Photochemical Aerobic Upcycling of Polystyrene Plastics to Commodity Chemicals

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Abstract

Since United Nations has set goals dealing with climate change, the chemical industry has focused on recycling the already-used polymers, targeting the reinsertion of plastic waste to market via new products through reforming. Upcycling of polystyrene plastic waste is becoming one of the hottest field of research in plastic upconversion. Herein, we introduce a novel, green, organocatalytic and photochemical aerobic upcycling process of polystyrene to benzoic acid, utilizing anthraquinone as the photocatalyst, LED 390 nm as the irradiation source and air as the sole oxidant. The developed protocol was applied successfully to the upcycling of daily-life used polystyrene products, leading to yields varying from 25-58%. Moreover, the obtained upcycled product from the polystyrene materials was employed to the successful synthesis of bioactive molecules, such as acetylsalicylic acid.
Introduction

During the last century, the quality of every-day life of humanity has improved exponentially and Chemistry has played a vital role in this upgrading process via its key developments in the fields of pharmaceuticals, agrochemicals, plastics, every-day commodities, etc. A pivotal innovation in this process was the introduction of polymers and plastics in particular, in basic every-day activities. Nowadays, the global economy is based on polymers, since they present numerous uses, such as in health-care products, packaging, electronics, transportation, constructions, etc. Plastics, due to their low cost, light weight, diverse properties and easy manufacturing procedures, have the lion’s share in polymer’s global market and constitute most frequently the material of choice for the production of daily-life products. Unfortunately, the exponential burst in massive production of plastics, along with their usual single-use, short-time of use after purchase (for example, food packaging) and slow decomposition, have contributed significantly in the planet’s pollution and climate change. Since the 1950s, where the annual production of plastics was 1.5 million metric tonnes, a sharp and constant increase in the production of plastics is observed and in 2021, the production of plastics was 380 million tonnes, while being projected to rise to 900 million tonnes by 2050. This sharp increase in production has constituted the vast accumulation of plastic waste as a matter of great concern, which has already created environmental implications, economic problems and waste management crises. In order to address these issues, the recycling of plastic waste [close-loop, mechanical, chemical and energy recovery] became the key weapon in scientist’s armbox to tangle these problems. Unfortunately, only 16% of polymer waste is recycled, while around 40% of it is ending up in waste landfills, producing in 2015, 4.9 billion tonnes of plastic waste, which are projected to rise to 12 billion tonnes of plastic waste by 2030, creating myriad of problems in the environment and the planet. There different ways to perform the recycling of plastics, however, it has not provided the desired results, since in most cases, recycling of plastic waste leads to downgraded materials, which inevitably end up as plastic waste as well in waste landfills, not providing a solution to the problem. In an effort to overcome this issue, the substitution of plastic commodities by paper or other-type products was envisaged. However, again, the final recycled product is a downgraded material, while in some cases, the plastic substitute does not exhibit the same properties as the
original plastics. In another attempt to solve these problems, the last few years, the idea of plastic upcycling, the recycling of plastics to high-added value chemicals, has become very popular,\textsuperscript{6,14-16} ensuing that the basic principles of circular economy are followed.\textsuperscript{15}

Among different plastics, polystyrene (PS) is one of the most frequently-used polymers in every-day life products and along with polyethylene (PE) and polypropylene (PP) are accounting for more than 50% (around 60%) of the world plastic production.\textsuperscript{11} Polystyrene polymers are widely used in cutlery, food containers and drinking cups, having a short life cycle and their demand increases significantly year by year. Thus, there is an elevated need for more efficient and sustainable recycling methods, while humanity urgently requires to focus on routes of re-entering these types of waste, back to the chemical industry as sources of raw materials. In order to face these challenges, the chemical community has created opportunities for polystyrene recycling, via pyrolysis, which constitutes the most frequent approach used to date.\textsuperscript{17} In these processes, polystyrene can be transformed to arene derivatives via catalysed processes. Along these lines, in 2021, Wang, Yan and coworkers reported a catalytic protocol for the reductive upcycling of aromatic polymers, such polystyrene (PS), polyethylene terephthalate (PET) and polycarbonate (PC) over a Ru/Nb$_2$O$_5$ catalyst (Scheme 1, A).\textsuperscript{17d} The process was effective for the formation of reduced aromatic species, which were obtained as a mixture, with indane being the major product. Despite the efficiency of the method, the need of high temperature (200 °C) and the high hydrogen pressure is a concern for the adaptability of the process in the chemical industry. Alternatively, microwave chemistry was employed to promote the recycling of polystyrene and other plastic materials,\textsuperscript{18} while in an alternative approach for upcycling of polystyrenes, Leibfarth and coworkers reported the modification of plastics via a C-H fluoroalkylation process.\textsuperscript{19}

Photochemistry, the use of light to promote organic transformations, is not a new concept, since Ciamiclan proved that sunlight can promote organic reactions.\textsuperscript{20} Since then, a century passed, in order the field to receive massive attention and a literature explosion on photochemical promoted reactions occurred.\textsuperscript{21,22} In particular, the area of photochemistry dealing with radical species to perform Hydrogen Atom Transfer (HAT) processes, creates the opportunity to cleave strong C-H bonds.\textsuperscript{23} The use of light in polystyrene upcycling has been known since 1984, when Mita, Horie and
**Scheme 1.** Upcycling protocols for polystyrene plastics.
coworkers reported the use of a benzophenone-catalysed process using a high-pressure mercury lamp at 60 °C, studying mainly the mechanism of action of the process regarding benzophenone and reporting that products of lower molecular weight were obtained.\textsuperscript{24} In 2021, two different research groups, on their way to study the Fe-catalysed photochemical oxidation of alkyl aromatics, they reported that the catalytic system FeCl\textsubscript{3}-TBACl (tetrabutyl ammonium chloride)\textsuperscript{25} or FeCl\textsubscript{2}\textsuperscript{26} can promote the degradation of polystyrene into benzoic acid. In both cases, an oxygen atmosphere was necessary to promote the photochemical degradation, while an irradiation reaction time of 3-5 days was necessary. Benzoic acid is an important commodity chemical.\textsuperscript{27} In 2021, the global market of benzoic acid surpassed 1 billion USD, while there is a projection that will reach 2 billion USD by 2028. It is a valuable feedstock, that can be used as a food additive in almost all kind of food products.\textsuperscript{27} Benzoic acid is the starting raw material for the synthesis of various bioactive compounds, since the benzene ring is abundant in nature. In 2022, Stache and coworkers build on earlier contributions and utilized FeCl\textsubscript{3} as the photocatalyst for the upcycling of polystyrenes (Scheme 1, B).\textsuperscript{28} This elegant contribution ensured the formation of chlorine radicals, which are known to be capable of performing HAT of strong C-H bonds (ca. 103 kcal/mol),\textsuperscript{23} and via this indirect HAT process, the authors were able to upcycle polystyrene into benzoic acid.\textsuperscript{28} The process enabled the use of 10w/t\% FeCl\textsubscript{3} as the photocatalyst under white LED irradiation for 20 h, using an oxygen atmosphere (Scheme 1, B). A mixture of products was obtained (23 mol\% overall yield), with benzoic acid being the major product. Unfortunately, when everyday polystyrene plastics were used, the overall yield varied from 2.2-22.9 mol\%, while the benzoic acid yield varied from 1.6-16 mol\%.\textsuperscript{28} The same time, McInnes, Qi, Xiao and coworkers presented the use of p-toluenesulfonic acid as the photochemical promoter to perform the oxidative upcycling of polystyrene, under 405 nm light irradiation and an oxygen atmosphere (Scheme 1, C).\textsuperscript{29} The authors supported that a [PS···H\textsuperscript{+}] adduct is the species that gets excited and further decomposes to furnish the final arene derivatives. Similar yields (36-51\%) of benzoic acid were observed, when everyday polystyrene plastics were employed, while a large-scale synthesis (18 gr) was demonstrated.\textsuperscript{29}

Also in 2022, Das and coworkers reported another photocatalytic system that employs an indirect-HAT protocol to afford the products of the aerobic upcycling of PS
(Scheme 1, D).\textsuperscript{30} The authors proposed that the use of $N$-bromosuccinimide (NBS) (15 mol%), along with sodium triflinate (CF$_3$SO$_2$Na) (50 mol%). The catalytic system, upon irradiation at 390 nm, can form various radicals, that are able to perform a HAT with PS, upon an oxygen atmosphere. The need though for the presence of both radical precursors is crucial for the fate of the reaction.

Our group has a long experience in photochemical processes and during the last years, we have demonstrated the power of small organic molecules as promoters of photochemical processes.\textsuperscript{31} Following our interest in merging photochemistry with aerobic processes\textsuperscript{31e,32} we questioned whether a commercially available small organic molecule can be employed as a potential promoter for the photochemical aerobic upcycling of polystyrenes (Scheme 1, E). Herein, we present a mild protocol, that is free of metal additives or toxic intermediates such as bromine, for the photochemical aerobic upconversion of polystyrene to benzoic acid in good yield. Utilizing 10 mol% of anthraquinone as the catalyst, LED 390 nm as the irradiation source and air as the oxidant, a variety of every-day plastic products were converted into benzoic acid. Furthermore, we studied the potential of post-upcycling modification of benzoic acid to every-day commodities, like salicylic acid and acetylsalicylic acid.

**Results and Discussion**

We initiated our studies using a commercially available polystyrene [98% styrene, 2% divinylbenzene, (CAS Number: 9052-95-3) 200-400 mesh] as the polystyrene model substrate and screened a variety of photocatalysts-photoinitiators in a search for the ideal molecule that can promote the photochemical aerobic cleavage of the benzylic moieties of the polystyrene chain (Scheme 2). We employed acetonitrile as the solvent and air as the oxidant, using a LED 390 nm irradiation source. At the beginning, we employed aromatic ketones that are known to perform HAT reactions, like thioxanthone (2a)\textsuperscript{33} or benzophenone (2g), which was presented in literature to work (under mercury lamp irradiation though)\textsuperscript{24} or acenaphthoquinone (2h), but in all cases, the yield of benzoic acid was 1.89-5.98% (Scheme 2). Aryl ketones that perform as photoinitiators, such as phenylglyoxylic acid (2e)\textsuperscript{34} or 2,2-dimethoxy-2-phenylacetophenone (2f) led to a slight increase in yield (Scheme 2). Organic dyes that are known as singlet oxygen generators or can perform HAT processes\textsuperscript{35} were
also tested, however similar yields were obtained (Scheme 2, 2i or 2j). The family of anthraquinones was tested as well, and anthraquinone (2b) proved to be the optimum photocatalyst, leading to 18.78% yield of isolated benzoic acid (1) (Scheme 2). Other derivatives of anthraquinone did not perform as well as 2b. Other typical photocatalysts, like 2k and 2l were tested for comparison purposes. In all cases, the desired benzoic acid was isolated after acid-base wash and extractions, without the need for further purification.

After identifying the optimum photocatalyst, we studied the importance of the
Table 1. Study of the irradiation source for the photochemical aerobic upcycling of polystyrene.[a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Irradiation Source</th>
<th>Yield (%)[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CFL lamps</td>
<td>0.38</td>
</tr>
<tr>
<td>2</td>
<td>370 nm</td>
<td>6.17</td>
</tr>
<tr>
<td>3</td>
<td>390 nm</td>
<td>18.78</td>
</tr>
<tr>
<td>4</td>
<td>427 nm</td>
<td>2.83</td>
</tr>
<tr>
<td>5</td>
<td>440 nm</td>
<td>1.40</td>
</tr>
<tr>
<td>6</td>
<td>456 nm</td>
<td>0.64</td>
</tr>
<tr>
<td>7</td>
<td>467 nm</td>
<td>0.39</td>
</tr>
</tbody>
</table>

[a] Reaction Conditions: In an open schlenk flask, PS (100 mg, 0.96 mmol), 2b (20 mg, 0.096 mmol) and MeCN (1 mL) were added and irradiated for 20 h. [b] Yield of isolated benzoic acid.

irradiation source (Table 1). First, household lamps were used, but proved ineffective (Table 1, entry 1). Similarly, no other LED irradiation led to similar high yield of benzoic acid as the 390 nm (Table 1, entry 3 vs entries 2 and 4-7). Following the discovery of the optimum irradiation source, we probed the optimum solvent for the photochemical aerobic upcycling of polystyrene (Table 2). We observed that when we doubled the amount of the solvent, the yield of benzoic acid increased (Table 2, entry 2 vs entry 1). Among the tested solvents, acetonitrile (Table 2, entry 2) and benzene (Table 2, entry 7) led to the best results. We decided to use acetonitrile instead of benzene in our studies, since acetonitrile is less toxic solvent compared to benzene. The optimum reaction conditions were found after a series of experiments and employ
**Table 2.** Screening of solvents for the photochemical aerobic upcycling of polystyrene.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1[c]</td>
<td>MeCN</td>
<td>18.78</td>
</tr>
<tr>
<td>2</td>
<td>MeCN</td>
<td>21.34</td>
</tr>
<tr>
<td>3</td>
<td>CH₂Cl₂</td>
<td>5.97</td>
</tr>
<tr>
<td>4</td>
<td>CHCl₃</td>
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</tr>
<tr>
<td>5</td>
<td>AcOEt</td>
<td>Traces</td>
</tr>
<tr>
<td>6</td>
<td>Acetone</td>
<td>4.41</td>
</tr>
<tr>
<td>7</td>
<td>Benzene</td>
<td>21.34</td>
</tr>
<tr>
<td>8</td>
<td>DMF</td>
<td>n.d.</td>
</tr>
<tr>
<td>9</td>
<td>DMSO</td>
<td>n.d.</td>
</tr>
<tr>
<td>10[d]</td>
<td>MeCN</td>
<td><strong>28.18</strong></td>
</tr>
</tbody>
</table>

[a] Reaction Conditions: In an open schlenk flask, PS (100 mg, 0.96 mmol), 2b (20 mg, 0.096 mmol) and solvent (2 mL) were added and irradiated under 390 nm LED for 20 h. [b] Yield of isolated benzoic acid. [c] Reaction performed with 1 mL of MeCN. [d] The reaction was performed with 2b (10 mg, 0.048 mmol, 10 mol%) for 48 h.

10 mol% of 2b, LED 390 nm irradiation for 48 h under open air, leading to 28.18% yield of benzoic acid (1) (Table 2, entry 10).³⁶
After finding the optimum reaction conditions for the photochemical aerobic upcycling of polystyrenes, we decided to probe its substrate scope. We initially tested the use of other commercially available resins that are based on polystyrene (Scheme 3). Aminomethylpolystyrene resin, as well as the commonly employed Wang resin were used successfully, leading to a similar yield of benzoic acid as our model substrate. However, the use of commercially available chlorotrietyl chloride resin did not perform equally well and led to a diminished yield of 13%.

Since the use of commercially available resin based on polystyrene was amenable in our photochemical aerobic upcycling process, we then decided to employ every-day products that are polystyrene-based (Scheme 4). Interestingly, the commercially available plastic commodities proved to work better than our model substrate and could be perfectly incorporated to our protocol, furnishing the desired oxidation product, benzoic acid, after an aerobic cleavage promoted by light (Scheme 4). The yields refer to isolated benzoic acid after the reaction took place, using acid-base wash and extractions, without taking into consideration the formation of other volatile oxidation products. Polystyrene-based plastic knife worked well, leading to 31.5%

**Scheme 3.** Photochemical aerobic upcycling of commercially available resins, used in organic synthesis and are based on polystyrene.
Scheme 4. Photochemical aerobic upcycling of commercially available PS products and daily life PS wastes.

yield of benzoic acid, while the corresponding plastic spoon led to an excellent 51.4% yield. In the market, a variety of different polystyrene-based plastic cups exist. We started by employing a small transparent plastic cup and a high yield of 50.6% was obtained. Similarly, using a big transparent plastic cup led to a further increase in the
Large Scale Experiment

**Scheme 6.** Large-scale photochemical aerobic upcycling of polystyrene.

yield and benzoic acid was isolated in 58.8%. However, the use of colored plastic cups (yellow or red) led to similar or higher yields than our model substrate (38.8% and 26.8%, respectively), but lower than the transparent plastic cups. The use of polystyrene-based plastic coffee cup led to 29.6% yield, while the use of a microwavable food container afforded benzoic acid in 31.1% yield. Two different kinds of polystyrene foams that are employed in packaging industries led to 43.5% and 49.5% yields, respectively. The use of a polystyrene CD case led to a decreased yield of 24.9%. Finally, the use of polystyrene beads or commercially available polystyrene polymer (MW 10,000) led to 41.8% and 49.2% yield, respectively.

In order to probe the industrial application of the process, a large scale experiment was performed (Scheme 5). We utilised a 2-gr scale and the reaction time had to be prolonged to 96 h, along with the use of 2 × 35W LED 390 nm irradiation source. A similar yield was obtained as in the smaller scale for benzoic acid. Interestingly, herein, we were also able to monitor the reaction by $^1$H-NMR and probe the presence of formic acid (3) and benzaldehyde (4). In the former case, a significant amount of 3 was observed, in line with literature observations.29 Furthermore, from the initial organic layer after quenching the reaction, we were able to isolate via column chromatography a small amount of acetophenone (5).

In an effort to further expand the applicability of this protocol, we envisaged the application of the delivered upcycled product into pharmaceuticals, like salicylic acid 6 and acetylsalicylic acid 7 (Scheme 7). Salicylic acid 6 constitutes a plant hormone37 and it has a long story as a bioactive compound, that dates back ancient Greece.38 Even though it demonstrates a potent activity against cardiovascular diseases, its
Scheme 7. Photochemical aerobic upcycling of polystyrene to salicylic acid and aspirin.

modern application is not recommended due to side-effects,\textsuperscript{38} although, it is employed against acne.\textsuperscript{39} The side effects of 6 were surpassed by a simple acetylation, forming the corresponding acetylsalicylic acid, a compound which later became extremely popular under the name aspirin. Since then, it is being used to treat, apart from cardiovascular issues, pain, fever, inflation and others and constitutes one of the most consumable drugs around the globe as its consumption rises to 40 hundred tons per year.\textsuperscript{40} Using a modified literature procedure for the C-H hydroxylation of benzoic acids,\textsuperscript{41} we were able to convert benzoic acid to salicylic acid in a single step and in 60\% yield (Scheme 7). Then, a simple acetylation with acetic anhydride led to aspirin (Scheme 7).

We then turned our attention in elucidating the reaction mechanism of the photochemical aerobic upcycling of polystyrene plastics. As in earlier studies,\textsuperscript{28-30} when the reaction was performed either under argon, or under dark or without catalyst, the reaction did not proceed.\textsuperscript{36} Furthermore, the radical nature of the process was probed with the presence of BHT or TEMPO. Anthraquinone (2b) is a well known photocatalyst, used in literature for the production of hydrogen peroxide, a process known as the anthraquinone process.\textsuperscript{42} We performed a control experiment where polystyrene was treated with hydrogen peroxide, but no photodegradation occurred, stating that hydrogen peroxide generated in the process is not responsible for the upcycling process.\textsuperscript{36} Also, anthraquinone is known to participate in HAT processes,\textsuperscript{23} while it can also generate singlet oxygen.\textsuperscript{32} Fluorescent quenching studies were then performed (Figure 1). After irradiation of anthraquinone (2b) (1 mM in MeCN) at 358 nm, its fluorescence was measured at 404 nm. Increasing the added amount of polystyrene, a decrease in the fluorescence was observed. The
Figure 1 Fluorescence quenching studies of anthraquinone (2b) by polystyrene and the corresponding Stern-Volmer plot.

The corresponding Stern-Volmer plot is also presented in Figure 1. Thus, there is a clear interaction between excited anthraquinone and polystyrene, which proves the direct HAT from the excited catalyst to the polystyrene. This is in agreement with the mechanism that are proposed in literature. In addition, when the reaction was performed in the presence of singlet oxygen quenchers, such as sodium azide or DABCO, the reaction was completely inhibited, stating that a secondary pathway involving singlet oxygen might be in operation. This is also in accordance with
literature, however, this is probably a secondary and minor pathway, since Rose Bengal (2i), which is a known singlet oxygen generator led to a very low yield (see Scheme 2). Finally, UV-Vis absorbance studies, following the reaction demonstrated an augmentation of the absorbance in the region of 200-250 nm, indicating the formation of aromatic compound bearing the characteristic absorption band.

Bringing all these data together, a plausible reaction mechanism is proposed in Scheme 8. After irradiation, triplet state excited anthraquinone I is capable of performing a hydrogen atom abstraction, forming anthraquinone ketyl radical II and an alkyl benzyl radical III (Scheme 8, A). The latter reacts with ground state oxygen, forming peroxy radical intermediate IV. Upon further irradiation, the unstable intermediate degradates to intermediate V and then through a β-scission into two polymeric chains VI and VII. This is in accordance with literature. Polymer chain VI reacts with a second excited molecule of anthraquinone, entering in a new cycle of oxidation, leading finally to benzoic acid (1). Intermediate VI can also be envisaged to be leading to acetophenone in a small degree, via a direct HAT, followed by a β-scission. Polymer chain VII reacts with oxygen, forming the more stable benzylic radical VIII and formic acid. Radical VIII upon oxygen incorporation and rearrangement furnishes benzaldehyde, which can be further oxidized to benzoic acid.

Scheme 8. Proposed reaction mechanism.
Since our control experiments showed that singlet oxygen could also play a role in the process, a secondary pathway is also proposed (Scheme 8, B). The triplet state anthraquinone is capable of generating singlet oxygen, leading to the mechanism proposed in Scheme 8, B. Singlet state oxygen is capable to perform a direct insertion in the activated benzylic C-H bond of PS, leading to IX. Also, the decomposition of the high energy peroxy intermediates can lead to reactive oxygen species (ROS), including hydroxyl radical and superoxide anion, which are highly oxidative and potent hydrogen atom abstractors. Then a similar β-scission can occur leading to VI and VII, following then the same pathway as in Scheme 8, A.

**Conclusion**

A green, mild, metal-free photochemical aerobic upcycling process of polystyrene was developed using anthraquinone (10 mol%) as the photocatalyst and LED 390 nm as the irradiation source. In contrast to recent developed methodologies, this protocol does not require the use of an oxygen atmosphere and the process is occurring under air. An easy-to-work procedure leads to the isolation of benzoic acid from the polystyrene degradation process in good yields, after simple base-acid wash and extractions. The protocol can be performed in a large-scale, while the use of everyday polystyrene-based commodities led to higher yields than the model substrate, which could be up to 58%. Moreover to the upcycling of polystyrene to benzoic acid, which is a key food additive, the process was applied in the simple and straightforward synthesis of two pharmaceuticals, salicylic acid and acetylsalicylic acid. We believe this process can have a huge impact in recycling processes and upconversion of plastic waste, which could help in the fight of mankind against pollution and climate change.

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Conflict of Interest

The authors declare no conflict of interest

References


36. For detailed optimization studies, mechanistic studies and synthetic procedures, see supporting information.


