

Selective degradation of styrene-contained plastics catalyzed by iron under visible light

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Efficient degradation of plastics, the vital challenge for a sustainable future, stands in need of better chemical recycling procedures that help produce commercially valuable small molecules and redefine plastic waste as a rich source of chemical feedstock. However, the corresponding chemical recycling methods, while being generally restricted to polar polymers, need improvement. Particularly, degradation of chemical inert nonpolar polymers, the major constituents of plastics, are reported to have suffered from low selectivity and very harsh transformation conditions. Herein, we report an efficient method for the selective degradation of styrene-contained plastics under gentle conditions through oxidative multiple sp^3 C-C bond cleavage. The unpresented procedure is catalyzed with inexpensive iron salts under visible light, using oxygen as the green oxidant. Furthermore, simple iron salts can be used to degrade plastics in the absence of solvent under natural conditions, highlighting the potential application of iron salts as additives for degradable plastics.

Plastics, being indispensable for everyday life, have greatly benefited the modern world with their safety, convenience, and wide applicability. While being essential for advanced technology development, plastics, because of their economy in pricing, are facing the challenges brought by casual disposal and the consequent plastic pollution to the environment¹⁻⁵. By 2015, around 6,300 million tons of plastic waste has been generated and expanded around the world, and the amount is quickly increasing every

year⁵. In contrast to this, the current procedure of plastic production is still largely unsustainable, due to its reciprocal relation with the oil industry which is also consumptive and contaminative^{2,6}. Moreover, the inert nature of polymers, resulting in a long degradation period of several hundred years under natural conditions, is the fundamental reason for plastic pollution. Based on that, despite the developments of new sustainable plastics^{1,7-9}, the relevant pollution remains a big challenge, so long as the existing plastic system stays regular in the foreseeable future². To solve the problem, many methods have been tried on plastic recycling and degradation, for example, reuse of plastic that suffers from deterioration of material properties¹⁰; chemical recycling which transforms polymers into valuable small molecules^{11,12}. Among these efforts, chemical recycling is viewed as an evolving solution to the plastic pollution challenge. However, because harsh conditions are usually required for chemical recycling of plastics, and low selectivity and poor product yields are generally observed¹³⁻¹⁵, especially for the chemical inert polymers such as polyethylene (PE), polypropylene (PP), and polystyrene (PS), those methods are not considered efficient enough (less than 10% plastic has been recycled in 2018)⁵. So, it is an urgent task to develop efficient methods for chemical recycling of plastics under gentle and energy saving conditions, which redefine plastic waste as a source of chemical feedstock, and as themselves benefits to a greener future (Fig. 1a)¹⁻³.

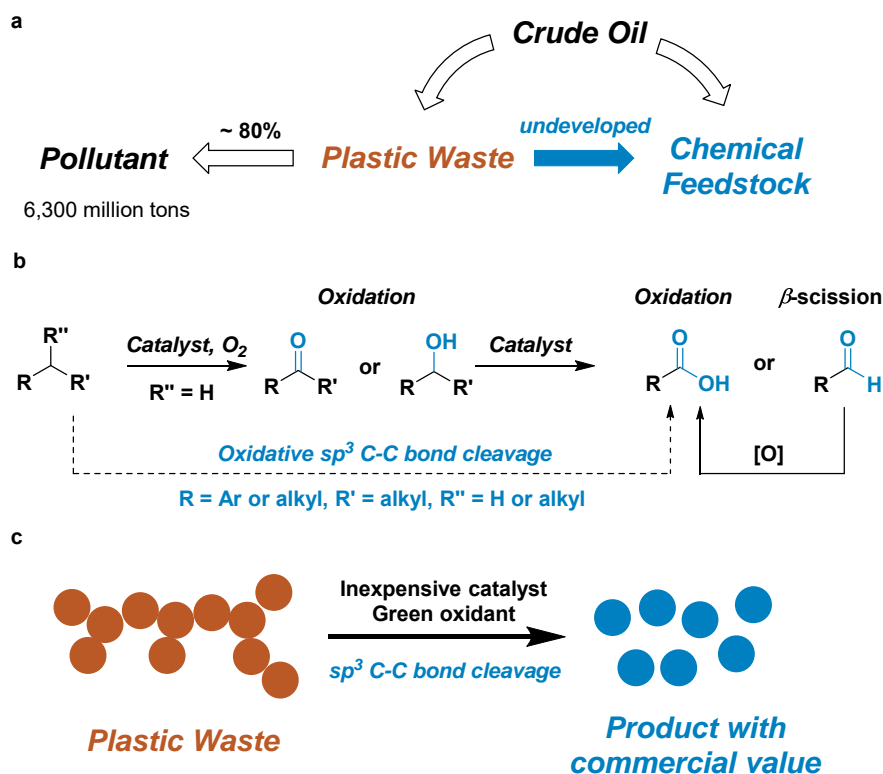


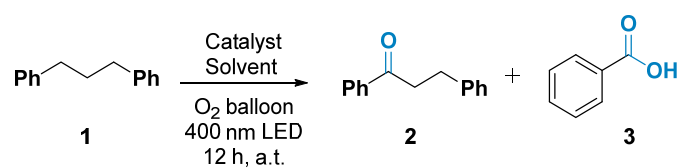
Fig. 1 | Selective degradation of plastic waste. **a**, Undeveloped transformation of plastic waste to chemicals. **b**, Design of oxidative sp^3 C-C bond cleavage. **c**, Design of selective degradation of plastic waste through oxidative sp^3 C-C bond cleavage.

Efficient chemical recycling of plastic usually means efficient cleavage/transformation of C-C bonds, especially for the nonpolar polyolefins, which account for approximately two-thirds of the whole plastic system^{1,16}. Because of the large dissociation energy of the C-C single bond (around 356 kJ/mol), selective C-C cleavage is always a tough challenge for chemists¹⁷⁻²³ and hinders polymer recycle procedures^{2,3,9,13}. For a sustainable chemical recycling system of plastic, economical and energy saving methods to dissociate C-C bond with high efficiency are highly desired. Earth abundant metals were found to transform alkanes to alcohols and ketones under oxygen atmosphere²⁴⁻³³. In addition, C-C bond scission of alcohols and ketones through alkoxy radical intermediates applying inexpensive catalysts were reported recently³⁴⁻⁴³. Though with limitations, these results illustrate us the possibility of developing an economic system for oxidative C-C bond cleavage in an environmentally friendly way (Fig. 1b). Especially, iron may be a good catalyst candidate, which can

perform both C-H bond oxidation^{25,26,28} and oxidative C-C bond cleavage⁴³ through photocatalysis⁴⁴⁻⁴⁹. The two kinds of transformations may proceed in a one-pot procedure to realize the degradation of plastics through multiple C-H bond oxidation and C-C bond cleavage (Fig. 1c). Herein, we report an unrepresented procedure for plastic depolymerization through oxidative cleavage of sp³ C-C bond, using iron as the catalyst under visible light in air/oxygen atmosphere. A simplified approach can be applied in the absence of solvent and additives under natural conditions, showing a significant accelerated speed of depolymerization. As far as we know, the method presented the gentlest conditions for the nonpolar polymer degradation ever reported.

Results

Initial investigation. The research begins with the study of the model substrate 1,3-diphenylpropane (Table 1). A variety of conditions were tested, and iron salts were found to be effective catalysts. The reaction was firstly performed in MeCN under the irradiation of LED light (400 nm, see Supplementary Fig. 1-3) in the atmosphere of 1 atm of oxygen. Iron salts with different anions were investigated, many of which showed catalytic activities, presenting ketone and the targeted C-C bond cleavage product benzoic acid as the products (entries 1-6). Benzoic acid and its additives are important chemical feedstock and widely used as food additives and precursors for industry and pharmacy. The global demand for benzoic acid is 480 kilotons in 2014 and will expand to 640 kilotons by 2024⁵⁰. When FeCl₂ was applied, full conversion and 90% NMR yield (86% isolated yield) of benzoic acid was observed in 12 h (entry 6). Good conversions were observed when applying other solvents, and a 71% yield of benzoic acid was achieved when ethyl acetate or acetone was used (entries 7-9). Increasing the reaction time to 16 h led to an isolated yield of 88% (entry 10). Decreasing the catalyst loading to 2 mol% resulted in full conversion of the substrate but a lower benzoic acid yield of 73% (entry 11); while longer reaction time presented a good isolated yield of 87% (entry 12). The combination of Fe(OTf)₃ and TBACl in a 1: 2 mol ratio resulted in a similar result as applying FeCl₂ (entry 13). Without catalyst (entry 14) or LED light (entry 15) led to no conversion of the substrate.

Table 1 | Optimized study of oxidative C-C bond cleavage

Entry	Catalyst	Time (h)	Conversion (%) ^a	Yield (2, %) ^a	Yield (3, %) ^a
1	Fe(NO ₃) ₃ • 9H ₂ O	12	73	22	32
2	Fe ₂ (SO ₄) ₃	12	0	-	-
3	Fe(OTf) ₃	12	88	22	49
4	FeBr ₃	12	24	22	2
5	FeCl ₃	12	100	2	67
6	FeCl ₂	12	100	4	90 (86) ^b
7 ^c	FeCl ₂	12	90	10	32
8 ^d	FeCl ₂	12	100	24	71
9 ^e	FeCl ₂	12	100	22	71
10	FeCl ₂	16	100	-	(88) ^b
11 ^{f,g}	FeCl ₂	12	100	12	73
12 ^f	FeCl ₂	24	100	-	(87) ^b
13 ^h	Fe(OTf) ₃	12	100	-	86
14	-	12	0	-	-
15 ⁱ	FeCl ₂	12	0	-	-

Reaction conditions: 1,3-diphenylpropane (0.1 mmol), catalyst (10 mol%) and MeCN (2 mL) were stirred under O₂ (1 atm) at ambient temperature for 12 h, irradiated by LED (400 nm, 20 W). ^aDetermined by ¹H NMR using dibromomethane as an internal standard. ^bIsolated yield. ^cDCM was used as the solvent. ^dEthyl acetate was used as the solvent. ^eAcetone was used as the solvent. ^f2 mol% FeCl₂ was used. ^g4% yield of 1,3-diphenylpropan-2-one was observed. ^h20 mol% TBACl (tetrabutylammonium chloride) was used. ⁱWithout LED.

Degradation of plastic. With the optimized conditions of the model substrate in hand,

we started to study the degradation of PS. It's noteworthy that PS is usually discarded directly after use, and the relevant chemical recycling methods are overly underdeveloped². Unfortunately, the transformation was failed at first when applying MeCN as the solvent, which cannot dissolve polystyrene. Plenty of solvents were tested, and dichloromethane (DCM) and acetone showed good solubility for PS. Surprisingly, the degradation of dissolved PS easily happened under the gentle optimized conditions for the model substrate. The mixed solvent with a volume ratio of 3: 2 (DCM: MeCN) led to good performance. When applying 2 mol% FeCl₂ as the catalyst, depolymerization was quickly preceded with the formation of carbonyl bonds (entries 1-5, Fig. 2a), and the polymer molecular weight (Mw) was dropped from 145 kg/mol to 5 kg/mol in just 1 h (entry 1). Full conversion of oligomer (Mw > 1 kg/mol) was achieved in 6 h (entry 6, Fig. 2b). A longer time was required for better reaction selectivity, and 63% isolated yield of benzoic acid was produced after 66 h (entries 7-9). Side products in small amounts, such as benzaldehyde and acetophenone, were observed by GC-MS. No oligomer or large molecule was observed. When acetone was applied as the solvent, a yield of 61% was presented (entry 10). Using FeCl₃ as a catalyst led to a similar yield of 62% (entry 11). Different combinations of iron salts and TBACl were also investigated, yields between 49% to 58% were observed (entries 12-15), and Fe₂(SO₄)₃ resulted in the best NMR yield of 66% (entry 16). Interestingly, when the reactions were performed under air in different solvents, good results were also achieved with higher FeCl₂ loading of 10 mol% (entries 17, 18). Decreasing the catalyst loading to 0.1 mol% didn't reduce the conversion, resulting in a 26% isolated yield of benzoic acid as the product. This result highlights the efficiency of the catalysis system for PS degradation.

Table 2 | Degradation study of polystyrene through oxidative C-C bond cleavage

Entry	Catalyst	Time (h)	Conversion (%) ^a	Yield (%) ^b
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1	FeCl ₂	1	14	0
2	FeCl ₂	2	24	0
3	FeCl ₂	3	41	0
4	FeCl ₂	4	60	0
5	FeCl ₂	5	95	0
6	FeCl ₂	6	100	4
7	FeCl ₂	12	100	29
8	FeCl ₂	48	100	55
9	FeCl ₂	66	100	65 (63) ^c
10 ^d	FeCl ₂	66	100	61 (59) ^c
11	FeCl ₃	66	100	62
12 ^e	Fe(OAc) ₂ OH	66	100	49
13 ^e	Fe(acac) ₃	66	100	56
14 ^e	Fe(OTf) ₃	66	100	57
15 ^e	Fe(NO ₃) ₃ · 9H ₂ O	66	100	58
16 ^e	Fe ₂ (SO ₄) ₃	66	100	66
17 ^f	FeCl ₂	66	100	62
18 ^f	FeCl ₂	66	100	63 ^d
19 ^g	FeCl ₂	66	100	(26) ^c

Reaction conditions: polystyrene (Mw is around 145 kg/mol, 0.5 mmol based on C₈H₈), catalyst (2 mol%), DCM/MeCN (v: v = 3: 2, 2 mL) were stirred under O₂ (1 atm) at ambient temperature (a.t.) for 12 h, irradiated by LED (400 nm, 20 W). ^aBased on the isolated yield of oligomers. ^bYield of benzoic acid determined by ¹H NMR using dibromomethane as an internal standard. ^cIsolated yield. ^dAcetone was used as solvent. ^e4 mol% TBACl (tetrabutylammonium chloride) was used. ^fAir was used instead of oxygen, 10 mol% FeCl₂ was applied. ^g1,2-dichloroethane was used as solvent, 0.1 mol% FeCl₂ was applied.

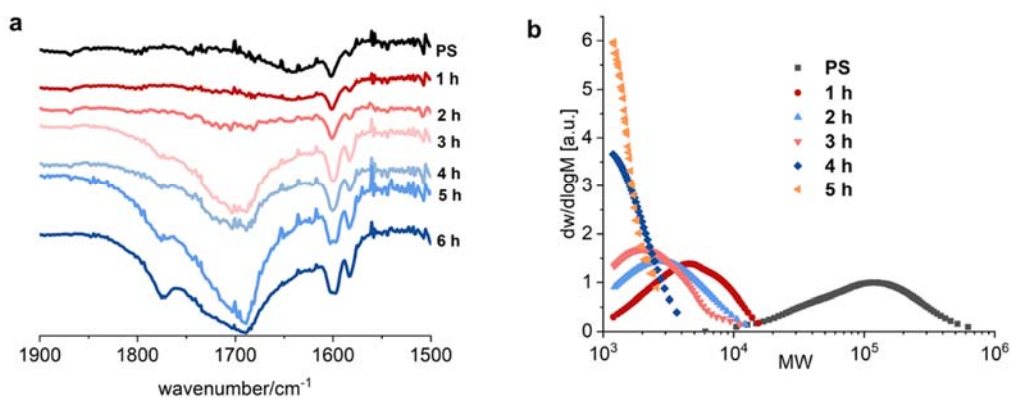
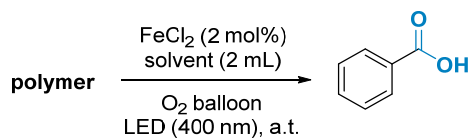


Fig. 2 | Spectra of degradation of PS in mixed DCM/MeCN (3: 2). a, FT-IR spectra of PS degradation reaction in 1-6 h. b, GPC traces of PS degradation reaction in 1-5 h.

Later, the simple system was applied to degrade different kinds of plastics (Table 3). FeCl_2 was applied as the catalyst, and two solvent systems (DCM/MeCN, acetone) were investigated. Generally, full conversions were observed. PS particles with different molecular weight were smoothly depolymerized, producing benzoic acid selectively in moderate isolated yields in the mixed solvent DCM/MeCN. PS with lower molecular weight resulted in better isolated yield of benzoic acid when acetone was applied as the solvent (entry 1 vs. 2). Syndiotactic PS and atactic PS were also successfully transformed to benzoic acid in DCM/MeCN, with 68% and 67% isolated yield, respectively (entries 3 and 4). Different copolymers of styrene were also tested under lower catalyst loading of 1 mol% or 0.8 mol% (entries 5-8), styrene-allyl alcohol copolymer presented a similar reactivity and selectivity as PS (entry 5). Poly(styrene-co-acrylonitrile) (entry 6), ABS (acrylonitrile butadiene styrene polymer) (entry 7) and styrene-maleic anhydride copolymer (entry 8) presented lower yields of benzoic acid with full conversion. Delightfully, commercial plastic waste produced from PS (see Supplementary Fig. 4), such as PS foam board (entry 9) and PS cup (entry 10), can also be depolymerized in full conversion, yielding a similar amount of benzoic acid as compared to pure PS. The results are attractive since commercial plastics usually containing additives such as antioxidants to extend the plastic life, which don't decrease the catalytic activity.

Table 3 | Depolymerization of different polymers through oxidative C-C bond cleavage



Entry	Substrate (Mw, kg/mol)	Conversion	Yield	Yield
		(%) ^a	(%) ^{b,c}	(%) ^{b,d}
1	PS particle (35)	100	56	62
2	PS particle (350)	100	56	51 ^e
3	syndiotactic PS (222)	100	68	61
4	atactic PS (202)	100	67	66
5 ^{f,g}	Styrene-allyl alcohol copolymer (4)	100	56	57
6 ^h	Poly(styrene-co-acrylonitrile) (106)	100	33	23
7 ^{g,i}	ABS (124)	100	31	3 ^j
8 ^{g,k}	Styrene maleic anhydride copolymer (74)	100	44	43
9	Waste PS foam board (222)	100	61	67
10	Waste PS cup (166)	100	63	65

Reaction conditions: polymer (0.5 mmol based on monomer), FeCl₂ (2 mol%), and solvent (2 mL) were stirred under O₂ (1 atm) at ambient temperature (a.t.) for 12 h, irradiated by LED (400 nm, 20 W). ^aBased on isolated yield of oligomer. ^bIsolated yield. ^cDCM/MeCN (3: 2) was used as the solvent. ^dAcetone was used as the solvent. ^eThe conversion was 62%. ^f0.96 mmol styrene-allyl alcohol copolymer (based on (C₈H₈)_{0.57}(C₃H₆O)_{0.43}) was used. ^g1 mol% FeCl₂ was applied. ^h1.26 mmol Poly(styrene-co-acrylonitrile) (based on (C₈H₈)_{0.6}(C₃H₃N)_{0.4}) was used. 0.8 mol% FeCl₂ was applied. ⁱ1 mmol acrylonitrile butadiene styrene polymer (ABS, based on (C₈H₈)_{0.5}(C₄H₆)_{0.25}(C₃H₃N)_{0.25}) was used. ^jThe conversion was 18%. ^k1 mmol of styrene maleic anhydride copolymer (based on (C₈H₈)_{0.43}(C₄H₂O₃)_{0.57}) was used.

Degradation of plastic in the absence of solvent in air. Furthermore, a more simplified procedure was tried to check the degradation ability of PS in the absence of solvent in the air (Table 4). PS was dissolved and mixed with FeCl₂, the solvent was then evaporated and the resulting film was irradiated with 400 nm LED or sunlight in the air (Supplementary Fig. 5). Interestingly, the samples with FeCl₂ showed significantly faster degradation speed (Mw₁, entries 1-3) than the samples without (Mw₂, entries 1-3) under LED (Fig. 3a-d). The depolymerization also happened observably under natural conditions for the iron-containing samples (Mw₃, entries 1-4), while no degradation was observed for iron-free samples (Mw₄, entries 1-4) (Fig. 3e-f). In addition, for samples with iron, signals of carbonyl groups, which can further improve the degradation of the polymer, were detected by IR (Fig. 3c,g). Iron is one of the most abundant and environmentally friendly metals in the earth. These observations highlight the potential application of iron salts as additives for disposable plastics and plastics used for a short period, which don't change the properties when use and can be degraded fast by simple treatment or just discarded in the natural environment.

Table 4 | Degradation of polystyrene in solid state

Entry	Time (day)	Mw ₁ ^b	Mw ₂ ^c	Mw ₃ ^{d,e}	Mw ₄ ^{e,f}
1	1	55	112	129	144
2	3	50	95	105	147
3	6	43	89	101	148
4	12	- ^g	- ^g	97	144

^aReaction conditions: polystyrene, FeCl₂ (2 mol%), DCM: MeCN (3: 2) were mixed and well dissolved. Then the solution was separated and transferred to different vials. After the solvent was removed, the vials were irradiated by 400 nm LED (50 W) or natural sunlight under air. The unit of Mw is kg/mol. GPC was applied to measure Mw. ^bLED was used. ^cLED was used without FeCl₂. ^dUnder natural sunlight. ^eThe time of daylength is around 13 h, and the latitude is 23 degrees, the temperature is between 23-31 °C. ^fUnder natural sunlight without FeCl₂. ^gNot tested.

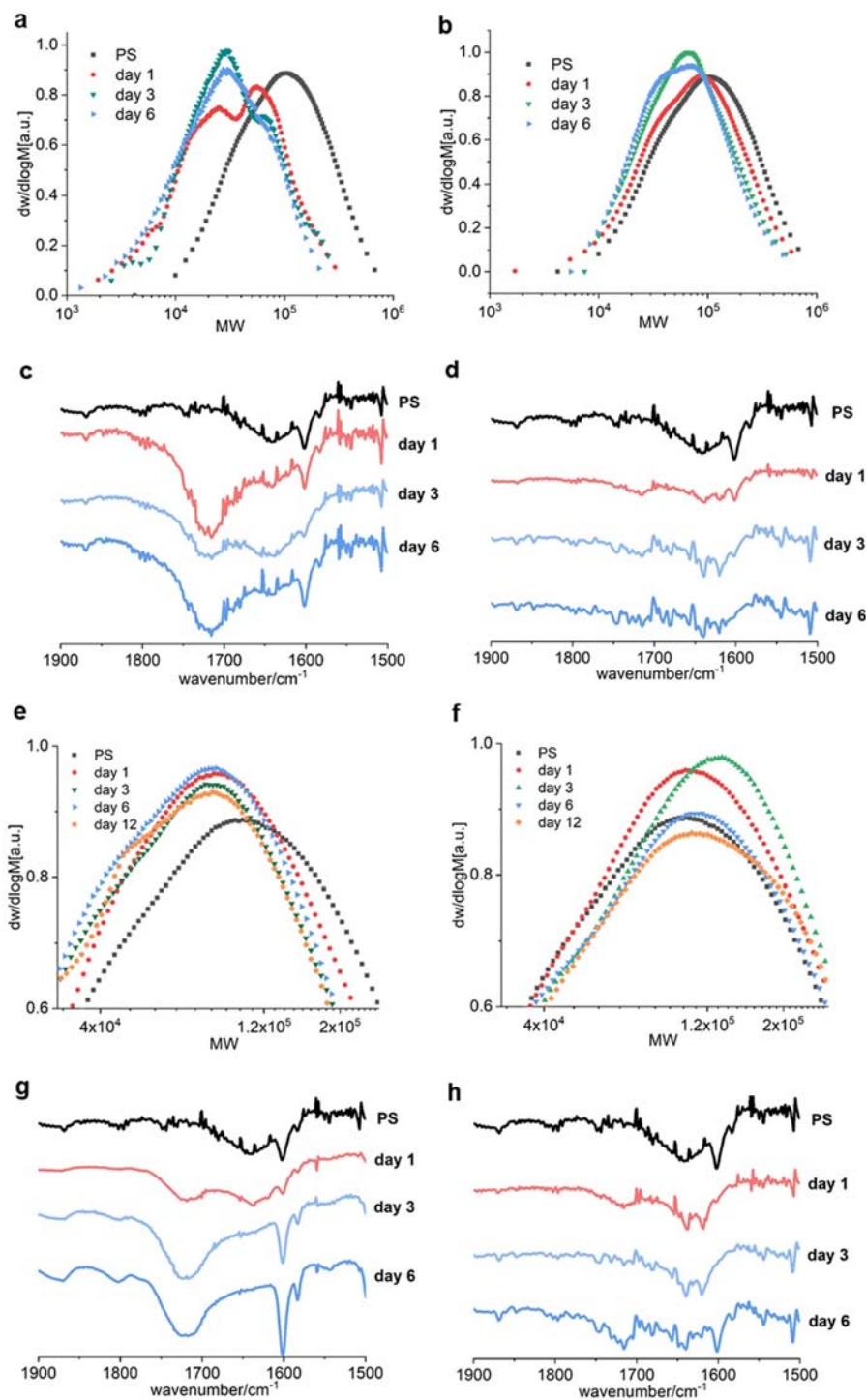


Fig. 3 | Spectra of degradation of PS in solid state. a, b, GPC traces of PS containing (a) or without (b) 2 mol% FeCl₂ after irradiation with 400 nm LED. c, d, FT-IR spectra of PS containing (c) or without (d) 2 mol% FeCl₂ after irradiation with 400 nm LED. e, f, GPC traces of PS containing (e) or without (f) 2 mol% FeCl₂ after irradiation with sunlight outdoors (see Supplementary Fig. 6,7 for detailed spectra of GPC traces). g, h, FT-IR spectra of PS containing (g) or without (h) 2 mol% FeCl₂ after irradiation with

sunlight outdoors.

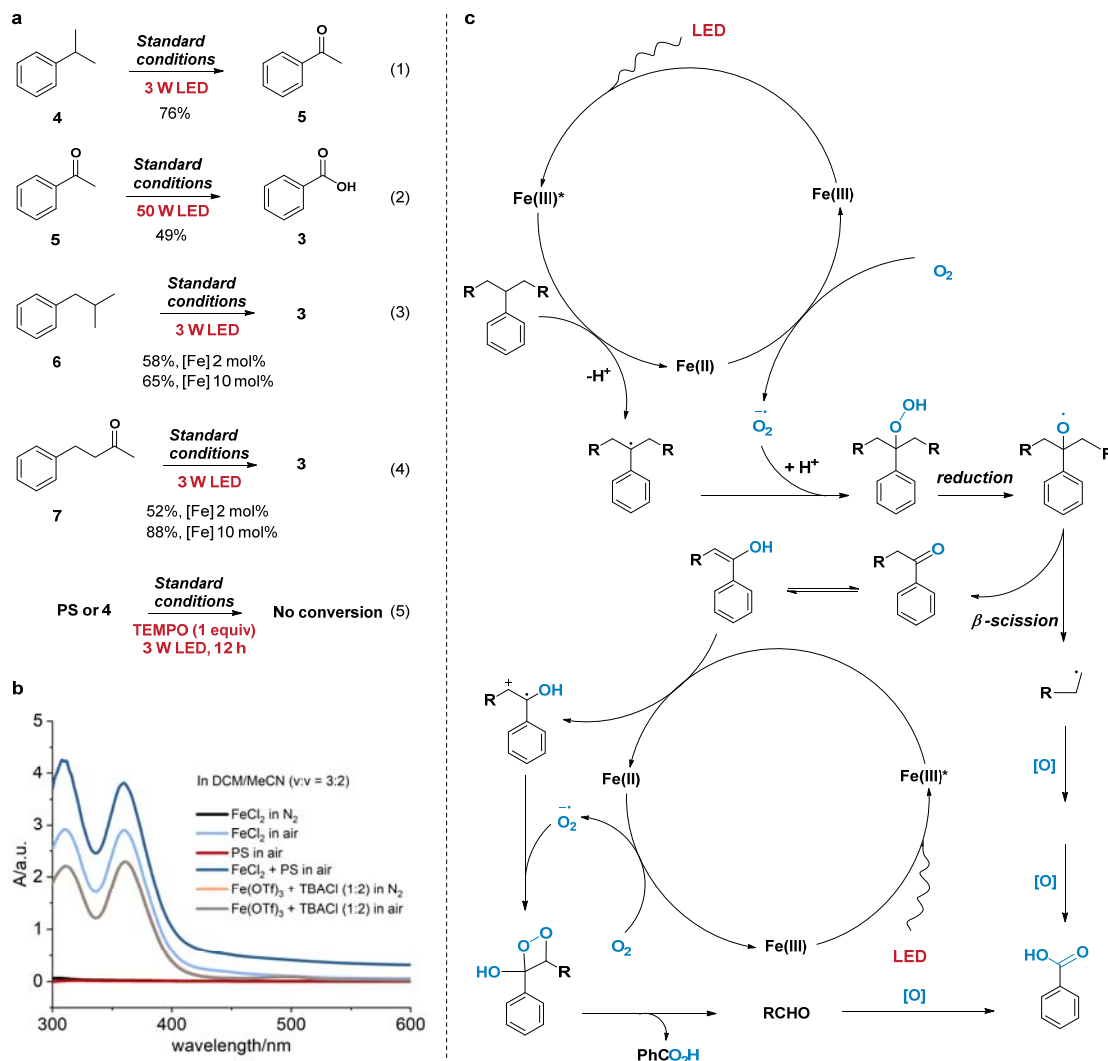


Fig. 4 | Mechanism study. **a**, Substrate performance under LEDs with different power. Standard conditions: substrate (0.1 or 0.2 mmol), FeCl₂ (2 mol%) and MeCN (2 mL) were stirred under O₂ (1 atm) at ambient temperature for 24 h, irradiated by LED (400 nm) (see Supplementary Fig. 8 for detailed condition). Acetophenone yield was measured by GC-MS using mesitylene as an internal standard. Other yields are isolated yields. **b**, UV-vis spectra under N₂ or air. DCM/MeCN (v: v = 3: 2) was used as the solvent (in the case of using acetone as the solvent, see Supplementary Fig. 9). Concentration: 5×10^{-4} mol/L [Fe], 2.5×10^{-2} mol/L PS. **c**, Proposed mechanism.

Mechanistic investigation. To study the mechanism, we set some reactions using

simply substituted arenes as substrates (Fig. 4a, Supplementary Fig. 8). For reactant with a tertiary benzylic carbon, such as isopropyl benzene (**4**), full conversion and 76% GC-MS yield of acetophenone (**5**) was easily achieved under the irradiation of 3 W LED. However, only trace benzoic acid was observed. The higher power of LED was found to be an essential factor for further oxidation of acetophenone. When 50 W LED was used, benzoic acid was generated from both isopropyl benzene (see Supplementary Fig. 8) and acetophenone. In addition, isobutylbenzene (**6**) and 4-phenylbutan-2-one (**7**) were transformed to benzoic acid smoothly when applying 3 W LED. Based on the optimized study and our observation of the above reactions, ketone is surely a key intermediate product of the oxidative C-C bond cleavage procedure. Both sp^3 C-C bond oxidative cleavage of tertiary benzylic carbon (such as **4**) and C-H oxidation of benzylic C-H bonds to produce ketones can be easily achieved under the standard conditions. However, oxidation of acetophenone is much harder than the other ketone intermediates (see Supplementary Fig. 8). One major difference between these ketones that affect the reactivity should be the ratio of their enol forms, which may be oxidized easily under the reaction conditions⁵¹. From the reaction condition studies and the UV-vis spectra (Fig. 4b and Supplementary Fig. 9), Fe (III) is believed to be the real photocatalyst, which can be oxidized from Fe (II) simply under oxygen atmosphere. Based on the above observations and the relevant mechanism studies reported^{28,43,51-55}, the proposed mechanism is shown in Fig. 4c. The irradiated Fe(III) oxidizes the benzylic C-H bond, generating the corresponding radical, which is then captured by superoxide radical and proton to produce the hydroperoxide^{28,52,53}. Reduction of the hydroperoxide by Fe(II) and the following beta-scission leads to the formation of the ketone. The enol form of ketone then reacts with oxygen to generate a four-membered ring, which decomposes to yield benzoic acid as the product⁵³⁻⁵⁵. Benzaldehyde can transform to benzoic acid smoothly under the reaction conditions (see Supplementary Fig. 8). Phenyl alkyl radicals can also produce benzoic acid through similar multiple oxidation procedures.

Conclusion

In conclusion, we developed a procedure to enable efficient oxidative multiple sp^3 C-C bond cleavage, which can be applied to depolymerize plastics containing styrene

selectively, generating commercial valuable benzoic acid as the product. The system is also inexpensive and environmentally friendly. Performed under visible light, the method uses iron, one of the most abundant metals on the earth, as the catalyst, oxygen or air as the oxidizing agent. Many commercial plastics, besides polystyrene waste, show outstanding conversions and very high selectivity of benzoic acid production. In addition, the system can be applied to degrade plastics under solvent free conditions, even in natural conditions, suggesting the potential application of iron salts as additives for degradable plastics.

Methods

General. All reagents were obtained from commercial vendors and used as received unless otherwise noted. Acetonitrile and dichloromethane were dried using calcium hydride. Flash column chromatography was performed using silica gel (300-400 mesh). ^1H NMR spectra were recorded at 400 MHz, using a Bruker AVANCE III 400 (400 MHz) spectrometer. Measurements were done at ambient temperature. Fourier-transform infrared (FT-IR) spectra were obtained on an interferometer of IRAffinity-1S. DCM solution of the sample was dropped on the surface of a KBr plate and dried. Then the IR spectrum was collected. UV-vis spectra were recorded on a HORIBA Duetta compact spectrofluorometer. The cuvette used was a standard 1 cm width quartz cuvette. Gel-permeation chromatography (GPC) was performed on a Waters Breeze 2 GPC equipped with a refractive index detector at 35 °C. Samples were run in tetrahydrofuran with a speed of 1.0 mL/min. GC-MS data were detected on an Agilent 8890-5977B gas chromatography-mass spectrometry.

General procedure for transformation of arene substrates. A 25 mL Schlenk tube with screw-cap was added 100 μL FeCl_2 solution (0.1 mol/L dissolved in acetonitrile), aromatic substrate (0.1 mmol), and 1.9 mL acetonitrile. The tube was blown with oxygen for several seconds and maintained in oxygen atmosphere by adding an oxygen balloon. Then the Schlenk tube was irradiated with 400 nm light emitting diode (LED, 20 W) and stirred at 500 rpm for 12 h. Subsequently, the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography using petroleum ether and dichloromethane as the eluent.

General procedure for selective degradation of plastics in DCM/MeCN. A 25 mL Schlenk tube with screw-cap was added 800 μL FeCl_2 solution (0.0125 mol/L dissolved in acetonitrile), polystyrene (0.5 mmol), and 1.2 mL dichloromethane. The tube was blown with oxygen for several seconds and maintained in oxygen atmosphere by adding an oxygen balloon. Then the Schlenk tube was irradiated by 400 nm LED (20 W) and stirred at 500 rpm for 66 h. Subsequently, 15 mL MeOH was added, the solution was filtered and the resulting residue was dried and weighed to calculate the conversion of polystyrene. Then, the filtrate was evaporated under reduced pressure and the residue was purified by flash chromatography using petroleum ether and dichloromethane as the eluent.

General procedure for selective degradation of plastics in acetone. A 25 mL Schlenk tube with screw-cap was added 1 mL FeCl_2 solution (0.01 mol/L dissolved in acetone), polystyrene (0.5 mmol), and 1 mL acetone. The tube was blown with oxygen for several seconds and maintained in oxygen atmosphere by adding an oxygen balloon. Then the Schlenk tube was irradiated by 400 nm LED (20 W) and stirred at 500 rpm for 66 h. Subsequently, 15 mL MeOH was added, the solution was filtered and the resulting residue was dried and weighed to calculate the conversion of polystyrene. Then, the filtrate was evaporated under reduced pressure and the residue was purified by flash chromatography using petroleum ether and dichloromethane as the eluent.

Procedure of degradation of PS using low catalyst loading. A 25 mL Schlenk tube with screw-cap was added 40 μL FeCl_2 solvent (0.0125 M dissolved in acetonitrile). Acetonitrile was evaporated under reduced pressure, and then polystyrene (0.5 mmol) and dichloroethane (2 mL) were added. The tube was blown with oxygen for several seconds and maintained in oxygen atmosphere by adding an oxygen balloon. Then the Schlenk tube was irradiated by 400 nm LED (20 W) and stirred at 500 rpm for 66 h. Subsequently, 15 mL MeOH was added, the solution was filtered and the resulting residue was dried and weighed to calculate the conversion of polystyrene. Then, the filtrate was evaporated under reduced pressure and the residue was purified by flash chromatography using petroleum ether and dichloromethane as the eluent.

General procedure for solvent free experiment. A 20 mL vial was added 1.6 mL

FeCl₂ solvent (0.0125 mol/L dissolved in acetonitrile), polystyrene (0.5 mmol), and 2.4 mL dichloromethane. The vial was then shaken violently to get a homogeneous solution. Then 80 µL solution was added into a 4 mL headspace bottle. The solvent was removed and the bottle was irradiated by 400 nm LED (20 W) or sunlight. The FT-IR spectra and gel-permeation chromatography (GPC) were determined for different samples. At the same time, the control experiments without FeCl₂ were carried out.

Data availability

The data supporting the findings of this study are available within the paper and its Supplementary Information.

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Competing interests

There are no competing interests to declare

Additional information

Supplementary information is available for this paper.

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