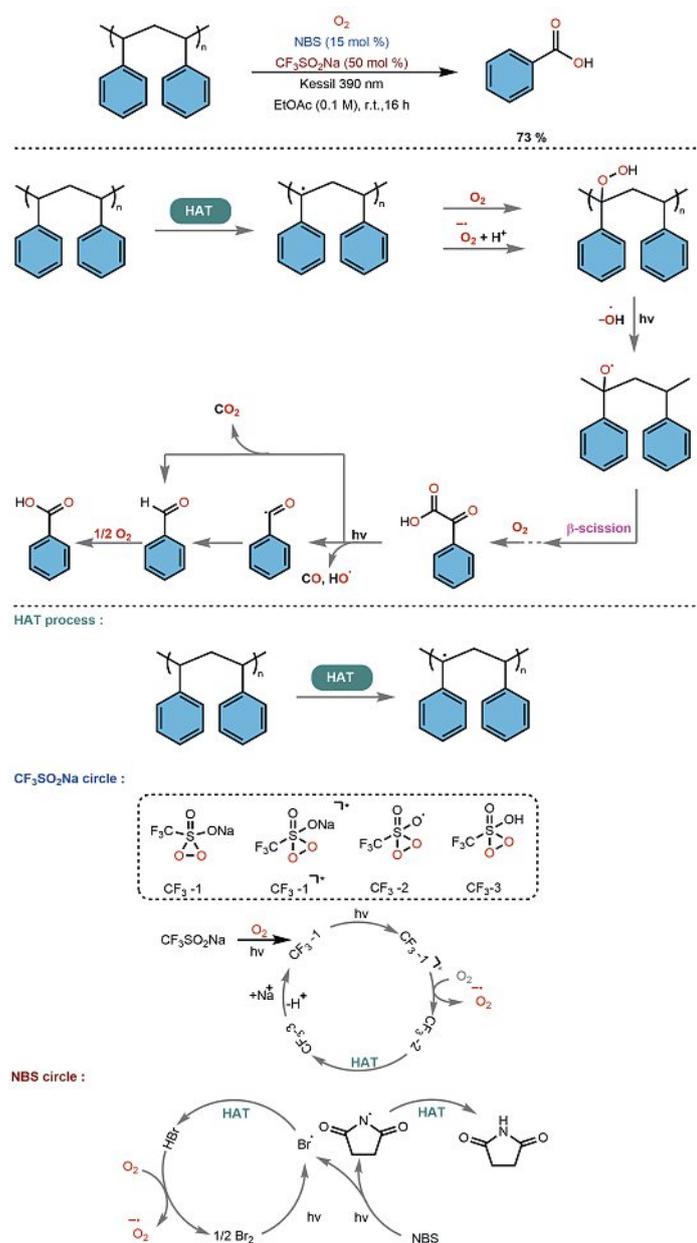

Scheme 5. Acid-catalyzed upcycling of PS.

radical then reacted with O$_2$, followed by the decomposition step to generate benzoic and formic acid as the coproducts of the degradation process.

Recently, our group also devised a metal-free dual Hydrogen Atom Transfer (HAT) strategy for the production of benzoic acid from polystyrene-based plastic wastes with exceptional selectivity and efficiency (Scheme 6).[52] In this innovative approach, both N-bromosuccinimide (NBS) and trifluoromethanesulfonic acid sodium salt (CF$_3$SO$_2$Na) were capable of functioning independently and simultaneously to act as HAT agents under the irradiation of 390 nm Kessil light. The reaction proceeded at room temperature and resulted in a remarkable yield of 73% of benzoic acid after 16 hours. Furthermore, we evaluated 13 different types of daily-life plastic waste, some of them containing different colors as additives (flower pot, stationery, foam, lining material of refrigerator, transparent CD case, yogurt box, foamy cushioning material, disposable cup, food package, sound and heat insulation material, toy gun, and fresh-keeping box in the refrigerator, and styrofoam cup), and all were selectively transformed into benzoic acid up to 68% yield. Scaling up the reaction to a gram-scale was also successful and produced benzoic acid >60% yield under optimal conditions, thus highlighting the practicality and scalability of this strategy for the industrial applications. Moreover, by employing a tandem approach, the obtained benzoic acid was further converted into high-valued aromatic building blocks and aromatic rings containing bioactive molecules to demonstrate the versatile nature of this strategy.

In this system, three distinct species served as HAT agents. N-bromosuccinimide (NBS) generated bromine radicals (Br·) and succinimide radicals, while trifluoromethanesulfonic acid sodium salt (CF$_3$SO$_2$Na) produced CF$_3$-2 radicals upon being oxidatively quenched by O$_2$ in its excited state. The concerted action of these species facilitated the efficient upcycling process. The C-centered radical, generated in the initial steps, was quenched by either O$_2$ or the superoxide radical anion, followed by protonation, resulting in the formation of a superoxide compound. With light illumination and subsequent β-scission, the key intermediate, phenylglyoxylic acid (PGA) was produced, which was successfully detected by

Scheme 6. NBS and CF₃SO₂Na catalyzed upcycling of PS.

an O-centered radical. Secondly, H_2SO_4 significantly reduced the kinetic energy barrier during the cleavage of the C–C bond to enhance the overall reaction rate. Thirdly, H_2SO_4 played a crucial role in assisting the reduction of O_2 to generate H_2O_2. Moreover, the successful capture of the key intermediate, phenylglyoxylic acid (PGA), through GC-MS analysis, provided solid experimental evidence to support the proposed reaction mechanism.

4. Conclusions

In conclusion, the utilization of photocatalysis for the upcycling of polystyrene-based plastic waste holds immense promise to address the growing environmental concerns which are associated with the plastic pollution. The rapid expansion of plastic waste, particularly polystyrenes, presents significant challenges in waste management and recycling. In this aspect, photocatalysis emerges as a powerful and sustainable tool by offering the potential to convert waste into valuable chemicals and building blocks and also to contribute to a more circular and resource-efficient economy.

The comparison between PPM and upcycling strategies reveals distinct advantages and challenges. While PPM provides a straightforward route to modify the polymer structure by diversifying its properties, the products obtained may have diminished quality compared to pristine monomers. In contrast, upcycling strategies enable the transformation of polystyrene-based waste into valuable chemicals or building blocks which potentially offers higher economic incentives. However, the activation of inert covalent bonds in polystyrenes poses tremendous challenge for efficient and selective upcycling. Thus, the upcycling of plastic-based waste is captivating. Certainly, the exploration and advancement of photocatalytic upcycling strategies for polystyrene-based plastic waste offer a mid-term hope for sustainable waste management of plastics. By understanding the strengths and limitations of

High Resolution Mass Spectrometry (HRMS). This intermediate was captured for the first time by our group and offered a comprehensive understanding of this degradation step. The formation of benzaldehyde occurred through two pathways. The first step involved decarboxylation, while the second step entailed PGA to undergo decarbonylation which led to the formation of an acyl radical, CO, and OH radicals. The acyl radical then abstracted a hydrogen atom to produce benzaldehyde which subsequently reacted with O_2 to form benzoic acid as the final product.
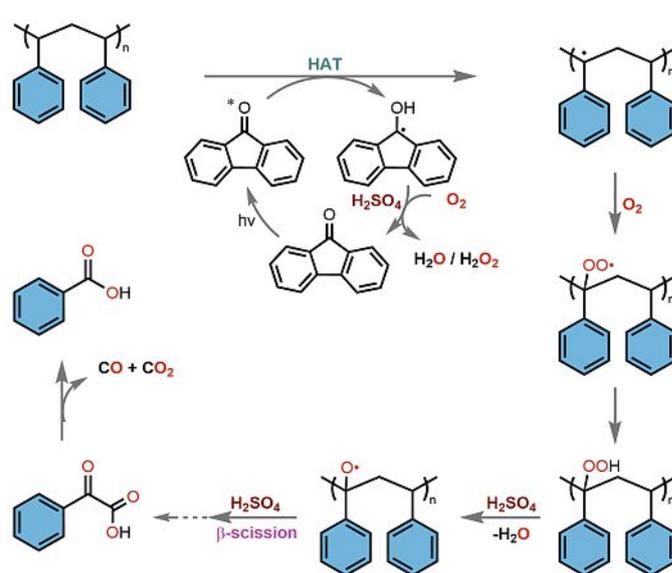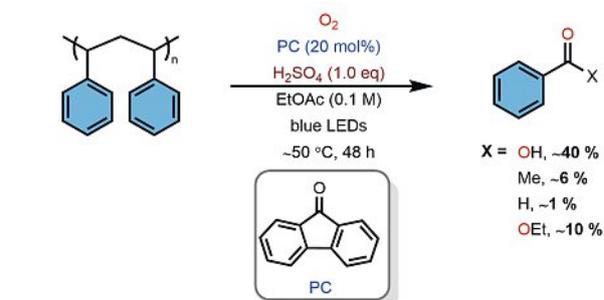
Around the same period, the Reisner group showcased a fluorenone-catalyzed deconstruction method for polystyrene into valuable chemicals (Scheme 7).[53] This process involved the utilization of equivalent quantity of H_2SO_4 as an additive. The reaction took place under the irradiation of blue LED light and resulted in the formation of aromatic products with an approximate yield of ~60% after 16 hours of reaction at 50 ºC. The author extensively explored the influence of each parameter through comprehensive reaction studies and density functional theory (DFT) calculations. Particularly intriguing was recognising the distinct roles of H_2SO_4 in this system. Firstly, H_2SO_4 acted as a proton source to facilitate the release of H_2O from the peroxide and to generate

Scheme 7. Fluorenone-catalyzed upcycling of PS.

each approach, we can develop novel photocatalytic approaches to overcome current limitations and promote the transition towards a more circular and environmentally conscious plastic economy. Ultimately, by leveraging the potential of photocatalysis, we can pave the way for a cleaner and greener future.

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