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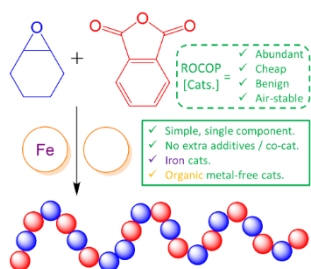
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Ring opening copolymerization using simple Fe(III) complexes and metal- and halide-free organic catalysts

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ABSTRACT. A comprehensive range of fourteen synthetically simple, air-stable and structurally diverse Fe(III) complexes, comprising of salalen, salen, salan and thioen frameworks, were applied as catalysts to the ring opening copolymerization of phthalic anhydride (PA) and cyclohexene oxide (CHO) without the need for extra additives, such as co-catalyst, as part of a newly discovered unary system. Alternating poly(1,2-cyclohexylene-1,2-phthalate) {poly(CHO-*co*-PA)} was obtained with reasonable molecular weights, narrow dispersities and with high % ester linkages. Structure-activity-relationships have been investigated and discussed. The most interesting discovery was when performing ‘ligand control’ ROCOP experiments (highlighting the importance of such checks in catalysis) that all these organocatalysts

outperformed their Lewis acidic Fe(III) analogues; these results are significant as a simplistic, metal- and halide-free, organocatalytic single component approach to ROCOP was developed. There are few examples of organocatalysts in literature, examples tending to rely on two component systems with harsher, air-sensitive chemicals and these results provide hope that more reactive, effective organo-initiators are possible in an area very much in its infancy, but will no doubt emerge and potentially prove vital to future sustainable polymerization research. Thermal properties were accessed *via* DSC analysis and, for the amorphous copolymers, the T_g values ranged by 35 °C from 100 °C to a respectable 135 °C.

INTRODUCTION

Globally, with our overreliance on diminishing fossil fuels, using alternative biomaterials, from biomass-derived resources and utilizing waste streams, as part of a sustainable, circular and bio-economy, will be vital to the future as we seek to replace petrochemical derivatives which dominate areas such as the plastics economy, *ca.* 99% in 2015 with the industry consuming *ca.* 6% of global oil production.¹⁻⁵ Due to the rapidly growing environmental concerns with their use, at both ends of their life cycle, there is need for change. To succeed, these future biopolymers will crucially need to hold similar or superior physical and chemical properties to act as more sustainable alternatives for any commercial application. Polyesters are one such ideal class of materials that hold potential because of their general biocompatibility, potential for being renewably sourced and the benign products formed from their facile hydrolytic degradation.⁶⁻¹¹ Their most common route of synthesis is in the step-growth polymerization of diacids and diols, which suffers from multiple drawbacks such as the requirement of forcing conditions to overcome the high activation energy barrier, precise stoichiometry of the monomers and complete removal of the produced water required to access high molecular weights and the overall process lacking polymerization control. The ring opening polymerization of cyclic esters to aliphatic polyesters is an alternative method and provides superior control but is limited by the availability of polymerizable cyclic monomers and sometimes unsuitable, inferior thermal properties. For example, polylactide (PLA) is the most commercially used

aliphatic ester formed *via* this method and holds many applications in beverage and food materials, packaging and for biomedical applications.^{3,12,21,13-20} However, it suffers from a low / modest glass transition temperature ($T_g = 50-72$ °C) which limits its suitability to replace petrochemically derived polymers, such as polystyrene ($T_g = 100$ °C), and therefore its use in further applications.^{12,16,29-31,20,22-28} Another promising and more versatile method is the ring opening copolymerization (ROCOP) of epoxides and anhydrides; this method is highly attractive as allows access to the combination of a broad range of both epoxides and anhydrides (both potentially obtained *via* renewable means for certain monomers) and to amorphous, rigid aromatic / semi-aromatic polyester backbones with varying and superior thermal and mechanical properties.²³ There is hence potential for facile, fine-tuning *via* the anhydride / epoxide combination sets for any polymeric application.²²

Despite the attractive benefits of iron, such as low toxicity (in case metal residue remains in the polymer products), high natural abundancy, low cost (commercially and industrially) and potential for air-stable systems, examples of Fe-mediated ROCOP in literature are scarce. Indeed, as far as we are aware, we only found five relevant and effective examples of Fe systems in literature for epoxide / anhydride ROCOP.^{6,32-35} Nozaki and co-workers briefly touched on Fe systems based on the corrole ligand framework with PPNC1 {*bis*(triphenylphosphoranylidene)ammonium chloride} co-catalyst but exploration focused on the manganese analogues.³² Following on from the high success achieved using salen ligand frameworks, with metals such as Al and toxic metals Cr and Co, Mundil *et al.* reported the first example of the ROCOP of epoxide and anhydride; specifically phthalic anhydride (PA) and cyclohexene oxide (CHO), using Fe(III)-salen-chloride complexes with either PPNC1 or DMAP {4-(dimethylamino)pyridine} co-catalyst to form alternating polyester.³³ However, it was shown that the co-catalysts being used solely were able to carry out the reaction more effectively at the employed reaction conditions, maintaining a 100% ester linkage, and the Fe complexes were in fact uncooperative with the PPNC1 co-catalyst and inhibiting overall reactivity. Likewise, this observation that PPNC1 can catalyze the polymerization has been reported in other cases.^{7,23,35-39} This was unlike the case for the Cr-salen-chloride complex that was employed as a benchmark

catalyst and showed cooperativity and enhanced activity when combined with co-catalyst.³³ Kleij and co-workers have made significant and interesting progress in this area using their highly effective Fe(III)-aminotriphenolate catalyst and varying both the epoxide and anhydride monomer sets to access more renewable, aliphatic or semiaromatic polyesters with high chemoselectivity and thermal properties.^{6,34} In 2016, using both their Fe(III)- and Al-aminotriphenolate catalysts, entirely alternating, aliphatic polyesters were afforded using CHO or propylene oxide (PO) with partially or fully renewably, synthesized tricyclic anhydrides. This was performed using mild reaction conditions (60 °C), PPnCl co-catalyst and either solvent-free conditions (for PO, reaction time = 3.5-18 h) or in toluene solvent (for CHO, reaction time 10-168 h). Through variation of the monomer, the fine-tuning of the T_g value was demonstrated across a remarkable 120 °C range from 66 to 184 °C; indeed to the best of our knowledge these values are the highest T_g values reported for entirely aliphatic polyesters to date.⁶ In 2017, focus shifted to the epoxides and, rigid PA or naphthalic anhydride (NA) were coupled with a range of renewable terpene oxides to form semiaromatic, fully alternating polyesters. The T_g values ranged and were tuned between 59 to 243 °C. Again the reaction conditions generally remained mild (65 °C) using a binary system with PPnCl co-catalyst and a low Fe catalyst loading (0.50 mol%) and reaction times between 24-100 h depending on the monomers employed.³⁴ Recently, Gao and co-workers further modified this aminotriphenolate ligand framework by introducing a rigid phenylene linker bridge between two such moieties to synthesize a range of dinuclear Fe(III) complexes that were applied, alongside their corresponding mononuclear analogue, to the ROCOP of CHO and PA or CO₂.³⁵ All the complexes were remarkably active and selective forming perfectly alternating polyester. The dinuclear complex bearing the 1,2-phenylene linker backbone and the mononuclear analogue were the most active and observed TOF values above 1100 h⁻¹ in neat conditions and above 240 h⁻¹ in toluene solvent both at 100 °C; the near identical reactivity observed between these two complexes suggested the synergistic interactions between the two Fe(III) centers in the dinuclear variant were minimal as a result from the significant steric hindrance of the growing polymer chain. However, there was cooperativity with the PPnCl co-catalyst in this study and the binary Fe(III) / PPnCl

systems were catalytically more active than PPnCl being applied solely.³⁵ Additionally, unlike that for Mundil, the PPnCl control, benchmark reactions did not produce fully alternating polyester and ether linkages were observed with an oligomeric molecular weight.³⁵

Recently, we reported the simple synthesis and application of a large range of air-stable, Fe(III)-acetate complexes, consisting of varying salalen, salan and salen ligand frameworks, for the selective coupling of CO₂ with multiple epoxides, predominately CHO, to exclusively form the *cis*-cyclohexene carbonate product (*cis*-CHC).⁴⁰ We have also reported the synthesis and application of Fe(III)-salalen {ONNO} and -thiolen-chloride {ONSO} complexes to both the isoselective ring opening polymerization (ROP) of *rac*-lactide (*rac*-LA) and CO₂ / epoxide coupling to again form cyclic organic carbonate (COC) products.⁴¹⁻⁴³ Due to the success we have found in these reactions, the limited examples of Fe-mediated ROCOP, and the growing importance of this area coupled with the benefits Fe holds, we decided to explore the coupling of PA and CHO herein. Additionally, with the large range of Fe(III) catalysts at our disposal, we wanted to partake in a comprehensive study using fourteen different structural frameworks to determine structure-activity-relationships; similar to that recently achieved by Kerton and co-workers in CO₂ / epoxide ROCOP to form polycarbonates, and as far as we are aware this has not been attempted to such scale before in this area.⁴⁴ Interestingly, we stumbled upon organo-initiated systems using the 'ligand' exclusively as will be presented. The use of simple metal-free, organic compounds as initiators has only recently attracted attention in polymerization chemistry and is certainly in its infancy for the area of ROCOP.^{7,45} With the benefits associated, it will no doubt grow in importance and potentially prove vital to our research endeavors for a sustainable future in the area of polymer chemistry.²³ This was recently well-reviewed by Dagorne, Le Bideau and co-workers.⁷

RESULTS AND DISCUSSION

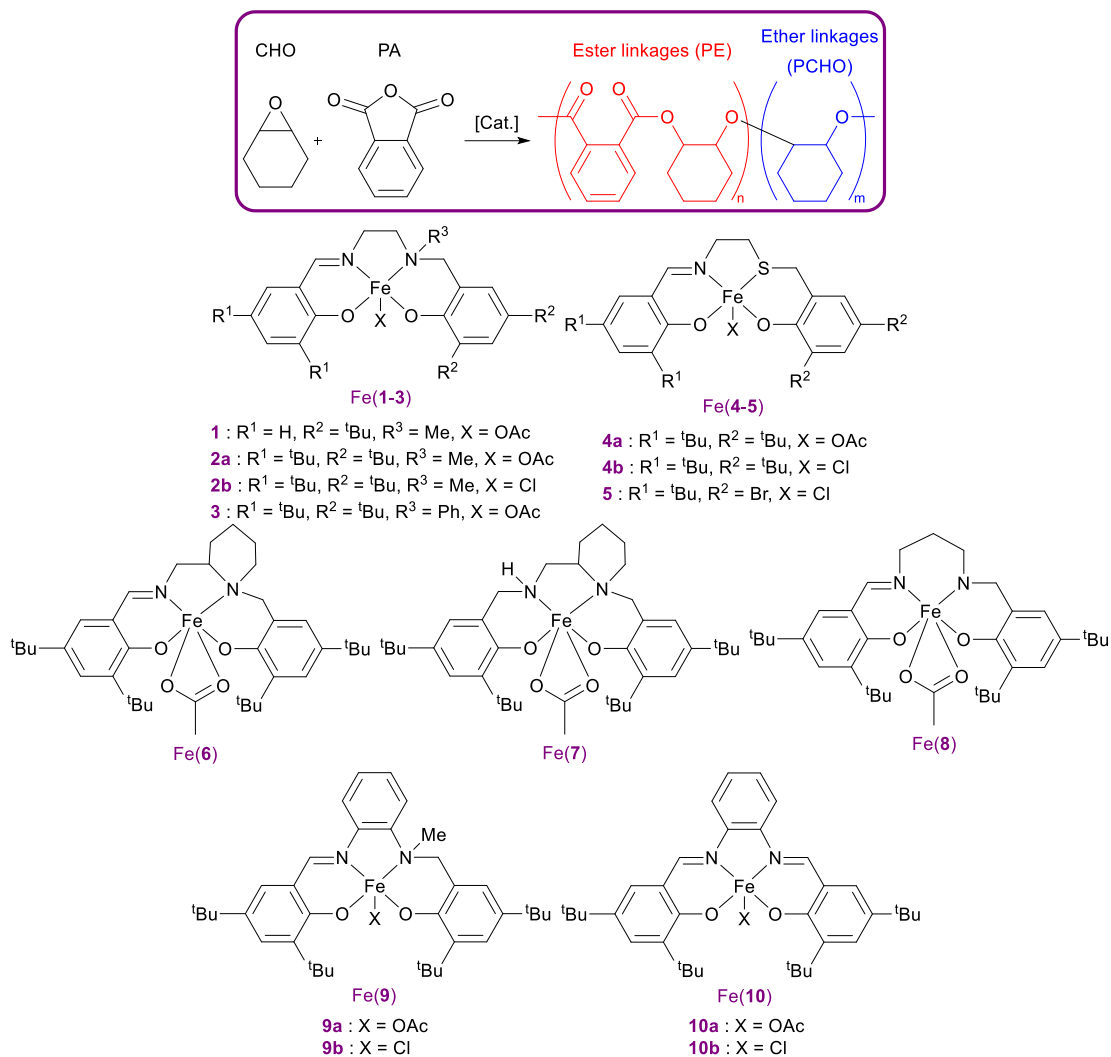
ROCOP of cyclohexene oxide and phthalic anhydride in toluene solvent. Initial investigations into the ring opening copolymerization of the internal epoxide, cyclohexene oxide (CHO) and aromatic phthalic

anhydride (PA) was conducted using Fe(7) catalyst and PPnCl co-catalyst as part of a binary catalytic system (see ESI, **Table S1**) to target the formation of the polyester, poly(1,2-cyclohexylene-1,2-phthalate) {poly(CHO-*co*-PA)}; as is commonly employed in literature for both Fe and other elements, in toluene solvent.³³ Although, the internal epoxide, CHO is a more challenging substrate compared to alternatives due to the high steric hindrance, this more rigid and sterically bulky framework allows access to polyesters with higher and more favorable T_g values. For this reason and because this monomer combination has been well explored and characterized, they were selected. Both substrates currently are not renewably sourced, but it has been shown both can be synthesized from either furans or 1,4-cyclohexadiene sourced from biomass.^{6,22,31,46–50} Fe(7) was chosen as recently we found it to be the most effective catalyst for the coupling of CO₂ with CHO to form the *cis*-CHC organic product exclusively.⁴⁰

Although moderate to high conversions and high degrees of ester linkage were observed after a few hours at 100 °C, low molecular weight, oligomeric polymer was produced. Additionally, it is important to note, the molecular weight increased as the CHO was further distilled and purified (from singly distilled to triply distilled); this agrees with that reported in literature.^{7,37,51} Also triply recrystallized PA using toluene solvent was found to be more effective than purification *via* hot filtration using chloroform and subsequent sublimation of the PA. It was discovered that the PPnCl could carry out the reaction solely; in agreement with other reports, and the [Fe] was not participating cooperatively with the PPnCl in the reaction.^{33,35,36} The rationale was while the PPnCl was more reactive than the [Fe], this was resulting in the oligomeric / low molecular weight polymer produced. There are examples in literature whereby co-catalyst; mainly for the purpose of initial ring opening of the epoxide, is not required.^{52,53} Williams' dimeric complexes using Mg and Zn are such an example and the acetate auxiliary ligands bear resemblance to our mononuclear Fe(III)-acetate catalysts.⁵²

Therefore, our hypothesis was the acetate auxiliary ligand in our case must have been able to initiate the reaction without the presence of PPnCl; albeit slower catalysis due to the use of a mononuclear catalyst and Fe in comparison, with higher molecular weight polymer growing on the Fe(III) center while

maintaining a high % ester linkages. The added benefit of this would also be the avoidance of an extra additive, trying to find simpler, 'greener' alternative catalytic systems such as using the abundant, non-toxic Fe and avoiding phosphine; a potentially endangered element in the future. This approach was successful and it was found after 3 days at 100 °C, [Fe] was able to catalyze the reaction, without any co-catalyst, in toluene solvent ([PA]:[CHO]:[Cat.]=[100]:[100]:[1]) to afford higher molecular weight polymer.



Scheme 1. The range of structurally diverse Fe(L)X initiators explored in this study for the simple alternating ROCOP of PA and CHO without any extra additives / co-catalyst. To note, when the ligands (L) are applied solely as organic initiators, these are the corresponding diphenol compounds and not diphenolate as is the case when complexed to Fe(III).

A range of structurally diverse Fe(L)X complexes (**Scheme 1**) were screened at these conditions to compare activities, molecular weights, dispersities and degrees of ester linkage (**Table 1**). Overall, although this approach is slower than the few alternative Fe systems in literature, high % ester linkages and reasonable molecular weight polymers were isolated without the need for co-catalyst by allowing the Fe more time to catalyze; there are scarce examples of metal systems without such additive and PPnCl is almost always required or used in conjunction with the metal catalyst.^{22,53,54} When discussing chemoselectivity or % ester linkages, with the structures of these two substrates it is possible to either form perfectly alternating polyester from sequential epoxide and anhydride ring opening copolymerization (ester linkages) or homopolymerization and sequential incorporation of only the CHO epoxide (ether linkages); therefore the catalytic system needs to be selective to target these desired ester linkages (**Scheme 1**). The PA conversion was determined by taking small aliquots of the crude reaction mixture and using ¹H NMR spectroscopy in CDCl₃ to compare the integrals of the observed aromatic resonance signals for unreacted PA and the polyester.^{33,52,55,56} To ensure any residual, paramagnetic Fe catalyst was removed, isolation of the purified copolymer was achieved *via* dissolving in CH₂Cl₂ and precipitating the white solid using acidified MeOH (1M, See ESI). The % ester linkages was determined using ¹H NMR spectroscopy in CDCl₃ on this polymer and integrating the observed resonance signals for the ester linkages respectively to the ether linkages.^{52,55} Williams' suggested using DMSO-d₆ to minimize overlap between the end groups for the poly(CHO-*co*-PA) and ether resonance signals; this was attempted in cases as a confirmation but the chemoselectivity values were equal here and the strong residual water peak in the DMSO-d₆ perturbed detection of the poly(CHO-*co*-PA) end group and, further to this, we found the polymer was unexpectedly less soluble in this solvent.⁵²

Table 1. Solution ROCOP of CHO / PA using Fe(L)X and organic initiators.

Entry	Catalyst (Cat.)	Framework class	PA conv. ^a (%)	Isolated yield (%)	% ester linkages ^b	$M_{n,theo}^c$ ($gmol^{-1}$)	M_n^d ($gmol^{-1}$)	\bar{D}^d
1	None	-	5	-	46	-	-	-
2	Fe(OAc) ₂	-	42	51	39	10,500	6100	1.24
3	FeCl ₃	-	- ^e	51	40	12,700 ^e	6400	1.05
4	Fe(1)	Salalen	93	82	92	23,100	11,250	1.14
5	2	Salalen	72	58	93	17,750	15,200	1.13
6	Fe(2a)	Salalen	43	38	92	10,750	10,300	1.21
7	Fe(2b)	Salalen	57	38	91	14,150	8900	1.04
8	Fe(3)	Salalen	58	61	47	14,450	9400	1.13
9	Fe(4a)	Thiolen	71	57	72	17,650	8600	1.15
10	Fe(4b)	Thiolen	53	32	95	13,200	13,750	1.08
11	Fe(5)	Thiolen	55	41	86	13,700	10,100	1.19
12	6	Salalen	89	77	95	21,950	16,200	1.15
13	Fe(6)	Salalen	41	33	91	10,250	8650	1.18
14	7	Salan	98	80	96	24,150	14,300	1.12
15	Fe(7)	Salan	45	49	41	11,250	6000	1.16
16	Fe(8)	Salalen	61	46	92	15,200	10,150	1.18
17	9	Salalen	77	56	95	19,000	19,600	1.12
18	Fe(9a)	Salalen	82	72	97	20,350	15,300	1.19
19 ^f	Fe(9a)	Salalen	39	44	49	9750	7350	1.21
20	Fe(9b)	Salalen	77	70	96	19,100	13,600	1.14
21	10	Salen	95	81	96	23,450	29,100	1.09
22	Fe(10a)	Salen	46	32	94	11,500	11,550	1.06
23	Fe(10b)	Salen	55	49	95	13,700	12,550	1.19

Conditions: 3 x recrystallized PA (0.3703 g, 2.5 mmol), 3 x distilled CHO (0.253 mL, 2.5 mmol), catalyst (1 mol%, 0.025 mmol), [PA]:[CHO]:[Cat.]=[100]:[100]:[1], toluene (1.0 mL), 100 °C, 3 days. ^a Determined by ¹H NMR spectroscopy (CDCl₃) by integrating the resonances of PA (δ 7.88–8.07 ppm) and the aromatic phenylene resonances in the polyester (δ 7.34–7.65 ppm). ^b Selectivity determined by ¹H NMR spectroscopy (CDCl₃) by integrating the resonances of the ester linkages (δ 5.04–5.26 ppm) and the ether linkages (δ 3.57–3.66 ppm) of the dried isolated polymer. ^c $M_{n,theoretical} = [(Conversion/100 \times [PA]/[Fe] \times M_r) + \text{end group MW from the corresponding auxiliary group of the complex (X) or whole structure if ligand (L)}] = [(Conversion/100 \times [PA]/[Fe] \times 246.26 \text{ gmol}^{-1}) + \text{end group MW}]$, assuming 100% ester linkages. ^d Determined *via* SEC (triple detection analysis) in THF solvent referenced against polystyrene standards with no correction factor. ^e $M_{n,theoretical}$ was calculated using isolated yield due to being unable to calculate PA conversion because of the highly paramagnetic FeCl₃ broadening the resonances of PA. ^f [PA]:[CHO]:[Cat.]=[100]:[600]:[1], 2 days.

Initially, control reactions using FeCl₃ or Fe(OAc)₂ synthetic metal precursor provided some activity but no control for the polymers' linkages; demonstrating the need for a ligand structural backbone to provide selective control (**Table 1**, entries 2 and 3). Using no catalyst and just both substrates resulted in no reactivity (**Table 1**, entry 1). Interestingly, having aromatic *tert*-butyl phenolate substituents or unsubstitution {Fe(**1**) vs. Fe(**2a**)} on the Fe(III)-salalen-acetate complexes made no influence on the % ester linkages with both resulting in high degrees of control (92%). Indeed, as would be expected, the less sterically hindered Fe(**1**) was more than twice as active and both produced reasonable molecular weights and narrow distribution {Fe(**1**), 93% PA conversion, $M_n = 11,250 \text{ gmol}^{-1}$, $\mathcal{D} = 1.14$ and Fe(**2a**), 43% PA conversion, $M_n = 10,300 \text{ gmol}^{-1}$, $\mathcal{D} = 1.21$ }. The *tert*-butyl substituted Fe(**2b**) chloride analogue; the complex that we previously reported to be highly selective for the ROP of *rac*-LA ($P_m = 0.80$), was more active, maintained the same % ester linkages and produced a better distributed polymer compared to Fe(**2a**) but was accompanied with a lower molecular weight {Fe(**2b**), 57% PA conversion, $M_n = 8900 \text{ gmol}^{-1}$, $\mathcal{D} = 1.04$ }.⁴¹ Installing an electron withdrawing phenyl group on the amine nitrogen donor atom ($R^3 = \text{Ph}$) also resulted in a higher activity but also poor selectivity (Fe(**3**), % ester linkages = 47%). Modifying this donor atom further and changing to a soft, hemilabile sulfur donor atom and a thiolen class of ligand backbone resulted in superior activity accompanied with a moderate degree of ester linkages for the Fe(**4a**) acetate complex (71% PA conversion, % ester linkages = 72%). The resulting polymerization remained controlled but yielded polymer with a reduced molecular weight {Fe(**2a**) vs. Fe(**4a**), $M_n = 8600 \text{ gmol}^{-1}$, $\mathcal{D} = 1.15$ }. Compared to the salalen backbone, changing to the chloride auxiliary group analogue for the thiolen, the opposite trend was observed with reactivity decreasing and a higher chemoselectivity (95%), molecular weight and more narrowly distributed polymer isolated {Fe(**4b**), $M_n = 13,750 \text{ gmol}^{-1}$, $\mathcal{D} = 1.08$ }.⁴² Attempting to

increase activity and the Lewis acidity of the Fe(III) center by introducing bromo-functionality to the Fe(III)-thiolen-acetate complex was unsuccessful and Fe(5) was both less active and selective (**Table 1**, entry 11).

Altering the ethylene ligand backbone and installing a rigid six-membered aminopiperidine ring into the salalen had a minimal influence on activity and selectivity, but the molecular weight was drastically reduced {Fe(2a) vs. Fe(6)}. Reducing the imine to an NH amine group and the corresponding salan Fe(7) complex slightly increased reactivity but a polymer with low % ester linkages and molecular weight was obtained (**Table 1**, entry 15). This result was surprising considering this complex was recently found to be the most effective catalyst for the coupling of CHO with CO₂ and the additional NH group was proposed to be advantageous in this case by possibly participating in additional H-bonding interactions with the substrates to improve activity, although this seems to have negatively impacted this reaction.⁵⁷ Alternatively, shifting to a more flexible propylene ligand backbone significantly increased the activity whilst maintaining high selectivity, reasonable molecular weight and narrow dispersity {Fe(8)}.

Most success was observed when a phenyl ring was employed in the ligand's backbone and these Fe(III)-salalen-acetate and -chloride complexes were the most active and selective (>96% ester linkages) systems studied {Fe(9a/9b), **Table 1**, entries 18 and 20}. The Fe(9a) acetate complex afforded the highest molecular weight observed for all Fe(III) catalysts and maintained a narrow distribution ($M_n = 15,300 \text{ gmol}^{-1}$, $\bar{D} = 1.19$). There was an attempt at decreasing the reaction time to two days using an excess of CHO ([PA]:[CHO]:[Cat.]=[100]:[600]:[1]), however the chemocontrol of the reaction was lost and significant ether linkages were formed (**Table 1**, entry 19). The corresponding phenyl bridged salen Fe(III) complexes were not as effective and active but still highly selective and resulted in reasonably high molecular weights {Fe(10a/10b), **Table**

1, entries 22 and 23}. Indeed, the combination of Fe(**10b**) and PPnCl or DMAP co-catalyst has already been reported by Mundil *et al.* at 110 °C in toluene ([PA]:[CHO]:[Cat.]:[Co-cat.]=[250]:[250]:[1]).³³ This usual binary method for ROCOP resulted in lower molecular weights (3700-9700 gmol⁻¹) and slightly broader dispersities ($\bar{D} = 1.27-1.33$) but dramatically quicker reaction times (1-5 h) compared to our method. Although, it was proven that PPnCl and DMAP could operate faster solely by themselves and the Fe(**10b**) was uncooperative with the PPnCl co-catalyst and actually inhibiting overall reactivity; therefore the [Fe] here was most likely not catalyzing the reaction. The blank reactions without co-catalyst and only [Fe] were tried but for only 24 h and hence no activity was observed for the two Fe-salophen complexes; however the Fe complex with a diaminocyclohexane backbone proved it was possible in 24 h and observed moderate reactivity with reasonable molecular weight but broader distribution (64% conversion, $M_n = 9700 \text{ gmol}^{-1}$, $\bar{D} = 1.52$).³³

The most interesting discovery of the study was realized when ligand control reactions were performed and it was found that they were more effective as organocatalysts than the Fe(III) complex analogues. North and co-workers recently reported examples of salophen ligands (salen ligands with 1,2-diaminophenyl bridges) that were able to carry out CO₂ / terminal epoxide coupling, without any metal and/or halide co-catalyst, *via* a proposed intramolecular H-bonding, dual activation mechanism.⁵⁷ Whereby, the hydrogen atoms are shared between the imine and phenol groups on each side of the phenyl bridge. These structures acted as organocatalysts *via* hydrogen-bonding interactions with the incoming substrate molecules. While we did not observe activity with our previously reported salalen and salan ligand control reactions for CO₂ / CHO coupling, this reactivity *via* H-bonding interactions and a dual activation mechanism seems to be at play for this ROCOP reaction.⁴⁰ This in contrast to the more traditional metal-mediated ROCOP

mechanism; generally accepted in literature, believed to be occurring when the Lewis acidic Fe(III) complexes $\{\text{Fe}(\text{L})\text{X}\}$ were applied as the initiators and ring opening of the monomer *via* the labile, auxiliary acetate or chloride ligands (X).^{22,31}

Additionally, the phenyl bridged ligands / organocatalysts were the most effective here and these observations agree with that discussed by North (indeed salophen **10** was one such example used by North for CO₂ / epoxide coupling) that the phenyl moiety seems to be crucial; and more specifically how the diamine plane aligns and arranges itself in relation to the phenol rings and the point group symmetry (*C*₁ vs. *C*₂ symmetry) to maximize the H-bonding interactions. These factors may contribute to differences in catalytic activity.⁵⁷ Ligands / organocatalysts: **2**, **6**, **7**, **9** and **10** all observed high conversions (72-98% PA conversion), % ester linkages (93-96%), narrow dispersities ($\text{Đ} = 1.09\text{-}1.15$) and, despite no presence of a Lewis acidic metal center for the growing polymer chains, reasonably high molecular weights ($M_n = 14,300\text{-}29,100 \text{ gmol}^{-1}$). The rigid aminopiperidine salalen framework was moderately more active than the salalen with the ethylene backbone (**2** vs. **6**). Unlike for the corresponding Fe(III) complexes, using the reduced aminopiperidine with an NH group (salan, **7**) further improved reactivity (98% PA conversion), as would be expected from the potential for additional H-bonding interactions occurring with the PA and CHO, and maintained the high selectivity (96%). As was the case for the Fe(III) complexes, the salalen and salen frameworks with phenyl bridged backbones were the most effective with high selectivity, activity and afforded the highest molecular weight polymer. Remarkably, the molecular weight observed using the salophen **10** was 29,100 gmol⁻¹ and the phenyl salalen **9** was 19,600 gmol⁻¹ while narrow distribution was maintained.

As far as we are aware, this is the first-time these simple types and classes of ligand; salen, salalen, salophen and salan, have been applied to epoxide / anhydride ROCOP. This is despite the

corresponding, analogous metal catalysts, covering a range of elements, being heavily used.^{33,53,54,56,58–60} These results seem significant as a simplistic, metal- and halide-free, organocatalytic approach has been stumbled upon that forms highly alternating polyester with low dispersities and reasonable molecular weight. This provides hope that certainly other, more reactive organic compounds may be efficient initiators for ROCOP. Additionally, there are few examples of organocatalysts in literature and these tend to rely on two component systems (for example Lewis pairs) and harsher, air-sensitive chemicals based on phosphine and boron.^{7,23,64–68,36–39,45,61–63} Whereas here, there is only one component with no extra additives. Of course, as was the case for North, this further highlights the need for ligand control reactions throughout all catalysis studies.⁵⁷ The area of metal-free, organo-initiators for copolymerization is in its infancy and will no doubt emerge, and potentially prove vital to future sustainable polymerization research.^{7,23,45}

DOSY NMR analysis confirmed the copolymers isolated were one polymeric species and MALDI-ToF analysis provided evidence that there were ester and ether linkages present. However, the systems were complicated and a range of potential end groups were proposed relating to the auxiliary ligands (X = OAc or Cl) or hydrolysis and chloro-functionalization; indicative of chain transfer reactions occurring upon termination and isolating the polymers with the acidified MeOH / HCl work-up (See ESI, **Figures S37-S42**), or possibly cyclohexane / cyclohexene from potential Meerwein-Ponndorf-Verley reduction / Oppenauer oxidation (MPVO) side reactions.^{35,52,62,69} IR analysis was consistent with literature (**Figures S23 and S24**).³³

ROCOP of cyclohexene oxide and phthalic anhydride in neat cyclohexene oxide. In an effort to reduce the reaction time, because the phenyl bridged frameworks were the most effective, these were applied to neat reaction conditions using CHO in excess (800 eq.) to act as both the substrate

and solvent (**Table 2**). It is shown in literature that neat conditions can substantially increase the rate of reaction and in cases improve selectivity to ester linkages.^{35,52} Fe(**9a**) was initially explored to gauge the length of reaction time required (**Table 2**) and it was found that the 3 days could be significantly reduced to 30 h to result in complete reactivity (100% PA conversion). It was observed that the crystalline PA was more soluble in the neat CHO mixture and this could contribute to the enhanced reactivity. However, this was a less controlled polymerization, compared to the solution ROCOP reaction in toluene solvent (**Table 1**, entry 18), and was accompanied with broadening in the resonances in the ether linkage region resulting in a decreased selectivity (69% ester linkage).⁵⁵ A higher molecular weight polymer was observed, compared to that in toluene conditions and a narrow dispersity was still achieved ($M_n = 18,900 \text{ gmol}^{-1}$, $\mathcal{D} = 1.20$ vs. **Table 1**, entry 18). Reducing the reaction time to 24 h resulted in a lower PA conversion of 34%; indicating for this particular initiator the optimum reaction time falls between this 24-30 h period, together with a significantly lower ester linkage selectivity and molecular weight. Interestingly, the SEC analysis for the 24 h reaction observed 3 peaks in the chromatogram (**Figure S16**); an unknown extra peak along with the usually observed bimodal peak that is common in literature and was also the case for the reactions in toluene solvent (**Table 1** and see ESI).^{33,35,37,70} This was also observed when attempting to reduce the temperature to 80 °C for 3 days (30% PA conversion) to unsuccessfully improve selectivity (**Figure S17**). This extra peak cannot result from a separate PCHO polyether species as DOSY NMR analysis on the polymers afforded from both toluene solvent and neat conditions showed the ether and ester resonances being part of the same, single polymer entity. However, this extra peak does disappear for the 30 h reaction at 100 °C (100% PA conversion, **Figure S18**) implying the possibility that chain exchange reactions were occurring and this is consistent with the MALDI-ToF analysis; where complicated systems, with

multiple series of ether linkages, with a range of potential end groups were observed (See ESI, **Figures S43** and **S44**).

All the phenyl bridged structures, both the Fe(III) complexes and ligands solely, were screened at this 30 h, neat reaction condition (**Table 2**). The chloride analogue Fe(**9b**) was both less reactive and selective and, unlike for the toluene reactions, the organocatalyst **9** was as active with the same % ester linkages but afforded a lower molecular weight polymer compared to both the Fe(III) complexes (**Table 2**, entry 1 vs. entries 4 and 5). All the corresponding phenyl bridged salen variants were not as effective as the phenyl bridged salalen frameworks and all reactions were similar; **10** being disappointing in expectation from the toluene reaction (**Table 1**, entry 21), the result being half as active as Fe(**10a/10b**). Additionally, along with the lower PA conversions (both 66% PA conversion), three peaks were again observed in the SEC analysis with only one species observed *via* DOSY NMR. The reduced control in the polymerization, for the reactions in the neat compared to in toluene solvent, is evident in the MALDI-TOF analysis where multiple series with a range of potential end groups were observed. Ether linkages are most common, in agreement with ¹H NMR spectroscopy, but ester repeating units are noted in cases; however, this may be related to their propensity to ionize and therefore not representative of the actual polymer sample. Overall, despite the % ester linkages dropping significantly in comparison (45-69%) to the toluene reactions, the neat reactions are considerably faster (30 h) and reasonable molecular weights are achieved while narrow distribution was maintained ($M_n = 10,100-18,900 \text{ gmol}^{-1}$, $\text{Đ} = 1.10-1.35$).

Table 2. Neat ROCOP of CHO / PA using Fe(L)X and organic initiators.

Entry	Catalyst (Cat.)	Temp. (°C)	Time (hours)	PA conv. ^a (%)	Isolated yield (%)	% ester linkages ^b	$M_{n,theo}^c$ (gmol ⁻¹)	M_n^d (gmol ⁻¹)	\bar{D}^d
1	9	100	30	100	97	69	25,250	12,500	1.17
2	Fe(9a)	100	24	34	51	24	8550	8100	1.67
3	Fe(9a)	80	72	30	44	20	7650	5750	2.46
4	Fe(9a)	100	30	100	95	69	24,800	18,900	1.20
5	Fe(9b)	100	30	74	86	45	18,350	15,750	1.17
6	10	100	30	32	24	49	8450	10,400	1.10
7	Fe(10a)	100	30	66	71	50	16,400	13,250	1.28
8	Fe(10b)	100	30	66	74	49	16,400	10,100	1.35

Conditions: 3 x recrystallized PA (0.3703 g, 2.5 mmol), 1 x distilled CHO (2.0 mL, 20 mmol), catalyst (1 mol%, 0.025 mmol), [PA]:[CHO]:[Cat.]=[100]:[800]:[1]. ^a Determined by ¹H NMR spectroscopy (CDCl₃) by integrating the resonances of PA (δ 7.88–8.07 ppm) and the aromatic phenylene resonances in the polyester (δ 7.34–7.65 ppm). ^b Selectivity determined by ¹H NMR spectroscopy (CDCl₃) by integrating the resonances of the ester linkages (δ 5.04–5.26 ppm) and the ether linkages (δ 3.26–3.67 ppm) of the dried isolated polymer. ^c $M_{n,theoretical} = [(Conversion/100 \times [PA]/[Fe] \times M_r) + \text{end group MW}]$, assuming 100% ester linkages. ^d Determined *via* SEC (triple detection analysis) in THF solvent referenced against polystyrene standards with no correction factor.

Thermal properties of the copolymers. Thermal analysis on a range of selected copolymers samples, *via* differential scanning calorimetry (DSC), confirmed the polyesters were, as expected, amorphous with the lack of crystallization temperature (T_c) and melting temperature (T_m) peaks (**Table 3**). The T_g values were above the desired 100 °C, reasonably ranged from 100-135 °C and similar to others in literature.^{22,23,34–37,52,60,71,72} The results were interesting and revealed that in this study that the T_g values generally depended on not only the % ester linkages and molecular weight; as is commonly focused on in the literature, but also subtle changes in the dispersity and therefore

a balance of all three factors. Indeed, and concentrating on the copolymers obtained from solution ROCOP, the three highest values observed were 135 °C using Fe(**10a**), 131 °C using Fe(**9b**) and 130 °C using **10**, all with the narrowest distributions ($\mathcal{D} = 1.06-1.14$). However, this explanation falls short when considering the particularly disappointing result using **9** with the second highest molecular weight observed, high % ester linkages and narrow distribution. The value with **10** was promising considering the organo-initiator nature and is competitive with other organic examples reported in literature.^{23,36,37,65} The findings become more complicated when shifting to the neat ROCOP copolymers. Despite the low % ester linkages and broader dispersities, the T_g values were higher than expected and ranged between 110-126 °C. MALDI-ToF analysis displayed significant polyether linkages and complicated fragmentation patterns, however, pristine PCHO is reported to have a dramatically lower T_g value of around 67 °C therefore there must still remain regions of significant poly(CHO-*co*-PA) in the statistical copolymer to result in these >100 °C T_g values. Darenbourg proposed that a small degree of cross-linking can dramatically increase the T_g value when applying a binary Cr(III)-salen-chloride and PPnCl catalyst system and this could account for inconsistencies in our trends if it was occurring and why our system thermally outperformed Darenbourg's in this instance ($T_g = 48$ °C, $M_n = 18,000$ gmol⁻¹, $\mathcal{D} = 1.13$, % ester linkages = >99%).⁵⁶ This is in agreement with that recently reported by Kleij and co-workers where, using an Fe(III)-aminotriphenolate and PPnCl catalyst system, it was observed that the afforded crosslinked poly(β -elemene dioxide-*alt*-phthalic anhydride) displayed a higher T_g value than that of the linear, cross-link-free analogue synthesized *via* post-modification ($T_g = 125$ °C and 97 °C respectively).⁷³ Furthermore, Williams' mentions their T_g values may have been lower due to unoptimized purifications and so our CH₂Cl₂ / acidified MeOH purification protocol may also play a small factor here.⁵²

Table 3. Thermal properties of selected polymers.

Entry	Polymer	Catalyst (Cat.)	% ester linkages	M_n (g mol ⁻¹)	\bar{D}	T_g (°C)	T_d (°C)
1	Table 1 , entry 6	Fe(2a)	92	10,300	1.21	125	358
2	Table 1 , entry 17	9	95	19,600	1.12	106	355
3	Table 1 , entry 18	Fe(9a)	97	15,300	1.19	100	355
4	Table 1 , entry 20	Fe(9b)	96	13,600	1.14	131	356
5	Table 1 , entry 21	10	96	29,100	1.09	130	356
6	Table 1 , entry 22	Fe(10a)	94	11,550	1.06	135	351
7	Table 1 , entry 23	Fe(10b)	95	12,550	1.19	124	350
8	Table 2 , entry 1	9	69	12,500	1.17	110	354
9	Table 2 , entry 4	Fe(9a)	69	18,900	1.20	122	355
10	Table 2 , entry 5	Fe(9b)	45	15,750	1.17	114	354
11	Table 2 , entry 7	Fe(10a)	50	13,250	1.28	126	345
12	Table 2 , entry 8	Fe(10b)	49	10,100	1.35	120	341

CONCLUSION

To conclude, fourteen air-stable, synthetically simple Fe(III) complexes, consisting of salalen, salen, salan and thioen frameworks, were applied to CHO / PA ROCOP in toluene in a newly discovered, single component system with the need for no extra additives or co-catalyst. A more comprehensive range of complex frameworks were screened for solution ROCOP in an attempt to ascertain structure-activity-relationships and insight. Examples of Fe-mediated ROCOP in literature are extremely scarce despite the attractive benefits of the element. Alternating poly(CHO-*co*-PA) was isolated with high degrees of ester linkages, narrow distributions of chain length and reasonable molecular weights and Fe(**9a**) was particularly promising. The most interesting discovery of the study was realized when ligand control reactions were carried out and it was found that they were more effective as organocatalysts than the Lewis acidic Fe(III) complex

analogues. As far as we are aware, this is the first-time these simple classes of ligand have been applied to epoxide / anhydride ROCOP and bears resemblance to work recently conducted by North using salophen organocatalysts for CO₂ / epoxide coupling.⁵⁷ These findings seem significant as a simplistic, metal- and halide-free, organocatalytic approach has been investigated that forms modest to high molecular weight alternating polyester with low dispersities with no need for a nucleophilic co-catalyst. This area is very much in its infancy, but will no doubt emerge, and potentially prove vital to future sustainable polymerization research.^{7,45} Currently, there are few examples of organocatalysts in literature and these tend to rely on harsher and more air-sensitive two component systems and these results provide hope that certainly other, more reactive organic compounds out there may be more efficient initiators for ROCOP. Of course, it also reinforces the importance of ligand control reactions. Additionally, there is also potential to access higher molecular weights *via* further purification of the monomers, such as using Greiner and co-workers' NaH / MeI method of purifying epoxide to remove diol impurities.^{37,51} Reactions were attempted in neat, solvent-free conditions but unfortunately this resulted in significantly reduced control in the polymerization and ether formation. Thermal properties were accessed *via* DSC analysis and the poly(CHO-*co*-PA) was found to be amorphous with T_g values ranging from 100 °C to a respectable 135 °C. These values were proposed to depend on the subtle balance of a higher molecular weight and % ester linkages but also crucially a narrow dispersity. It was also possible small degrees of cross-linking was at play to account for discrepancies in trend.

ASSOCIATED CONTENT

Supporting Information. The Electronic Supporting Information (ESI) is available free of charge on the ACS Publications website. Experimental details, general considerations and procedures, the initial investigations into solution ROCOP, NMR spectra and polymer

characterization *via* NMR, IR and MALDI-ToF spectra, SEC chromatograms, DSC traces are provided. (PDF)

Conflicts of interest.

There are no conflicts to declare.

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Author Contributions

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