COMMUNICATION

Upcycling of Polystyrene to 1,2-Disubstituted Oxygenated Aromatics through Backbone Rearrangement and Oxidation Reactions

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Abstract: Upcycling polystyrene (PS) into economically-viable, industrially-relevant single- and multi-substituted oxygenated aromatic compounds is an attractive option to address the current unsustainable end-of-life of this high-volume waste plastic. However, 1,2-disubstituted aromatics (e.g. phthalic anhydride), possessing a multi-billion dollar annual market, have thus far been inaccessible from PS. This is due to unsurmountable steric constraints conferred by the polymer backbone hindering ortho-functionalisation of its pendant phenyl groups. Herein, to overcome this challenge, we report a versatile strategy to convert PS directly into 1,2-disubstituted aromatics, first by PS backbone rearrangement into polyindanes, followed by organocatalyzed aerobic oxidations. Our approach is applicable to mixed real-life PS waste on multi-gram scales, allowing convenient access to *ortho*-substituted aromatics used as catalysts, dyes and drug precursors with different structural complexities previously inaccessible from PS. Furthermore, this versatile strategy was also applicable on PS-like polymers such as poly(4-methylstyrene), producing trimellitic, terephthalic and isophthalic acids. This approach significantly expands the range of high-value substituted aromatic products accessible from PS, further enhancing its utility as a feedstock in a circular economy.

The upcycling of polystyrene (PS) into value-added, industrially-relevant chemicals is of great recent interest.[1-5] With an estimated global demand of 15 million tons in 2023 that is expected to further increase by ~2 million tons by 2028,[4] PS is one of the most-produced plastics in the world, yet amongst the least recycled (<1% in the US).[6] With recycled PS being more expensive than the virgin petroleum-derived polymer, PS upcycling into products of higher economic value repositions this high-volume waste material as feedstock in the chemical value chain, and has the potential to create an economically-viable post-use plastics economy.[3-4, 7] PS is especially attractive for chemical upcycling as its electron-rich phenyl groups are amenable to electrophilic substitutions (e.g. bromination and Friedel-crafts alkylation),[8-12] and can stabilize propagating reactive species during chain scission reactions to produce industrially-relevant oxygenated aromatics such as phenol, acetophenone and benzoic acid (BA).[13-24]

Although these mono-substituted aromatics are of industrial importance, strategies to synthesize multi-substituted aromatics directly from PS greatly expands the range of products accessible. For example, *in-situ* nitration during PS oxidative upcycling affords 4-nitrobenzoic acid (4-NBA),[16, 25] useful as a precursor in the dye and pharmaceutical industries. However, product selectivity is largely constrained by reagent accessibility during electrophilic substitution of the phenyl rings on PS. Despite both 2- and 4-positions of the phenyl groups on PS being electronically favored for electrophilic substitution reactions, *para*-substitution is almost exclusively achieved (**Figure 1A**): Friedel-Crafts alkylation of PS, followed by oxidation affords mainly terephthalic acid (TPA), with the conspicuous absence of phthalic acid (1,2-benzenedicarboxylic acid, PAc) reflecting the inability to alkylate the 2-position of the phenyl group on the polymer (**Figure 1A-i**).[9] Similarly, $AuCl_3$-catalysed PS bromination affords 4-bromo-polystyrene exclusively (**Figure 1A-ii**).[10] The steric inaccessibility of the 2-aromatic position resulting from the proximal PS backbone has thus far posed unsurmountable challenges for ortho-functionalization. Even under extremely forcing nitration-oxidation conditions, electronically-disfavored 3-nitrobenzoic acid and 3,5-dinitrobenzoic acid were preferentially formed over 2-nitrobenzoic acid (**Figure 1A-iii**).[25] This constraint has prevented access to

1,2-disubstituted aromatics such as phthalic anhydride (PAn) from PS, which is an important precursor for industrial production of plasticisers (e.g. phthalate esters), dyes (e.g. fluorescein, phthalocyanines), drugs (e.g. thalidomide), energy storage (e.g. lithium phthalates) and functional polymers.[26-29] With an annual production exceeding 5.5 million metric tons,[30] conversion of PS to PAn potentially allows direct access to its existing USD 4.5-billion market (2023) with projected unabated growth at nearly 4% compounded annual growth rate till 2030,[31] far exceeding that of BA, the most common oxidation product from PS (**Figure 1B**). Considering that PAn and PAc have thus far predominantly produced by oxidation of petroleum-based o-xylene and naphthalene,[32-33] their alternative production from post-use PS not only reduces dependency on these non-renewable resources, but also contributes towards addressing escalating plastic pollution.

To bypass the steric constraints of the PS backbone that has prevented access to 1,2-disubstituted C8 aromatics, we devised an alternative two-stepped strategy: First, acid-mediated backbone rearrangement of PS can form polyindanes (PIs),[34] possessing aromatic rings linked to the polymer backbone at the 1,2-position, which can be subsequently liberated via catalytic oxidation reactions to produce PAc or PAn (**Figure 1B**). Unlike C8 diacids (e.g. TPA) produced from PS through Friedel-Craft alkylation,[9] which incorporates an additional carbon atom from external alkylating agents, this approach utilizes PS as the sole carbon source, with all 8 carbon atoms of the 1,2-disubstituted aromatics derived entirely from the polymer itself. Herein, we demonstrate the viability of this approach to produce PAc or PAn directly from PS for the first time, including a non-chromatographic process to access PAn in high purity directly from various types of waste PS.

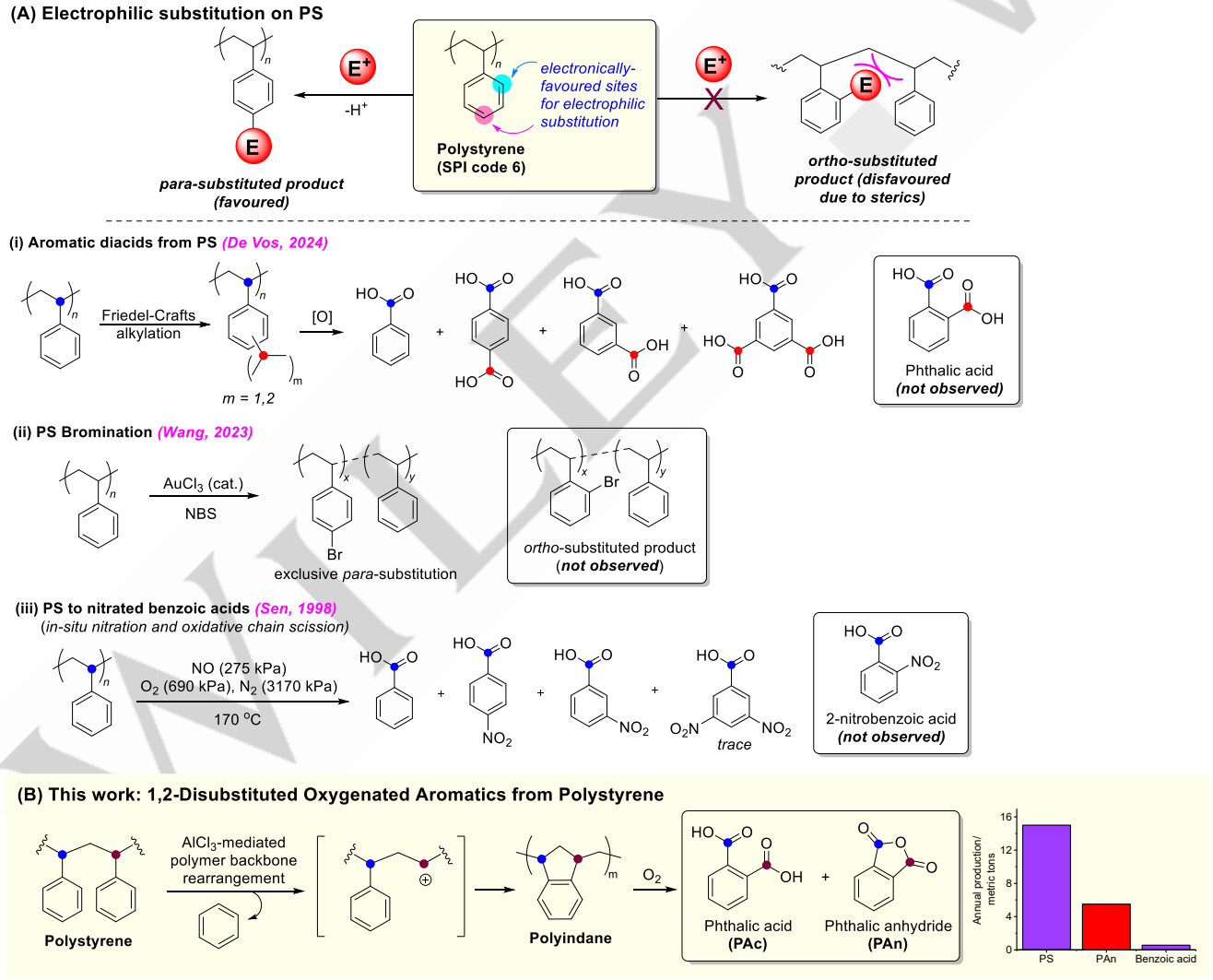

Figure 1. (A) Electrophilic substitution of PS favoring *para*-substituted products in (i) Friedel-Crafts alkylation; (ii) aromatic bromination and (iii) nitration; (B) Converting PS to 1,2-substituted aromatic oxygenates through sequential polymer rearrangement followed by oxidation. Colored circles indicate the source of carbon atoms on COOH groups of the final products.

To achieve backbone rearrangement of PS, we employed strong Brønsted acidic conditions at ambient temperature, using 1.0 weight equivalent of $AlCl_3$ relative to PS in the presence of trace amounts of water, which forms the strong Brønsted acid $[AlCl_3OH^-][H^+]$ in-situ.[34] Under these conditions, the pendant phenyl groups of PS can be protonated, followed by elimination of benzene to form a carbenium cationic site on the hydrocarbon backbone, which can then undergo intrachain rearrangement with a neighbouring phenyl groups to form the 1,2-substituted indane moiety (**Figure 1B**)[35]. We successfully achieved high extents of PS indanization, evident from ^{1}H NMR analysis (DCM-d_2) of the resulting isolated solids: In the aromatic region, the two characteristic PS aromatic signals centered at 6.50 and 7.10 ppm coalesced to form a single broad peak at ~7.20 ppm (**Figure 2A-B**). In the aliphatic region, the PS's methylene and methine proton signals were changed to a broad signal from ~1.00 - ~3.70 ppm. Additionally, the relative integrations of the aromatic and aliphatic signals changed from 5:3 expected for PS, closer to the 2:3 expected for fully-converted polyindane (**Figure S2**). Significant reduction of PS molecular weight resulted during the rearrangement reaction (**Figure S11**), indicating that chain scission reactions were competing with indane formation. Optimisation experiments (**Table S1**) showed that the presence of water that allows $[AlCl_3OH^-][H^+]$ formation was essential for achieving high extents of indanization, exemplifying the necessity of Brønsted acidity in driving the PS intrachain rearrangement, while lower loadings of $AlCl_3$ or excess water reduced the extent of indanization. Interesting, other strong Brønsted acids such as H_2SO_4, HCl and Amberlyst-15 failed to elicit significant PS rearrangement. Using our optimized conditions, multi-gram indanization of PS resins could also be achieved to afford a polymer (PI-resin) with 73% conversion of styrene to indan units. Although this also resulted in unavoidable mass loss (~32%, **Section S2**) from benzene detachment, the benzene may be recovered and recirculated as feedstock back into the petrochemical industry[36-37].

Thereafter, PI-resin oxidation was first investigated using *N,N',N''*-trihydroxyisocyanuric acid (THICA) with HNO_3 (aq.) under aerobic conditions. ^{1}H NMR analysis of the crude reaction mixture revealed that PAc was the major product (**Figure 2C**), which was further corroborated with ESI mass spectrometry (expected $[M+H]^+$ m/z= 167.0344; obtained 167.0338; 0.0006 ppm). No PAn was observed under these conditions, possibly due to the usage of aqueous HNO_3 that promoted hydrolysis of any PAn formed. Other than PAc, BA and 4-NBA were observed as minor products, likely arising from oxidation of the unreacted styrene units present on the polymer. The possibility that the PAc could have originated from phthalate-containing additives/ plasticisers in the PS starting material could be ruled out, as ^{1}H NMR characterization of the PS resin showed no detectable presence of these compounds (**Figure S1**). Control experiments (**Table 1 entries 2 and 3**) indicated the necessity of an aerobic atmosphere for PAc to be obtained, though a pure O_2 atmosphere did not substantially enhance PAc yields. The presence of light was not essential for the reaction (**entry 4**), achieving comparable yields of PAc and BA in the dark as under ambient lighting.

Under oxidative conditions, the *N*-oxyl radical intermediates generated from *N*-hydroxyl compounds are susceptible to degradation reactions such as radical disproportionation, ring-opening and oligomerization,[38-39] thus often necessitating high catalyst loadings to maintain reactivity.[40] Despite so, archetypical *N*-hydroxyl catalysts such as *N*-hydroxyphthalimide (NHPI) find applications in industrial-scale oxidation processes (e.g. production of adamantanol from adamantane, cyclohexane oxidation to adipic acid, alkylaromatic oxidation)[41], although ineffective catalyst recovery is still a key challenge. These degradation products are also often not recovered for catalyst regeneration, causing significant wastage and contributing to process costs. Motivated by the possibility of reducing wastage, we investigated replacing THICA with NHPI, an *N*-hydroxyl catalyst with similar 1,2-substitution as PAn/PAc, which was previously shown to exhibit similar catalytic efficiency for PS-to-BA conversion as THICA.[16] Moreover, the products of NHPI degradation during the reaction can be converted to PAc/PAn,[38] which can be isolated together with the same products from polyindane oxidation for NHPI catalyst regeneration (*vide infra*). Indeed, PI-resin oxidation with NHPI (0.1 mmol) afforded both PAc and PAn (**Table 1, entry 5**). Although NHPI degradation performed under identical reaction conditions was found to also produce PAc and PAn as the main decomposition products (**Figure S18**), the cumulative quantity of PAc and PAn from the reaction (0.32 mmol) exceeded the NHPI catalyst loading (0.1 mmol), clearly indicating that the majority of these products were obtained from the PI-resin instead of the catalyst.

To identify possible side products and intermediates formed during the reaction, GC-MS analysis of the NHPI-catalysed reaction was performed. Other than the expected products (BA, PAc and PAn), we observed a number of partially-oxidized intermediates and indane derivatives (e.g. 2-indanone and 1,3-indandione) from partial oxidation of the indan segments of the PI-resin, together with several nitrated aromatics (**Table S3**). These findings suggested that multiple hydrogen abstraction reactions[42] need to occur at different sites on the polymer-bound indane fragments, before subsequent β-scission reactions and/or combinations with oxygen or nitrogen oxides can occur to propagate oxidative degradation to PAc/PAn as the terminal aromatic oxidation products (see proposed mechanism in **Figure S19**). In all cases (**Table 1**), higher conversions of the styrene units to BA were observed compared to PAc/PAn from the indan moieties. This could be attributed to the greater number of elementary steps

needed to produce PAc/PAn from the indan units, as well as differences in electronic susceptibility and steric accessibility that affect both the thermodynamics and kinetics of hydrogen abstraction.

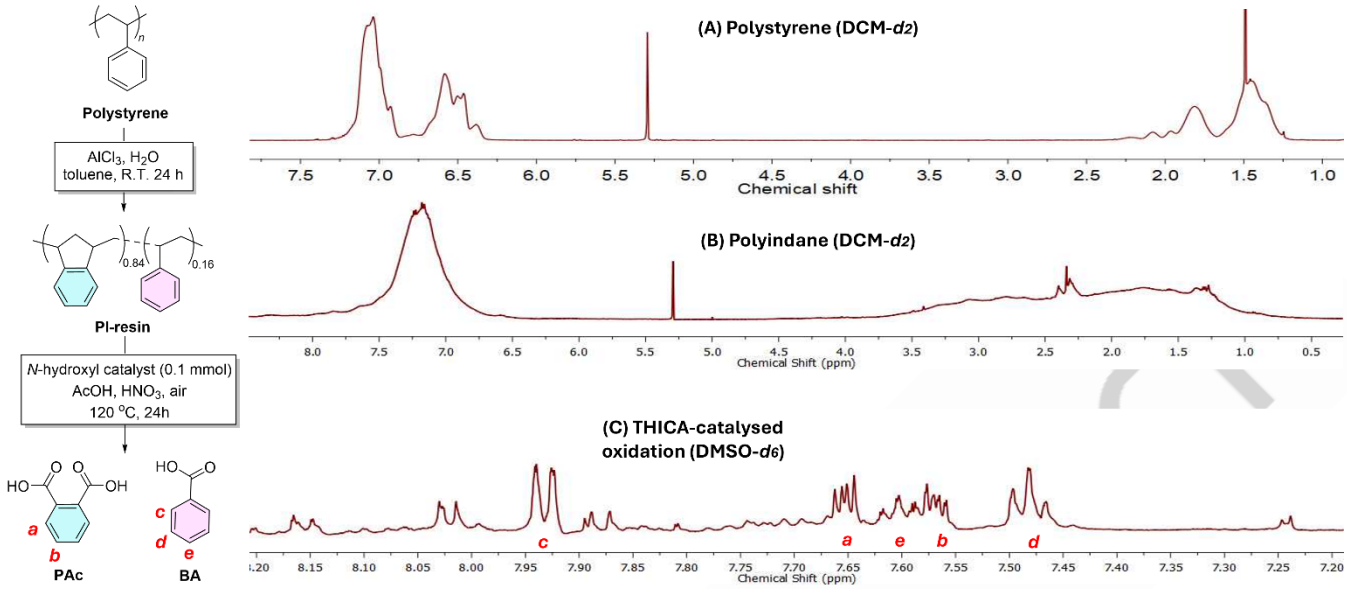

Figure 2. Conversion of PS resins to 1,2-aromatics with assigned partial ^{1}H NMR spectra (DMSO-d_6) of (A) PS and (B) PI-resin in DCM-d_2 and (C) post-oxidised unpurified reaction mixture in DMSO-d_6 (see **Figure S12** for full NMR spectrum).

Table 1. Oxidation of PI-resin through thermal catalysis

S/N	Catalyst	Deviation from std Conditions [a]	Conversion from indan/styrene segment on PI-resin (%) [b]		
			PAc	PAn	BA
1	THICA	-	39	-	60
2	THICA	Ar instead of air	-	-	18
3	THICA	O_2 instead of air	35	-	51
4	THICA	Dark	38	-	49
5	NHPI	-	38 (29) [c]	14 (8) [c]	50

[a] All reactions were performed using PI-resin (104 mg), N-hydroxyl catalyst (0.1 mmol; i.e. 17.7 mg THICA, 16.3 mg NHPI) AcOH: 70% HNO_3 10:1 *v/v*, air, 24 h, under ambient lighting conditions, unless stated otherwise. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture based on the quantity of each unit from PI-resin (i.e. PAc and PAn from 73% indan units, and BA from the 27% styrene units) (**Sections S2-3**). [c] Yields in parentheses exclude PAc and PAn produced via NHPI degradation (**Section S3**).

The success of photoredox catalysis in upcycling PS to BA[14-15, 17-19, 21, 23] prompted us to study the possibility of PI photocatalyzed oxidations under near-ambient conditions. Using indane as a model small-molecule substrate in ethyl acetate as a green solvent, *N*-bromosuccinimide (NBS) (10 mol%) was found to be the only catalyst that elicited significant oxidation under 390 nm irradiation, whilst other known catalytic systems for converting PS to BA (i.e. H_2SO_4, $TsOH{\cdot}H_2O$, $FeCl_3$) did not[14-15] (see **Section S4** for full screening details). Addition of aqueous HBr (20 mol%) to NBS resulted in nearly 3-fold increase in product yields from indane, though an equivalent amount of CF_3SO_2Na, previously shown to enhance PS-to-BA conversion[18] was ineffective. Unlike the THICA-catalysed thermal oxidations, unexpected selectivity for PAn over PAc was observed, even in the presence of aqueous HBr. While mechanistic details remain to be clarified, the photodehydration of PAc to PAn was likely brought catalysed by succinimide, formed from debromination of NBS during the photoredox oxidation,[18] with irradiation and O_2 shown to be necessary conditions for PAn formation (discussed in **Section S4**). Despite this success on indane, applying the NBS-HBr (20 mol%) catalytic system on the PI-resin was largely unsuccessful, affording BA and only trace amounts of PAn after 24 h under 390 nm irradiation (**Figure S47**). The stark contrast in susceptibility of PS

and polyindane towards photocatalytic oxidation is significant and unexpected, and may again result from differences in electronics between both polymers and their intermediates towards oxidative scissions.

Considering the ineffectiveness of photocatalytic reactions for polyindane oxidation, we then probed the practicality of converting multi-gram real-life PS waste into 1,2-disubstituted aromatic molecules under thermal batch conditions (**Figure 3**). 10 g of mixed PS waste, containing different dyes and additives (^{1}H NMR revealed absence of significant detectable phthalate-based compounds, **Figure S1**), underwent facile rearrangement with $AlCl_3$ to afford 70% indanization after 24 hours. Subsequently, NHPI-catalysed oxidation of the resulting isolated polymer (**Section S5**) afforded PAc as the major product alongside PAn. To isolate the 1,2-aromatics from these insoluble oligomeric byproducts of polyindane oxidation, the reaction mixture was then further subjected to an aqueous Soxhlet extraction, which also simultaneously hydrolysed any PAn and NHPI degradation products into PAc. After removal of the water through evaporation, sublimation of the extracted products led to *in-situ* PAc dehydration, forming PAn in high purity as white crystals. The use of only water for PAn isolation from the crude reaction mixture, coupled with scalable industrially-relevant processes (i.e. Soxhlet extraction, evaporation and sublimation) positions it for potential scale-up and industrial translation.

Next, the as-obtained PAn was then converted into several products of varying structural complexity to showcase its synthetic versatility (**Figure 3**). First, to recover the NHPI catalyst used for polyindane oxidation, PAn was subjected to dehydrative condensation with hydroxylamine hydrochloride to obtain the target product in 60% yield. A similar reaction with urea allowed direct conversion to phthalimide, an essential precursor for synthesis of various products of significant market demand, such as saccharin, insecticides (e.g. Phosmet) and drugs (e.g. (R)-thalidomide). Additionally, reaction of PAn with phenol, which could itself be obtained from PS using the Hock process,[13] allowed convenient access to the pH indicator phenolphthalein. The analogous reaction with resorcinol afforded the biomedically-versatile dye, fluorescein. These proof-of-concept transformations allow synthesis of diverse 1,2-aromatics previously inaccessible from PS.

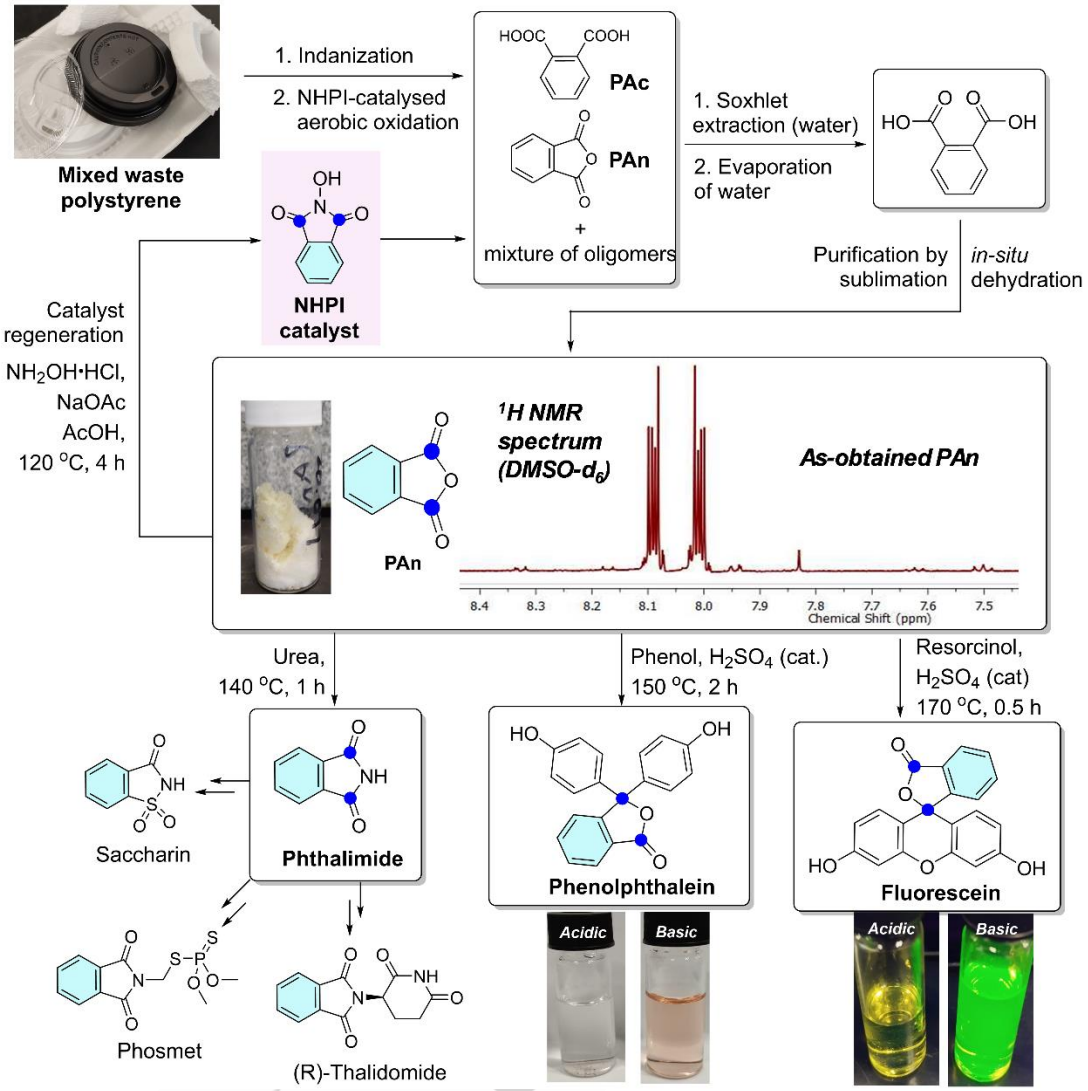

Figure 3. Conversion of mixed PS waste into PAn, and subsequent further upcycling into different products of varying structural complexity containing 1,2-substituted aromatics that were previously inaccessible from PS. Full ^{1}H NMR spectra of the PAc intermediate, PAn product and functionalized derivatives are shown in **Sections S5** and **S7**.

Finally, we extended our process to other commercial PS derivatives such as poly(4-methylstyrene) (P4MS, commonly used as coatings and engineering plastics (**Figure 4**). Indanization of P4MS (to form P4MS-I) was followed by THICA-catalysed oxidation to form trimellitic acid as the major product (**Section S6**), which is a precursor to plasticisers[43] and MOFs.[44-45] Other than the expected TPA by-product from unreacted 4-methylstyrene units, isophthalic acid (IPA) was also observed in significant yields. Time-course experiments (**Figures S61** and **S62**) show that very small quantities of TPA, IPA, or TMA (total yield < 5%) were produced in the first 3 hours, indicating that P4MS-I backbone activation and chain cleavage scission reactions dominated during this period.[16] Thereafter, the yields of all three compounds increased continually throughout the 24 h reaction. The unexpected IPA product suggested the possibility of reversibility during indanization: like the 4-methylstyrene units, the asymmetric methyl-substituted indan moieties may also be protonated under strong Brønsted acidic conditions, which can undergo scission of either bond attaching the aromatic ring to the polymer backbone (**Figure 4**). This forms pendant phenyl moieties substituted at both 1,3- and 1,4-positions, which are in turn precursors for IPA and TPA respectively. By extension, this also offers a potential route for production of TMA, TPA and IPA directly from PS, via successive *para*-selective Friedel-Crafts alkylation, indanization and oxidation.

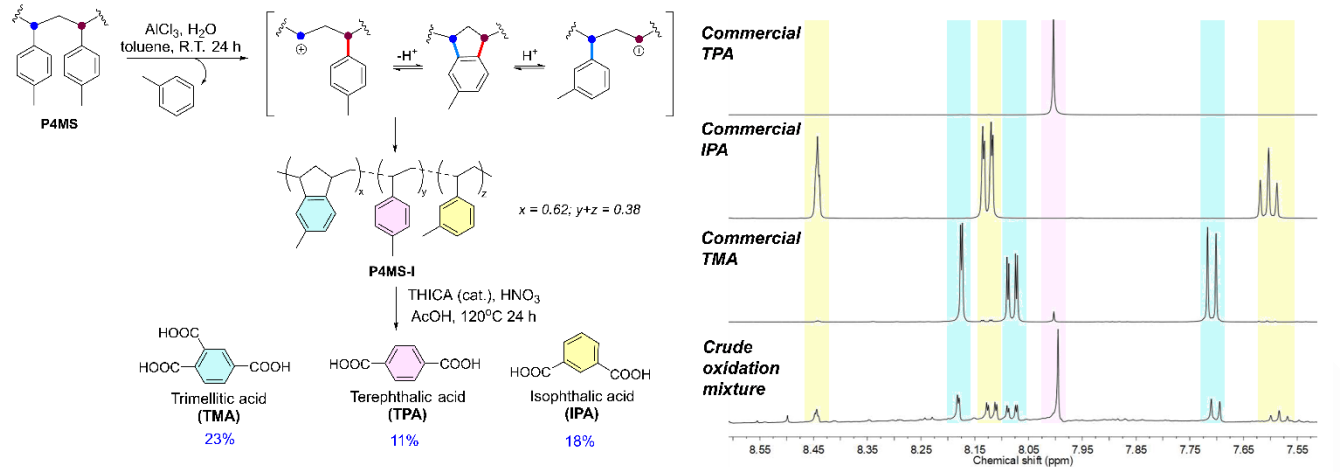

Figure 4. Conversion of P4MS into trimellitic, terephthalic and isophthalic acids, with stacked ^{1}H NMR spectra (DMSO-d_6) of the reaction mixture with spectra of the pure, commercially-available products.

In conclusion, we disclose a novel strategy for converting PS into previously-inaccessible 1,2-aromatic oxygenates through polymer backbone rearrangement, followed by aerobic oxidation. Although *N*-hydroxyl thermal catalysis proved effective in polyindane oxidation to PAc, the unexpectedly poor outcomes of photoredox catalysis highlights the inherent differences in susceptibility of polyindanes and PS towards oxidations. We also demonstrated effective gram-scale conversion of mixed PS waste into PAn, which was further transformed into 1,2-substituted dyes, phthalimide, and even the NHPI catalyst previously inaccessible from PS. Our method's success on substituted PS derivatives also allows convenient access to highly-functionalised aromatic oxygenates (i.e TMA) and even 1,3-substituted IPA from P4MS. By providing convenient access to a new class of products previously inaccessible from PS, our strategy greatly expands its utility as a feedstock for upcycling into high-value aromatics of high industrial demand.

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Conflicts of interest

A patent application has been filed by the authors based on the contents of this manuscript.

Keywords: Waste plastics • polyindane • organocatalysis • phthalic anhydride • circularity

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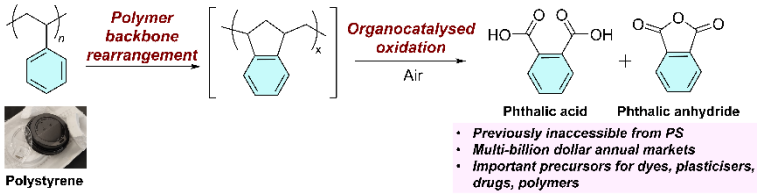
Entry for the Table of Contents



Industrially-important 1,2-disubstituted oxygenated aromatics (e.g. phthalic acid and anhydride) have been inaccessible from polystyrene due to sterics conferred by the polymer backbone. Herein, we overcome this constraint through acid-mediated polymer backbone rearrangement, followed by aerobic oxidation. These aromatics were further converted into economically- and industrially-relevant products previously-inaccessible from polystyrene.