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Benzaldehyde-mediated selective aerobic polyethylene functionalisation with isolated backbone ketones†

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Post-synthetic functionalisation of commodity polymers such as polyethylene (PE) is an increasingly important strategy for giving waste plastics new 'lease-of-lives' as functional polymers. In particular, installing oxygenated functional groups such as alcohols and ketones is valuable due to their chemical versatility for further chemical modifications. However, this is especially challenging for PE due to its unreactive nature, and often requires hazardous and environmentally damaging chlorinated solvents owing to PE's excellent solvent resistance. Herein, we demonstrate a highly selective method to install isolated carbonyl groups on PE using only benzaldehyde and O₂ as a terminal oxidant, without the need for stoichiometric organic oxidants or any hazardous organic solvents. This process relies on the aerobic auto-oxidation of benzaldehyde to benzoic acid, generating reactive radical intermediates in the process that are responsible for both C–H activation and exclusive carbonyl formation. Our method is compatible with copper(II) oxidation catalysts to enhance the extent of PE oxidation, and can also minimise the waste produced as the benzoic acid side product can be easily isolated and reused for different applications. The versatility of carbonyl-containing PEs for further chemical derivatisation offers many exciting options for transforming waste PE into diverse polymeric materials for a materials circular economy.

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Introduction

Polyethylenes (PEs) are the single most widely-produced class of plastics today due to their low cost, versatility, durability and processibility. Highly popular for many domestic and industrial applications, particularly as packaging materials,^{1,2} more than 100 million tonnes of PE waste were produced in 2015 alone, with the vast majority disposed in landfills or incinerated.³ The PEs' extremely linear and unsustainable cradle-to-grave life cycles are largely due to their chemical inertness towards hydrolysis and chemical degradation, as these polymers are exclusively made up of strong C–C and C–H bonds. This not only makes them highly environmentally persistent (taking up to 400 years to degrade),⁴ but it also severely

hinders attempts to chemically recycle and valorise them into new functional products.^{5,6}

In recent years, post-synthetic chemical modification of PEs has emerged as a promising enabling technology for transforming these commodity polymers into functional materials for targeted applications.^{6–8} On top of leveraging on the existing high-volume industrial PE production capabilities, post-synthetic functionalisation also offers opportunities to mitigate the global plastic waste crisis. In particular, methods to install oxygenated functional groups (*i.e.* alcohols and ketones) on the inert PE polymer are attractive. These groups can imbue PEs with new properties, such as enhanced adhesiveness.⁹ Furthermore, the well-established and versatile reactivity of these oxygenated functionalities allow further modifications (*e.g.* ring opening polymerisation on alcohols and reductive amination on carbonyls) to access new applications such as polymer blend compatibilisation.¹⁰ The presence of in-chain carbonyls can also enhance the PEs' photodegradability through Norrish-type photochemical chain-scission reactions.^{11,12} Installing these oxygenated groups, however, is challenging. Free radical chemistry often leads to excessive and uncontrollable chain cleavage, compromising on polymer strength and processibility.¹³ Although these undesirable side reactions can be elegantly circumvented by using organo-

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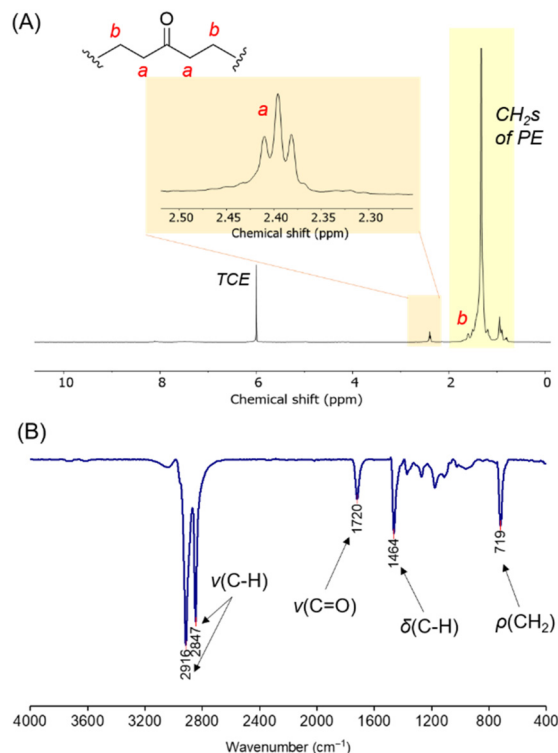


Fig. 2 (A) ¹H NMR spectrum of the isolated oxidised PE (C₂D₂Cl₄, 80 °C); inset: expanded region of the spectrum showing the methylene signals immediately adjacent to the in-chain carbonyls. (B) FTIR spectrum of the oxidised PE.

signals at 2.40 ppm to the signals of the unreacted methylene groups (0.8–1.6 ppm) (Fig. S3†), we obtained a total degree of PE functionalisation (TF) of 1.2% (Table 1, entry 1). This is notable for being the first known method to exclusively install carbonyl groups post-synthetically onto PE. Furthermore, benzoic acid could be easily isolated with excellent yields

(>80%) and purity (Fig. S4†) by simple recrystallisation using hot water without any organic solvents.

A series of control experiments were then performed to better understand the requirements for PE oxidation. The necessity of O₂ as an oxidant is evident from the lack of carbonyl formation under an argon atmosphere (entry 2), and a smaller extent of PE oxidation when air (21% O₂) was used instead of pure O₂ (entry 3). While a lower reaction temperature of 100 °C expectedly caused less oxidation (entry 4), raising the reaction temperature to 140 °C brought about increased PE oxidation (entry 5). The usage of less benzaldehyde (1 eqv. w.r.t. ethylene repeating units instead of 3) resulted in much lower TF, albeit also with exclusive carbonyl functionalisation (entry 6). Although PE can possess alkene defects that can result in the addition of hydroxyl, carbonyl and acid groups under aerobic oxidation,^{29,30} the lack of any functionalisation observed in O₂ when benzaldehyde was replaced with 1,2,4-trichlorobenzene solvent (entry 7 and Fig. S10†) showed that the PE starting material by itself could not be oxidised under these reaction conditions. This was further corroborated when no oxidation was detected when molten PE was heated at 120 °C for 24 hours in the absence of benzaldehyde (Fig. S17†). In addition, to prove that benzaldehyde was able to facilitate the oxidation of the saturated C–H bonds of PE, we used identical reaction conditions to those in Table 1, entry 1 on *n*-icosane (linear C₂₀H₄₂), which afforded a similar TF of 1.3 with exclusive carbonyl functionalisation (Fig. S18†). Finally, to exclude the possibility of trace metal contamination on the surface defects of stirrer bars acting as the active oxidation catalyst,³¹ the PE oxidation reaction was repeated on a larger scale (2.5 g of PE) using a new, unused stirrer bar that was soaked overnight with the glassware in aqua regia to simultaneously investigate the effect of reaction scale-up. Our results showed that a comparable degree of PE oxidation (TF = 0.8) could also be achieved with exclusive carbonyl group formation (Fig. S19†), where by the

Table 1 Aerobic oxidation of PE using benzaldehyde^a

S/N	Dispersant	Gas ^b	T/°C	Molar ratio of C=O : COOH : OH ^c	TF/% ^c
1	Benzaldehyde	O ₂	120	100 : 0 : 0	1.2
2	Benzaldehyde	Ar	120	—	0
3	Benzaldehyde	Air	120	100 : 0 : 0	0.7
4	Benzaldehyde	O ₂	100	100 : 0 : 0	0.5
5	Benzaldehyde	O ₂	140	100 : 0 : 0	1.3
6	Benzaldehyde (1 eqv.)	O ₂	120	100 : 0 : 0	0.5
7	1,2,4-TCB	O ₂	120	—	0
8	Benzaldehyde (in the dark)	O ₂	120	100 : 0 : 0	1.1
9	Furfural	O ₂	130	—	0
10	Benzaldehyde + benzyl alcohol (1 eqv)	O ₂	120	100 : 0 : 0	0.9
11	Benzaldehyde + benzyl alcohol (6 eqv)	O ₂	120	100 : 0 : 0	0.3
12	Benzaldehyde + [CuCl ₂ ·DCH18-crown-6] (1 mol%) ^d	O ₂	120	61.7 : 38.3 : 0	3.8
13	Benzaldehyde + CuCl ₂ (1 mol%)	O ₂	120	61.0 : 29.3 : 9.7	1.8

^a Reactions were performed under ambient lighting conditions for 24 hours (unless otherwise stated) under constant stirring, with 3 molar equivalents of benzaldehyde w.r.t. the number of PE repeating units present unless otherwise stated. ^b Under 1 atmospheric pressure delivered using a balloon. ^c Determined from the ¹H NMR spectra of the oxidised PE polymers (C₂D₂Cl₄, 80 °C) by relative integration of the peaks arising from CH–OH (3.6 ppm), CH₂COOH (2.3 ppm), CH₂C(O)CH₂ (2.4 ppm) and unreacted CH₂S (0.8–1.6 ppm). Spectra are shown in Fig. S3 to S16 in the ESI.† ^d DCH = dicyclohexyl.



slight diminution compared to that of Table 1, entry 1 is attributed to the less efficient O₂ mixing with the liquid-phase reaction upon scale-up. These control experiments demonstrated that benzaldehyde was essential for aerobic C–H oxidation to carbonyls on PE.

The properties of carbonyl-containing PE (from Table 1, entry 1) were compared against the pre-oxidised PE to evaluate the influence of the benzaldehyde-mediated oxidation. Water contact angle measurements showed a slight decrease in the contact angle from (101.5 ± 0.1)° to (99.2 ± 0.2)° after oxidation (Fig. S20†), which is consistent with a slight increase in the surface hydrophilicity of the polymer due to the presence of carbonyl groups. Although high-temperature GPC analysis revealed that some C–C chain scission occurred during the PE oxidation process (Fig. S21†), thermogravimetric analysis (TGA) of both polymers showed comparable degradation temperatures (*T_d*) (Fig. S22A†). Furthermore, differential scanning calorimetry (DSC) analysis revealed that the endothermic peak corresponding to the polymer melting temperature (*T_m*) did not shift considerably after oxidation (Fig. S22B†). These results indicated that the presence of carbonyl groups and changes in molecular weight distribution after oxidation did not adversely affect the stability of the PE towards thermal processing and melt properties of the oxidised polymer to a significant extent. With the versatile reactivity of carbonyls, there are ample opportunities for further chemical modifications of these PEs for transformation into functional polymers.

Finally, to verify that our benzaldehyde-mediated aerobic PE oxidation process could also be applicable to actual PE plastic waste, we reacted 300 mg of a commercial LDPE plastic bag with benzaldehyde at 120 °C under O₂. While the oxidised polymer product obtained after 24 hours was found to be similarly functionalised exclusively with carbonyl groups by ¹H NMR spectroscopy (Fig. S23†), a considerably higher TF of 2.4 was obtained. This could be attributed to the high degree of branching in LDPE, whose many tertiary carbon atoms are more reactive to activation by H-abstraction (*vide infra*), leading to more extensive subsequent radical chain scission and carbonyl formation (*vide infra*).

Mechanism of PE oxidation

The mechanism of PE oxidation by benzaldehyde was further probed through a series of experimental and computational studies. Firstly, we ruled out the involvement of triplet carbonyls generated by the irradiation of benzaldehyde in hydrogen abstraction from PE,^{32,33} as well as the contributions of singlet oxygen (¹O₂) produced by photosensitisation in PE oxidation,³⁴ as repeating the reaction in the dark did not decrease the resulting TF (Table 1, entry 8). Next, we determined that the auto-oxidation of benzaldehyde was responsible for PE oxidation by performing a negative control using furfural. Furfural undergoes auto-oxidation much more slowly compared to benzaldehyde, and it is known to proceed *via* a different mechanism which is not initiated by aldehyde H-abstraction³⁵ (Fig. S12C†), unlike the case with benz-

aldehyde.¹⁹ Indeed, no observable PE oxidation in O₂ was observed with furfural, even at a higher reaction temperature of 130 °C for 24 hours (Table 1, entry 9), despite some furfural oxidation occurring to form polyaromatics likely responsible for the dark colouration of the reaction mixture. Furthermore, when increasing quantities of benzyl alcohol—a known inhibitor of benzaldehyde auto-oxidation¹⁹—were added to benzaldehyde, the extent of PE oxidation was reduced considerably (Table 1, entries 10 and 11). Although the low TF of 0.3 (Table 1, entry 11) observed in the presence of 6 equivalents of benzyl alcohol could result from benzaldehyde dilution, we were able to rule out this effect by replacing the benzyl alcohol with a similar volume of 1,2,4-TCB solvent, which elicited a much higher TF of 0.9 (Fig. S24†). As the inhibitory effects of benzyl alcohol stem from intercepting the benzoylperoxy radical intermediates that play a key role in benzoic acid formation,¹⁹ these experiments suggested that these radicals, formed after initial formyl H-abstraction from benzaldehyde,³⁶ are likely primarily responsible for PE C–H oxidation.

Having gained some evidence that the oxidation was facilitated by radical species generated after the abstraction of the formyl hydrogen atom of benzaldehyde, we turned to computational modelling to determine which of such species were involved in the activation of PE. We also used modelling to gain insights into the exclusive carbonyl selectivity of the reaction, using *n*-pentane as a model compound for PE. § All calculations were performed using ORCA 5.0.3.^{37–39}

We first evaluated the reactivities of the various radical species known to be generated during benzaldehyde auto-oxidation,¹⁹ and their reactivities in hydrogen atom transfer (HAT) from both benzaldehyde and *n*-pentane (Fig. 3). The HAT from *n*-pentane by the benzoyl radical was found to proceed over a high activation barrier of 33.4 kcal mol^{−1} (**TS1**); hence this route is unlikely to be feasible for PE activation. Addition of O₂ to the benzoyl radical yields the benzoylperoxy radical, which was found to react with both *n*-pentane and benzaldehyde with almost equal reaction barriers (**TS2A** 28.5 and **TS3** 28.1 kcal mol^{−1}, respectively). This makes the benzoylperoxy radical a likely candidate for the active species in the PE activation, as it is consumed by both benzaldehyde and PE at similar rates.

Peroxybenzoic acid, generated from the HAT by the benzoylperoxy radical, would yield a benzoyloxy radical and a hydroxyl radical upon O–O bond homolysis. While the benzoyloxy radical was found to react with *n*-pentane with a low barrier of 19.2 kcal mol^{−1} (**TS4**), the HAT from benzaldehyde to the benzoyloxy radical was found to be barrierless; hence the concentration of the benzoyloxy radical would have been too low to be an active species in PE oxidation. Finally, both benzaldehyde and *n*-pentane undergo HAT to the hydroxyl radical without

§ We note that these preliminary computational studies should be interpreted qualitatively, due to the various limitations of using a short chain alkane as a model system for polyethylene (see ESI† for details)



The transfer of the electrophilic hydroxyl group of the peracid to the nucleophilic C-centred radical is highly exergonic, with the free energy of the alcohol and benzoyloxy radical being $-43.7 \text{ kcal mol}^{-1}$ downhill of the starting material. Subsequent abstraction of the alcohol C_{α} -H by the benzoyloxy radical proceeds without a barrier (see Fig. 3B), and this high reactivity can be attributed to the weakening of the C_{α} -H bond due to hydrogen bonding between the alcohol and the benzoyloxy radical.^{49–52} The barrierless abstraction of the C_{α} -H bond corroborates the experimental observation that no alcohols were observed in the final oxidised polymers. Finally, addition of O_2 to the carbon radical, followed by the elimination of a hydroperoxyl radical (TS2C), gives the product ketone. The reaction can then propagate through an attack of the hydroperoxyl radical on benzaldehyde.

Computational modelling also revealed useful insights into the lack of 1,2- or 1,3 diketones in the oxidised PE. Using 2-heptone as a model compound for a polyethylene chain bearing some ketones, we investigated the C-H activation step of the various positions along the 2-heptone chain by the benzoylperoxy radical (Scheme S1†). Although a HAT from the ketone's α -carbon to the benzoylperoxy radical leads to the most stable radical product due to carbonyl conjugation, the C_{α} -H activation barrier is high ($30.9 \text{ kcal mol}^{-1}$). Indeed, hydrogen abstraction barriers at all the positions ($C_{\alpha-\delta}$) are similar ($28\text{--}30 \text{ kcal mol}^{-1}$). This agrees with observations from prior studies, which report that the reactivity of electrophilic radicals with hydrogens near a ketone is kinetically disfavored.^{53–55} Thus, due to the absence of any specially activated methylene units on the carbonyl-containing PE towards HAT, methylene oxidation occurs at random along the PE chain.

Finally, we used computational modelling to investigate the reaction of peroxybenzoic acid with benzaldehyde, *via* a Baeyer–Villiger type mechanism. Baeyer–Villiger reactions can be acid-catalysed,⁵⁶ and the benzoic acid produced in the reaction might well facilitate such a reaction, which would compete with the hydroxyl transfer reaction described earlier. However, we found that the reaction barriers associated with such a reaction are too high ($56.7 \text{ kcal mol}^{-1}$ uncatalysed, 55.6 and $41.1 \text{ kcal mol}^{-1}$ catalysed); thus, the rate of consumption of peroxybenzoic acid by benzaldehyde can be considered insignificant (see Scheme S3† for details).

We then evaluated the influence of different benzaldehyde aromatic substituents on their efficacy for aerobic PE oxidation (see section S4†). Due to the high melting points of some of the resulting carboxylic acids beyond the reaction temperature, the reactions had to be performed in the presence of 1,1,2,2-tetrachloroethane (TCE) solvent to ensure PE solubility and effective stirring throughout their durations for access to O_2 .[¶]

[¶] Performing these reactions in the absence of TCE solvent resulted in the reaction solidifying after some time, which prevented stirring for mixing with O_2 . A control experiment where PE was stirred in TCE at $100 \text{ }^\circ\text{C}$ without any benzaldehydes under an O_2 atmosphere showed no discernible PE oxidative functionalisation.

The presence of TCE solvent resulted in less selective PE oxidation: even the reaction with benzaldehyde at a lower temperature of $100 \text{ }^\circ\text{C}$ resulted in additional chlorine functionalisation (3.9 ppm) in addition to isolated ketones. While isolated ketones remained the most abundant functional group in all cases, different benzaldehyde derivatives resulted in varying amounts of closely spaced carbonyls ($\delta \sim 2.7 \text{ ppm}$), esters (4.1 and 2.3 ppm), carboxylic acids (2.3 ppm), alcohols (3.6 ppm) and chlorine (3.9 ppm) substituents (Table S3†). We attribute this to the possibility of hydrogen and chlorine-abstraction from the haloalkane by the various reactive radicals^{10,36} formed during the course of the reaction. It is notable that when the reaction was performed using benzaldehyde in the presence of 1,2,4-TCB as mentioned earlier (*vide supra*), less selective carbonyl functionalisation was also observed (Fig. S24†). These findings showed that PE oxidation in neat benzaldehyde without additional chlorinated solvents clearly afforded superior carbonyl selectivity.

Generally, more electron-withdrawing substituents resulted in higher total degrees of PE functionalisation. As shown in Fig. 4, a good correlation was obtained when $\log_{10}(TF_R/TF_H)$ —the ratio of the TF values obtained with substituent R to that of benzaldehyde ($R = H$)—was plotted as a function of the Hammett substituent constant (σ_R).⁵⁷ While the electron-donating methoxy group of 4-anisaldehyde is expected to cause lower PE functionalisation, the exceptionally low TF observed on PE may be a result of competing oxidation of the methoxy groups of anisaldehyde. These findings further support our aforementioned mechanism, as more electron-withdrawing substituents are expected to increase the electrophilicity of the benzoylperoxy radical intermediates, making it more reactive for HAT from PE.⁵⁸

Compatibility with copper-containing oxidation catalysts

Having demonstrated the feasibility of catalyst-free aerobic PE oxidation with benzaldehyde, we then investigated the compat-

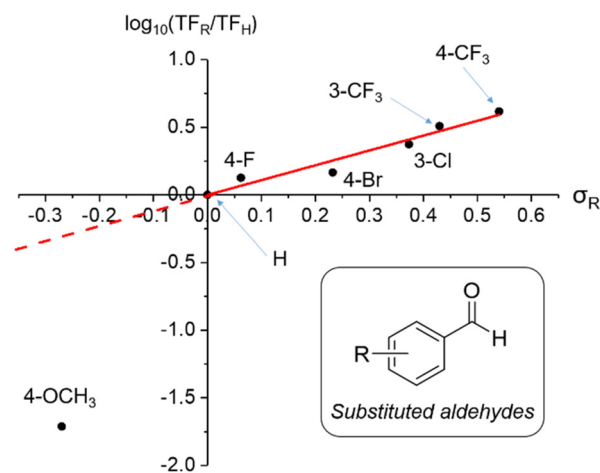


Fig. 4 Plot of $\log_{10}(TF_R/TF_H)$, the ratio of the TF values obtained when benzaldehyde bearing substituent R was used to that of benzaldehyde ($R = H$), as a function of the Hammett substituent constant (σ_R).



ibility of these reaction conditions with known oxidation catalysts. [CuCl₂-dicyclohexyl (DCH)-18-crown-6] (Table 1, entry 12) was chosen due to its known efficacy for alkane oxidation in O₂.⁵⁹ The ¹H NMR spectrum (Fig. S15†) of the resulting oxidised PE in the presence of this catalyst (1 mol% w.r.t. ethylene repeating units) revealed that other than carbonyls, a new prominent signal centred at $\delta = 2.30$ ppm was present, which we attributed to COOH groups due to the lack of a corresponding ester signal at ~ 4.1 ppm. FTIR spectroscopy (Fig. S25†) showed a C=O absorbance peak centred at 1724 cm⁻¹, which was considerably broadened compared with that of PE oxidised by benzaldehyde alone, as well as a prominent C–O absorption at 1248 cm⁻¹.|| These indicated that the presence of the [CuCl₂-DCH18-crown-6] complex could augment the degree of PE oxidation, also seen from the higher overall TF value obtained. Indeed, the likely presence of COOH groups also indicate that more extensive oxidative C–C chain cleavage occurred, which is further supported by high-temperature GPC analysis that showed considerable molecular weight reduction after oxidation (Fig. S21†). The efficacy of the crown ether complex for enhancing PE oxidation was evident when the reaction was repeated using anhydrous CuCl₂ alone (Table 1, entry 13), which gave a lower TF of 1.8, albeit with detectable OH, C=O and COOH functionalisation (Fig. S16†). Like the aforementioned metal-free PE oxidation (Table 1, entry 1), high-purity benzoic acid could be recovered after the reaction by recrystallisation from hot water. The ability to modulate the outcome of the benzaldehyde-mediated PE oxidation using metal catalysts further suggests the possibility of exploiting this green oxidation approach to upcycle PE into long-chain carboxylic acids, without the need for highly corrosive concentrated nitric acid⁶⁰ or nitrogen oxides⁶¹ as an oxidant. These long-chain carboxylic acids could find potential high-value applications as surfactants or chemical precursors for polymers and coatings.

Conclusions

In conclusion, we demonstrate a new and exceptionally simple approach for aerobic C–H oxidation of PE to achieve exclusive functionalisation with isolated carbonyl groups for the first time. Using just benzaldehyde as the reagent and bulk dispersant, with readily available O₂ as the stoichiometric oxidant, our approach bypasses the need for hazardous chlorinated solvents or stoichiometric organic oxidants typically required for PE post-synthetic chemistry. In fact, the presence of chlorinated solvents such as TCE was detrimental to achieving exclusive carbonyl selectivity. The potential of this method for minimal waste generation is evident from the easy isolation of the benzoic acid by-product in excellent yields and purity by recrystallisation from hot water for reuse in different applications. We also show that the extent and functional group

selectivity of PE oxidation can be modulated with the use of additional oxidation catalysts. Considering the versatility of carbonyls for further chemical derivatisation, this solvent-free method can offer new avenues for valorising waste PEs into functional materials for various applications for a sustainable materials economy.

Conflicts of interest

There are no conflicts of interest to declare.

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