



Zinc {ONO} complexes for the chemical recycling of PET and PLA

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ABSTRACT

Nine {ONO} ligands were prepared and treated with ZnEt₂ to form a range of complexes. The resulting complexes were characterised in solution through ¹H and ¹³C{¹H} NMR spectroscopy, and in the solid state through single-crystal XRD and elemental analysis. Moderate reactivity towards lactide polymerisation was demonstrated, with hydroxyl complexes reaching high conversion in 1–2 minutes at 300: 1: 1. All complexes successfully degraded PLA to methyl lactate and the effect of reaction time, temperature and catalyst loading was explored. Zn(4)₂ successfully produced ethyl and n-butyl lactate and was shown to work in ambient conditions, albeit with reduced yield and selectivity. The production of BHET from waste PET was demonstrated with a selection of the most active catalysts. Zn(4)₂ was shown to be capable of sequential PLA/PET degradation and to be tolerant of HDPE/PVC contaminants.

1. Introduction

Synthetic polymers are an incredibly valuable class of materials that have revolutionised almost every aspect of modern life [1]. However, there are serious environmental concerns associated with the production and disposal of these materials. Most commodity plastics are based on crude oil, the extraction and processing of which contribute greatly to climate change and global warming. At the other end of the life cycle, there are currently inadequate disposal methods for the enormous volume of plastic waste generated each year. As of 2017, it was estimated that 6300 Mt of plastic waste had been generated of which 79 % had accumulated in the environment or in landfill, causing immense ecological damage across most ecosystems and trophic levels [2–5]. Only 9 % of the total waste volume was recycled, and this was almost exclusively through mechanical processes, inevitably leading to material downcycling and eventual disposal after a finite number of cycles [6].

In contrast to the linear economy model described above, it is imperative to bring about a circular economy for polymers with the goal of retaining the inherent value and physical properties of the initial polymer over a theoretically infinite number of cycles. This could negate the effects of accidental release into the environment and create an intrinsic economic incentive for industry to take responsibility for their post-consumer waste [7]. This switch to a circular economy approach is

being further incentivised by changes to legislation such as Extended Producer Responsibility (EPR) [8] in the UK and EU directive 2019/904 [9].

One important step to realising a more sustainable relationship with plastics is the adoption of chemical recycling, wherein polymers are broken down chemically to give value added products (chemical upcycling or degradation) or virgin monomer. The latter being commonly known as depolymerisation or chemical recycling to monomer (CRM). Both of these processes fulfil the requirements of a circular economy whilst retaining, or enhancing, the value of the original product over an unlimited number of cycles [10].

Polyesters constitute an important class of commodity plastics and are ideal targets for chemical recycling due to the susceptibility of ester groups towards nucleophilic attack reactions such as alcoholysis. One increasingly important bio-renewable polyester is polylactic acid (PLA). It has many attractive properties, such as renewable feedstocks, biocompatibility and material properties competitive with polyethylene terephthalate (PET) and polystyrene (PS) for certain applications [11–14]. PLA is increasingly used as a packaging material and has also found extensive use in the biomedical industry. The most common industrial synthesis is through the ring-opening-polymerisation (ROP) of L-lactide catalysed by Sn(Oct)₂. [15] Research into the production of PLA has focused on developing more benign initiators and the improvement

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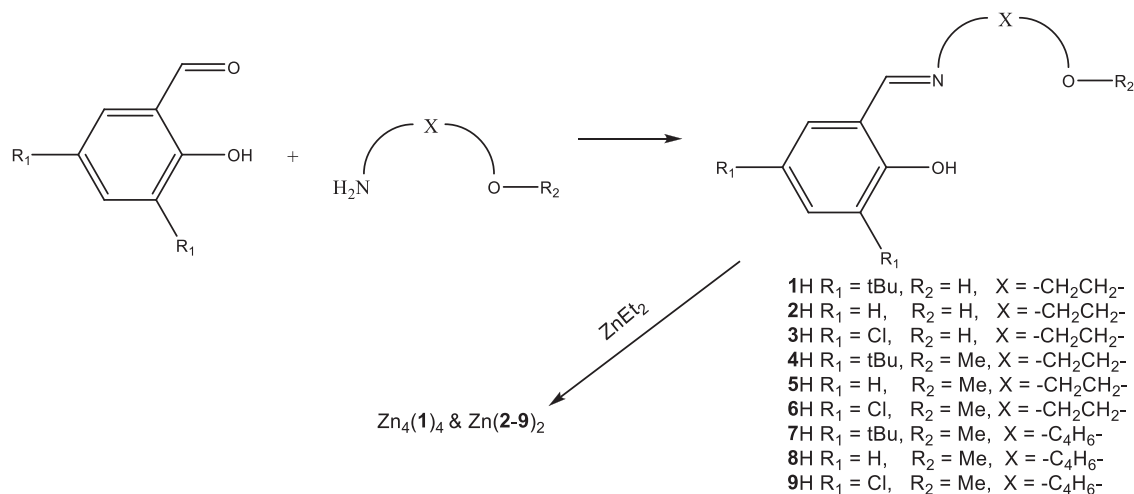
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Scheme 1. Synthesis of {ONO} ligands and Zn(II) complexes.

of physical properties through the stereoselective polymerisation of *rac*-lactide. There are literature examples of metal initiators from across the periodic table, including: Group I [16–18], Mg/Ca [19–22], Group IV [23–25], Fe [26–31], and group XIII.[32–36]

In recent years, zinc complexes have shown incredibly high activity for lactide polymerisation, in some cases comparable to Sn(Oct)₂. [27, 37–41] Our group has produced several zinc monophenolate complexes capable of rapid lactide polymerisation at low catalyst loadings [39–43]. Complexes based on propylenediamine monophenolate ligands achieved nearly full conversion of *L*-lactide in one minute at a ratio of [LA]: [Zn]: [BnOH] = 10,000: 1: 100 under solvent-free conditions [40]. Similar activity was recorded for a phenylene-bridged thioether complex with an unsubstituted phenolate group which achieved a turnover frequency of 249,000 h⁻¹. [43] Zinc complexes based on guanidine ligands have also displayed excellent activity towards lactide ROP [27,37,38, 44–46]. A zinc bisguanidine complex reported by Herres-Pawlis and co-workers was shown to be more active than Sn(Oct)₂ and produced highly crystalline PLA from technical grade lactide [44]. The same group has subsequently published a hybrid bisguanidine zinc complex based on a TMGeech ligand that outperformed Sn(Oct)₂ by a factor of ten in toluene. [47]

The alcoholysis of polyesters, particularly PLA and PET, has been extensively explored using zinc complexes [39–42,48–50]. Short-chain lactate esters find use as green solvents, food additives and synthetic precursors, and can also be converted to lactide for the synthesis of virgin PLA [51]. Many of these complexes have also been applied to the glycolysis of PET to bis(2-hydroxyethyl terephthalate) (BHET), comprising one of the raw ingredients for fresh polymer. Propylenediamine-based monophenolate complexes were capable of full PLA conversion in 30 minutes producing an 81 % yield of methyl lactate (Me-LA) [40]; this significantly outperformed the ethylenediamine-based analogue, suggesting an active role for the free amine group associated with this complex [41]. The same complex was able to break down PET with benzyl alcohol and an initial attempt at sequential degradation was reported. Similar complexes bearing a salan-type donor were reported by Payne and co-workers and the most active example gave a Me-LA yield of 76 % after 3 h at 50 °C at 8 wt% catalyst loading [49]. The upcycling of several polyesters and polycarbonates was also reported including PET and BPA-PC. Similar half-salan complexes with an ethyl spacer between the nitrogen donors were also shown to degrade PLA, PET and PCL [50]. A high rate was observed towards PLA methanolysis ($k_{app} = 0.23 \text{ min}^{-1}$) giving 85 % Me-LA yield after 30 minutes at 50 °C. Lamberti *et al.* reported {ONN} zinc monophenolate complexes with a pendent pyridine donor [52]. Room-temperature degradation was achieved over 2 hours with the

most active catalyst giving 100 % conversion of PLA and 74 % yield of methyl lactate.

One significant drawback of mechanical recycling is an intolerance of mixed plastic feedstocks which are unavoidable when dealing with realistic waste streams or when considering products based on multiple plastics [53]. Wang *et al.* used a Zn(HMDS)₂ catalyst to depolymerise polymer mixtures including PLA, PET, PBS and PBAT [54]. Selectivity was achieved through temperature control and a distinction was established between sequential depolymerisation, where different polymers are degraded in sequence with intermediate product removal steps, and “one-pot” depolymerisation where a mixture of polymers are degraded simultaneously and their products are separated downstream. [54] Klankermeyer and co-workers developed a Ruthenium catalyst for sequential hydrogenolysis of polyesters [55]. PLA was converted to 1, 2-propanediol without affecting PET which could be collected and depolymerised at an increased temperature. A three-component sequential glycolysis from the Dove group successfully degraded PLA, BPA-PC and PET with high conversions and excellent selectivity based on temperature and the catalyst choice. Despite all being commercially available, the necessity of adding three separate catalysts is a drawback of this approach [56]. Saito *et al.* used a simple organocatalyst to show that PET could be depolymerised in the presence of less reactive polymers such as PE, PP and cotton [57]. This is important as, in many cases, products contain plastics that are unsuitable for chemical recycling such as a PET drinks bottle with a HDPE lid.

Herein, we present a series of nine zinc monophenolate complexes with the potential for {ON} or {ONO} coordination depending on the role of the ether/hydroxyl pendant groups (Scheme 1). The complexes vary in monophenolate substitution, alkyl or aryl linkers and pendant donor. The complexes are characterised through ¹H NMR, ¹³C{¹H} NMR, elemental analysis (CHN) and single-crystal XRD where possible. The activity of these complexes towards *rac*-lactide polymerisation and the degradation of commercial polyesters is described.

2. Experimental

2.1. Materials

All chemicals were commercially obtained from Sigma-Aldrich and used as received, except for *rac*-lactide, which was recrystallised from dry toluene and stored under argon. PET samples were obtained from a Fanta™ bottle, washed with water and air-dried prior to use. HDPE and PVC were taken respectively from the cap and label of the same bottle. PLA samples were taken from Vegware™ cups and were not washed or dried prior to use. All polymers were cut into small pieces (approx. 5

×10 mm) prior to reaction. For the synthesis of metal complexes under anhydrous conditions, dry solvents, MBraun LABmaster dp glovebox, standard Schlenk line techniques and oven-dried glassware were used. Dried and degassed reaction solvents, used in the preparation of these complexes, were collected under inert gas conditions from a Solvent Purification System (SPS).

2.2. Analysis

^1H NMR spectra of ligands, complexes and polymerisations were recorded on a Bruker 400 II MHz or 500 MHz instrument and referenced to residual solvent peaks. Polymerisation conversion was recorded from the integration of the methine region of the polymer (5.12 – 5.20 ppm) against that of the monomer (4.94 – 5.01). The tacticity of polymers was determined from its $^1\text{H}\{^1\text{H}\}$ NMR spectrum, decoupling from the polymer doublet at 1.62 ppm. $^1\text{H}\{^1\text{H}\}$ NMR was recorded on a Bruker AV 400 MHz spectrometer. The following abbreviations are used in the report of spectra: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; m, multiplet.

Electrospray ionisation (ESI) mass spectra of ligands were collected using a MicroToF electrospray quadrupole time-of-flight mass spectrometer, with the sample dissolved in acetonitrile at approximately $1\ \mu\text{g mL}^{-1}$ concentration. Spectra were recorded in negative loop injection mode set for a range of 50 – 1500 m/z .

GPC was carried out on an Agilent 1260 Infinity series instrument at $1\ \text{mL min}^{-1}$ at $35\ ^\circ\text{C}$ with a THF eluent using a PL gel $5\ \mu\text{m}$ MIXED-D 300 × 7.5 mm column. Detection was carried out using a differential refractive index detector (referenced to 11 polystyrene standards of narrow molecular weight, ranging from M_w 615 – 568000 Da).

All crystallographic data was collected on a SuperNova or Excalibur, EOS detector diffractometer using radiation $\text{CuK}\alpha$ ($\lambda = 1.54184\ \text{\AA}$) or $\text{Mo-K}\alpha$ ($\lambda = 0.71073\ \text{\AA}$) radiation all recorded at 150(2) K. All structures were solved by direct methods and refined on all F 2 data using the SHELXL-2014 suite of programs. All hydrogen atoms were included in idealised positions and refined using the riding model.

2.3. Complex synthesis

Ligands were prepared through the imine condensation reaction and characterised by ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR and HR-MS. Ligands were reacted with ZnEt_2 in toluene to give catalysts. Further synthetic information can be found in [Section 3.1](#) and [supporting information](#).

2.4. Typical polymerisation procedure

Lactide (1.0 g, 6.94×10^{-3} mol) was added to a Young's ampoule with initiator (2.31×10^{-5} mol) in a glovebox. An oil bath was heated to the appropriate temperature and the polymerisation ran for one hour or until stirring was significantly slowed. Once complete, the solvent was immediately removed *in vacuo* and the crude product analysed via ^1H NMR. The pure polymer was obtained by washing with > 30 mL methanol and used for GPC and $^1\text{H}\{^1\text{H}\}$ NMR spectroscopy.

2.5. Typical PLA degradation procedure

Young's ampoule containing PLA (0.25 g, Vegware™, PLLA cup, $M_n = 45,510\ \text{g mol}^{-1}$), was taken into a glovebox and loaded with metal complex (4 – 8 wt%, 0.01 – 0.02 g). The polymer was then dissolved in THF (4 mL) with heating and stirring assisting dissolution. The flask was then submerged in a preheated oil bath ($50 - 80\ ^\circ\text{C}$) to which MeOH (1 mL, 7 eq. with respect to ester group) was added. Aliquots were taken for ^1H NMR (CDCl_3) analysis of the methine region. After the reaction, the solvent was removed *in vacuo* and the residual methyl lactate (Me-La) was analysed further. For reactions using ethanol and n-butanol, the 7: 1 molar ratio of alcohol to ester group and the 4: 1 vol ratio of THF to alcohol were maintained.

2.6. PET degradation procedure

The Young's ampoule containing PET (0.25 g of carbonated drinks bottle), was taken into a glovebox and loaded with metal complex (8 wt %, 0.02 g). Ethylene glycol (EG) (27.5 eq., 1.5 mL) was added, and the flask was submerged in a pre-heated oil bath at $180\ ^\circ\text{C}$. When full disappearance of the PET was observed, water was added, and the mixture was filtered. BHET crystallised from the mixture and was collected, dried at $100\ ^\circ\text{C}$ *in vacuo* for 4 hours and weighed to obtain isolated yields. When required, an aliquot was taken and analysed with a 1,3,5-trimethoxybenzene internal standard to obtain spectroscopic BHET yield.

2.7. Mixed plastic degradation procedure

Mixed-plastic PET degradation reactions were carried out in a Young's ampoule containing PET (0.25 g of carbonated drinks bottle) and a contaminant plastic (0.25 g HDPE bottle lid/0.125 g PVC label/0.25 g PLA cup) was taken into a glovebox and loaded with metal complex (8 wt% with respect to PET, 0.02 g). EG (27.5 eq., 1.5 mL) was added, and the flask was submerged in a pre-heated oil bath at $180\ ^\circ\text{C}$. When full disappearance of the PET was observed, an aliquot was taken and analysed with a 1,3,5-trimethoxybenzene internal standard to obtain spectroscopic BHET yield. Water was added, and the mixture was filtered. BHET crystallised from the mixture and was collected, dried at $100\ ^\circ\text{C}$ *in vacuo* for 4 hours and weighed to obtain isolated yields.

One-pot degradation of PLA and PET was carried out in a Young's ampoule containing PET (0.25 g of carbonated drinks bottle) and PLA (0.25 g of PLA cup). Catalyst (8 wt% with respect to PET, 0.02 g) was added in a glove box. EG (27.5 eq, 1.5 mL) was added, and the flask was submerged in a pre-heated oil bath at $180\ ^\circ\text{C}$. When full disappearance of the PET was observed, an aliquot was taken to analyse with 1,3,5-trimethoxybenzene to determine spectroscopic yield of BHET and observation of PLA degradation products. Water was added, and the mixture was filtered. BHET crystallised from the mixture and was collected, dried at $100\ ^\circ\text{C}$ *in vacuo* for 4 hours and weighed to obtain isolated yield.

Sequential degradation of PLA and PET was carried out in a Young's ampoule PET (0.25 g of carbonated drinks bottle) and PLA (0.25 g of PLA cup). Catalyst (8 wt% with respect to PET, 0.02 g) was added in a glove box. The polymer was then dissolved in THF (4 mL) with heating and stirring assisting dissolution of PLA. The flask was then submerged in a preheated oil bath ($80\ ^\circ\text{C}$) to which MeOH (1 mL) was added. After 8 hours, an aliquot was taken for ^1H NMR (CDCl_3) analysis of the methine region. EG (27.5 eq, 1.5 mL) was added to the reaction mixture, and the flask was submerged in a pre-heated oil bath at $180\ ^\circ\text{C}$. When full disappearance of the PET was observed, an aliquot was taken to analyse with 1,3,5-trimethoxybenzene to determine spectroscopic yield of BHET and observation of PLA degradation. Water was added, and the mixture was filtered. BHET crystallised from the mixture and was collected, dried at $100\ ^\circ\text{C}$ *in vacuo* for 4 hours and weighed to obtain isolated yields.

3. Synthesis and characterisation

3.1. Ligand synthesis and characterisation

Imine condensation reactions were performed in methanol between the relevant amines and salicylaldehyde derivatives, affording ligands 1–9H ([Scheme 1](#)). The reaction mixture was stirred at room temperature for 24 hours or until a precipitate formed. Ligands 1, 3, 6, 7, 8 & 9H were recrystallised from methanol to give a range of pink and yellow powders in moderate to good yields (58 – 92 %). Interestingly, all ligands containing chloro R1 substituents formed a precipitate immediately upon reactant addition. Ligands 2, 4 & 5H were isolated as yellow and red oils, with a >99 % yield assumed. Purity and structure were confirmed by ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and high-resolution

Table 1
Selected bond lengths (Å) and angles (°) for tetrahedral complexes, Zn(4,5,7)₂.

	Zn(4) ₂	Zn(5) ₂	Zn(7) ₂
τ_4 ^[a]	0.79	0.87	0.67
Zn – O(1)	1.9079(8)	1.9274(15)	1.9315(13)
Zn – O(2)	1.9392(9)	1.9274(15)	1.9315(13)
Zn – O(3)			2.9020(18)
Zn – N(1)	1.9812(10)	1.9892(15)	2.011(2)
Zn – N(2)	1.9920(10)	1.9893(15)	2.011(2)
O(1) – Zn – O(2)	108.40(4)	109.92(9)	123.68(8)
O(1) – Zn – N(1)	96.61(4)	96.62(6)	94.22(7)
O(1) – Zn – N(2)	126.03(4)	117.95(6)	106.28(7)
O(2) – Zn – N(1)	109.61(4)	117.95(6)	106.28(7)
O(2) – Zn – N(2)	94.55(4)	96.62(6)	94.22(6)
N(1) – Zn – N(2)	121.03(4)	118.97(9)	135.94(12)

mass spectrometry (HR-MS), which confirmed the condensation product in all cases (Figures S1–S18).

3.2. Complex synthesis and characterisation

Two equivalents of 1–9H were complexed with ZnEt₂ in anhydrous toluene to target the homoleptic ZnL₂ complexes (Scheme 1). Purification was achieved through crystallisation from varying mixtures of hexane and toluene and five complexes produced crystals suitable for XRD analysis. ¹H NMR analysis was consistent with the homoleptic structure for all complexes (Figures S19–S34), and there was no evidence of Zn-Et resonances throughout. However, the presence of the free alcohol group for complexes formed from 1–3H could allow for alkoxide-bridged oligomeric species which would be indistinguishable by ¹H NMR spectroscopy. The spectrum of Zn(2)₂ indicates two full sets of resonances at a 1:1 ratio (Figure S21). This could indicate an oligomeric structure in which two ligand environments exist or could be evidence of a diastereotopic conformation of ligands within a homoleptic structure. ¹³C{¹H} NMR spectra were consistent with the

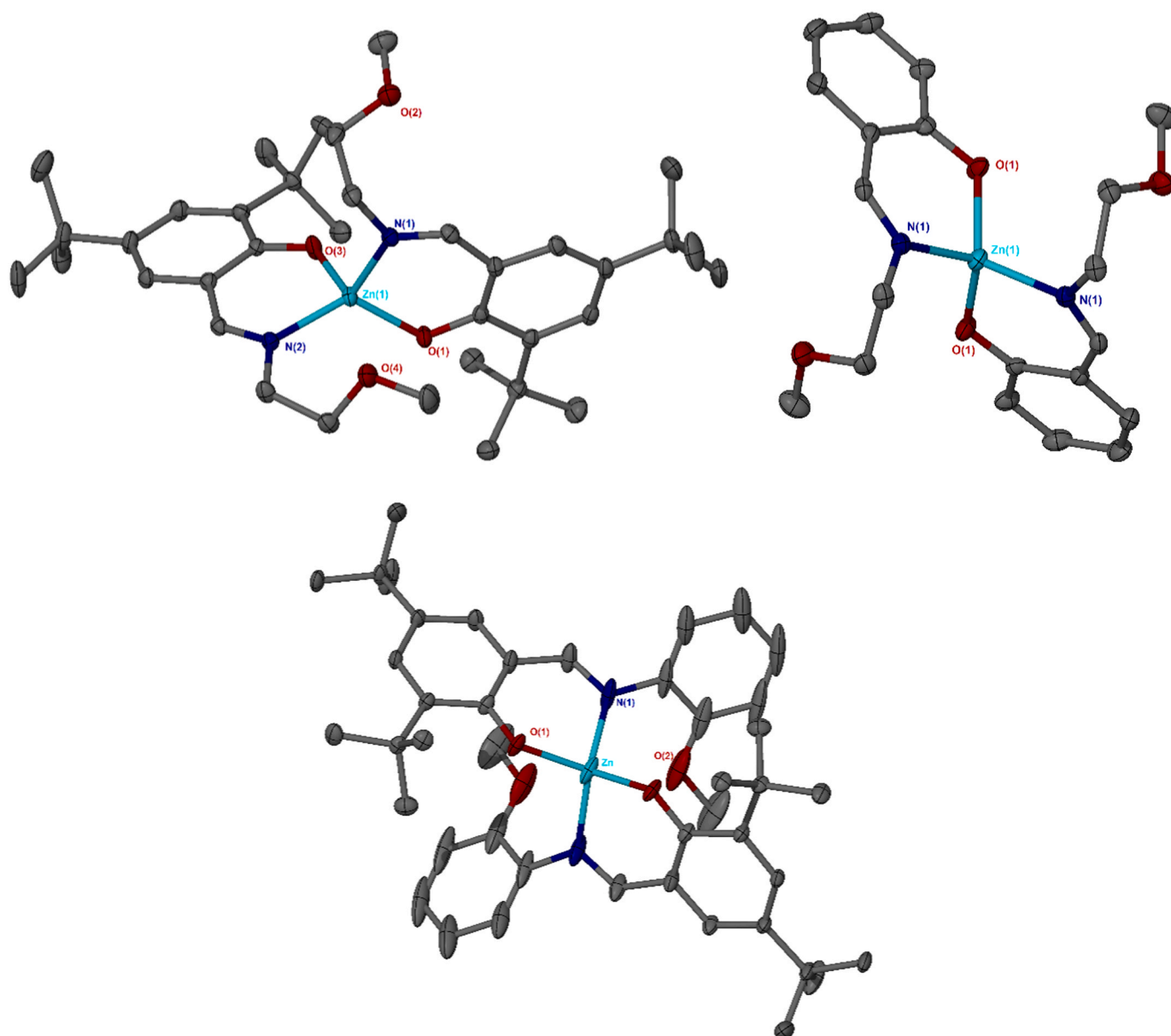


Fig. 1. Solid-state structures of Zn(4)₂ (left), Zn(5)₂ (right) and Zn(7)₂ (bottom). Ellipsoids shown at 30 % probability level. H atoms have been removed for clarity.

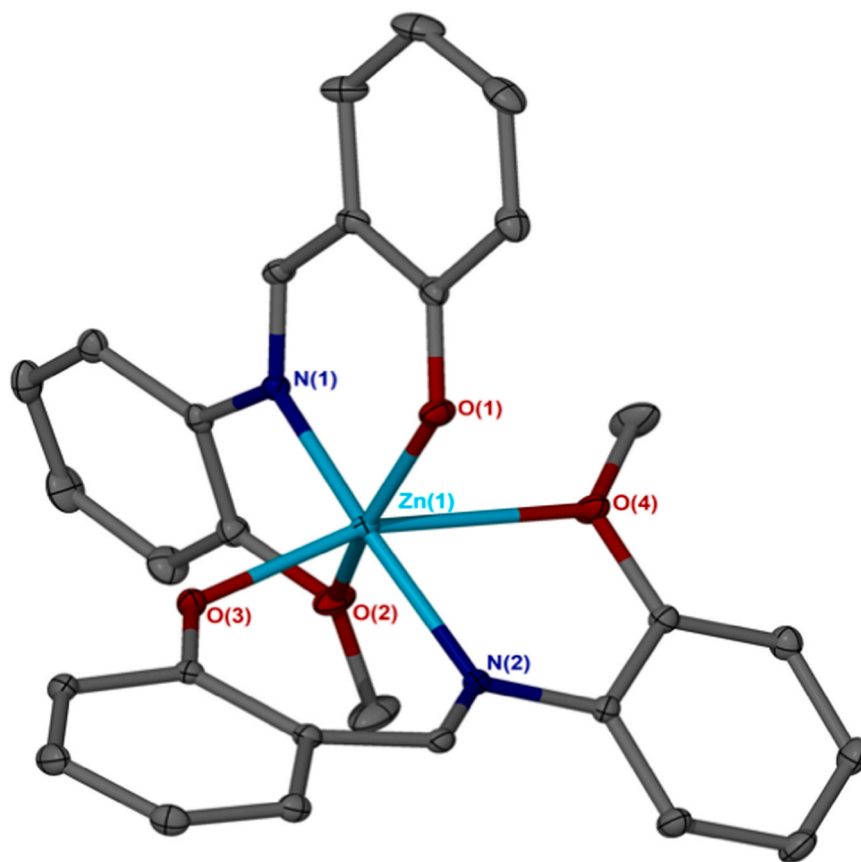


Fig. 2. Solid state structure of Zn(8)₂. Ellipsoids shown at 30 % probability level. H atoms have been removed for clarity. Key bond lengths (Å): Zn – O(1) = 1.9739(10), Zn – O(2) = 2.4225(10), Zn – N(1) = 2.0323(11), Zn – N(2) = 2.0545(11). Key bond angles (°): N(1) – Zn – N(2) = 163.23(5), O(3) – Zn – O(4) = 159.98(4), O(1) – Zn – O(2) = 154.30(4).

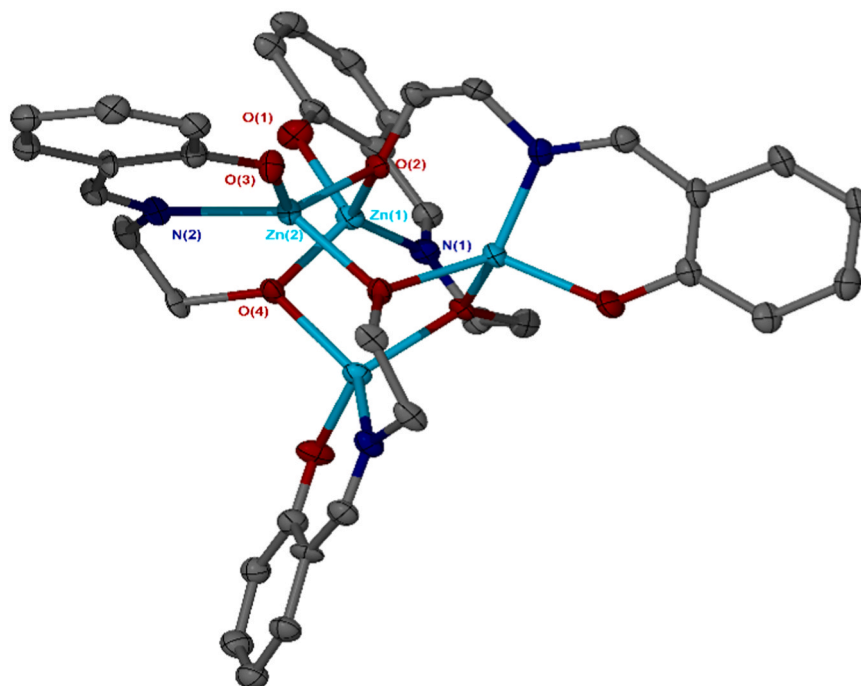


Fig. 3. Solid state structure of Zn₄(1)₄. Ellipsoids shown at 30 % probability level. H atoms have been removed for clarity.

Table 2Solvent-free polymerisation of *rac*-lactide at 130 °C with Zn₄(1)₄ and Zn(2–9)₂.

Init.	[LA]:[I]: [BnOH]	Time [min]	Conv. [%] ^a	P _m ^b	M _n [g mol ⁻¹] ^c	M _n Calc. [g mol ⁻¹] ^d	Đ ^c
Zn ₄ (1) ₄	300: 1: 1	1	80	0.53	15750	34700	1.99
Zn(1) ₂	3000: 1: 10	60	19	0.56	4850	8300	1.25
Zn(2) ₂	300: 1: 1	2	90	0.52	19300	39000	1.45
Zn(2) ₂	3000: 1: 10	60	22	0.58	4100	9600	1.11
Zn(3) ₂	300: 1: 1	2	82	0.54	19350	35550	1.65
Zn(3) ₂	3000: 1: 10	60	7	-	-	-	-
Zn(4) ₂	300: 1: 1	18	65	0.59	16800	28200	1.18
Zn(5) ₂	300: 1: 1	60	41	0.55	6100	17850	1.10
Zn(6) ₂	300: 1: 1	20	35	0.59	5300	15250	1.10
Zn(7) ₂	300: 1: 1	30	48	0.56	12450	20850	1.14
Zn(8) ₂	300: 1: 1	60	53	0.56	10050	23050	1.13
Zn(9) ₂	300: 1: 1	60	31	0.61	10850	13500	1.03

Conditions: *rac*-LA (1 g), [LA]/[Zn]/[BnOH] = 300:1:1, solvent free. ^a Determined by ¹H NMR spectroscopy. ^b Probability of racemic enchainment, determined by ¹H{¹H} NMR spectroscopy. ^c Theoretical molecular weight calculated from conversion (rounded to the nearest 50): {(conversion × 3 × M_n [LA]) + M_n [BnOH]}. ^d Determined from GPC (in tetrahydrofuran) referenced against polystyrene standards.

proposed structures with the exception of chlorinated analogues, Zn(3)₂ and Zn(9)₂, which were not sufficiently soluble to afford usable data. A further minor set of resonances could be attributed to a small amount of three coordinate Zn(2) being present. Elemental analysis (CHN) was consistent with the homoleptic structure for Zn(4–9)₂, as expected. For complexes formed from 1–3H, the measured values were compared with percentages calculated for a 2: 1 and 1: 1 ligand to zinc ratio. The values for 1H were much closer to a Zn_n(1)_n structure whereas 2H and 3H gave values closer to the expected ZnL₂ structure.

Solid state structures were obtained for Zn_n(1)_n and Zn(4,5,7,8)₂. Zn(4,5,7)₂ exhibited four coordinate structures which tended towards tetrahedral geometry (Table 1, Fig. 1). Zn(5)₂ was the closest to ideal tetrahedral geometry (τ₄' = 0.88) and this can be attributed to a lack of steric hindrance from the unsubstituted phenolate and the ethylene linking group. Zn(4)₂ and Zn(7)₂ gave τ₄' values of 0.78 and 0.74 respectively, suggesting that bulky tBu groups have the most significant impact on structure and that the inclusion of a rigid phenolate linking group in Zn(7)₂ causes a further deviation from ideal geometry (τ₄' = 0.67). This mirrors the trend observed with analogous {ONS} complexes. [43]

Zn(8)₂ (Fig. 2) shows a *pseudo*-octahedral structure with a *mer* ligand conformation. The apical nitrogen donors are situated *trans* to one another and constitute the largest coordination angle [N(1)–Zn–N(2) = 163.23(5)°]. This change in geometry can be rationalised by considering the proximity of the methoxy donor to the zinc centre enforced by the phenylene linker, coupled with a lack of bulky phenolate substituents.

The final structure can be represented as Zn₄(1)₄ and is a symmetrical tetramer that is consistent with the NMR and EA data previously discussed (Fig. 3). [58] The free alcohol group for 1H, in this case, becomes a bridging alkoxide allowing each zinc centre to adopt a distorted tetrahedral geometry (τ₄' = 0.70) with the deviation a result of structural constraints arising from the cyclic structure. DOSY NMR was consistent with the tetrameric structure being maintained in solution.

4. Results and discussion

4.1. Lactide polymerisation

All complexes were tested for the solvent-free polymerisation of *rac*-lactide at 130 °C at an initial ratio of [LA]: [Zn]: [BnOH] = 300: 1: 1 (Table 2). Hydroxyl complexes, Zn₄(1)₄ and Zn(2–3)₂ were by far the

Table 3Methanolysis of PLA to Me-LA using 8 wt% Zn₄(1)₄, Zn(2–9)₂ at 80 °C [a].

Cat.	Time [h]	Cat. Loading [wt %]	Y _{Me-LA} [%]	S _{Me-LA} [%]	X _{int} [%]
Zn ₄ (1) ₄	8	8	82	82	100
Zn(2) ₂	8	8	85	85	100
Zn(3) ₂	8	8	54	60	90
Zn(4) ₂	8	8	93	93	100
Zn(5) ₂	8	8	46	53	87
Zn(6) ₂	8	8	27	38	72
Zn(7) ₂	8	8	83	83	100
Zn(8) ₂	8	8	53	56	94
Zn(9) ₂	8	8	22	32	70

[a] Reaction conditions: V_{THF}:V_{MeOH} = 4: 1, 0.25 g of PLLA cup (M_n = 45 510 g mol⁻¹), n_{MeOH}:n_{ester} = 7: 1, 8 wt% cat. loading (0.5–1.5 mol% relative to ester linkages). Y_{Me-LA}, S_{Me-LA} and X_{int} determined by ¹H NMR upon solvent removal.

most active initiators, reaching high conversion in 1 – 2 minutes (conversion = 80 – 90 %). GPC analysis showed molecular weights around half (45 – 54 %) of the expected values. This implies an average of two polymer chains per zinc centre. This could result from the formation of different active species under reaction conditions facilitated by the hydroxyl group's ability to act as a bridging donor or to stabilise a three-coordinate complex. Dispersities were relatively broad (Đ = 1.45 – 1.99), which is likely a function of the rapidity of the reaction and a lack of control. Atactic PLA was produced, which is expected from zinc monophenolates of this type. When the catalyst loading was decreased ([LA]: [I]: [BnOH] = 3000: 1: 10), activity was significantly reduced for Zn₄(1)₄ and Zn(2–3)₂. Only low conversion was attained after 60 minutes (7 – 22 %) which is a much greater reduction than observed with similar Zn(II) complexes [43]. Dispersities were improved at this ratio (Đ = 1.11 – 1.25), but molecular weights remained low.

Of the methoxy complexes, Zn(4–9)₂, complexes bearing tBu substituents, Zn(4)₂ (Y = -CH₂CH₂-) and Zn(7)₂ (Y = -C₄H₆-), were the most active, achieving 65 % and 48 % conversion after 18 and 20 minutes respectively. This mirrors the trend seen with analogous thioether complexes, although they were significantly more active [43]. This suggests that the presence of the methoxy group in some way hampers the activity of the complexes towards lactide coordination or polymer propagation. Complexes bearing unsubstituted phenolate rings, Zn(5)₂ and Zn(8)₂, were significantly less active achieving moderate conversion after 60 minutes. Considering the lack of steric hindrance in these complexes, the poor activity is surprising, especially when comparing Zn(5)₂ to its thioether equivalent which was exceptionally rapid for this reaction at much lower initiator loading [43]. The crystal structures could offer some insight into this lack of activity with Zn(5)₂ adhering closely to tetrahedral geometry (τ₄' = 0.88) and Zn(8)₂ showing octahedral geometry. Both geometries could be considered a barrier to lactide coordination through steric crowding of the coordination sphere. Complexes bearing chloride substitution gave varied results. Zn(6)₂ reached low conversion after 20 minutes, whereas Zn(9)₂ achieved a similar conversion after 60 minutes. There are literature examples of halide-bearing complexes being the slowest examples of their series [40, 43, 48]. In this case, a lack of solubility was observed throughout the synthesis and in the molten lactide during polymerisation. In further contrast to the results seen with {ONS} complexes, the variation of the linking group did not appear to have a significant impact on polymerisation outcomes. As seen with the alkoxy complexes, Zn₄(1)₄ and Zn(2–3)₂, molecular weights tended to be significantly lower than expected and only atactic PLA was produced. Dispersities were relatively narrow for this series (Đ = 1.03 – 1.18).

4.2. Chemical recycling of PLA

Zn₄(1)₄ and Zn(2–9)₂ were initially tested for the methanolysis of

Table 4Methanolysis of PLA to Me-LA using 4 wt% Zn₄(1)₄, Zn(2–9)₂ at 80 °C [a].

Cat.	Time [h]	Cat. Loading [wt %]	Y _{Me-LA} [%]	S _{Me-LA} [%]	X _{int} [%]
Zn ₄ (1) ₄	8	4	64	64	99
Zn(2) ₂	8	4	54	60	91
Zn(3) ₂	8	4	65	66	100
Zn(4) ₂	8	4	44	47	93
Zn(5) ₂	8	4	8	18	45
Zn(6) ₂	8	4	13	24	54
Zn(7) ₂	8	4	78	78	100
Zn(8) ₂	8	4	7	15	48
Zn(9) ₂	8	4	11	29	37

[a] Reaction conditions: V_{THF}:V_{MeOH} = 4:1, 0.25 g of PLLA cup (M_n = 45 510 g mol⁻¹), n_{MeOH}:n_{ester} = 7:1, 4 wt% cat. loading (0.25 – 0.73 mol% relative to ester linkages). Y_{Me-LA}, S_{Me-LA} and X_{int} determined by ¹H NMR upon solvent removal.

commercial PLA (0.25 g, PLLA cup, M_n = 45,510 g mol⁻¹) at 80 °C for 8 hr with 8 wt% catalyst (Table 3). This is to provide a direct comparison to conditions used with equivalent zinc {ONS}, [43] {ONN} [40,59] and catam-based ligand systems [48,60]. Methyl lactate (Me-LA) has been shown to form via a two-step mechanism through oligomeric intermediates [41]. Me-LA is useful as a green solvent and can be converted to virgin lactide to retain the value in the polymer cycle [61]. Me-LA is also an alternative to lactic acid for many transformations, and is easier to store and process in some cases [62]. The composition of the product mixtures can be determined by ¹H NMR where methine resonances relating to PLA (internal methine), oligomers (chain end methine) and product (ester methine) can be observed and quantified (Figure S35). Three key parameters can be calculated from this data [41]. X_{int} refers to the conversion of internal methine units, synonymous with PLA. The yield of methyl lactate is denoted as Y_{Me-LA}, and the selectivity is shown as S_{Me-LA}. Table 4

The complexes bearing tBu substituents (Zn₄(1)₄, Zn(4,7)₂) were consistently active, all reaching 100 % conversion of internal methine. Of these, the ethylene-bridged complex, Zn(4)₂, gave the highest selectivity and yield of Me-LA (S_{Me-LA} = 93 %, Y_{Me-LA} = 93 %). This is in direct contrast to the results seen for {ONS} complexes where the thiol analogue performed poorly (X_{int} = 77 %, S_{Me-LA} = 33 %, Y_{Me-LA} = 24 %) [43]. Complexes with an unsubstituted phenylene ring, Zn(2,5,7)₂, also performed well, with Zn(2)₂ giving full conversion and an 85 % yield of Me-LA over 8 hours. Interestingly, Zn(8)₂ still performed well despite the steric hindrance imposed by the octahedral structure (Fig. 2). As noted with similar complexes [43,59], the addition of chloro groups led to a drop in activity; it has previously been suggested that this results from agglomeration of the active species [43]. Moreover, chloride complexes tended to be less soluble in the reaction mixture. This is particularly true of Zn(6)₂ and Zn(9)₂ which gave Me-LA yields of 27 % and 22 % respectively. Broadly, the linking group had less of an impact on reactivity than the phenolate substitution pattern. However, hydroxyl-containing complexes Zn₄(1)₄ and Zn(2–3)₂ appeared to be the most active, possibly implying an active, mechanistic role for the hydroxy group. Furthermore, if the tetrameric structure of Zn₄(1)₄ is maintained in solution, then the high conversion could be related to cooperative effects between two metal centres and work is ongoing to establish this [39]. With the ether containing ligands, varying from phenyl to ethyl had a minimal impact on conversion or selectivity.

The effect of catalyst loading was explored in a series of experiments at 4 wt%. As expected, due to the presence of fewer active species, yield and conversion were reduced for most complexes. The most pronounced reduction in activity occurred with the unsubstituted complexes, Zn(2,5,8)₂. The conversion and yield for Zn(8)₂ reduced from 94 % and 53–48 % and 7 % respectively. Conversely, a smaller effect was observed for the tBu-substituted complexes, Zn(1,4,7)₂, where a minimal effect on conversion was observed [X_{int}(8 wt%) = 100 %, X_{int}(4 wt%

Table 5Methanolysis of PLA to Me-LA Zn₄(1)₄ and Zn(3,4,7,8)₂ at 50 °C [a].

Cat.	T/ °C	Time [h]	Cat. Loading [wt%]	Y _{Me-LA} [%]	S _{Me-LA} [%]	X _{int} [%]
Zn ₄ (1) ₄	50	18	8 ^[b]	7	16	42
Zn(3) ₂	50	18	8 ^[b]	15	27	54
Zn(3) ₂	50	18	4 ^[c]	12	23	52
Zn(4) ₂	50	18	8 ^[b]	49	54	89
Zn(4) ₂	50	18	4 ^[c]	20	30	67
Zn(7) ₂	50	18	8 ^[b]	16	26	61
Zn(8) ₂	50	18	8 ^[b]	19	29	65

[a] Reaction conditions: V_{THF}:V_{MeOH} = 4:1, 0.25 g of PLLA cup (M_n = 45 510 g mol⁻¹), n_{MeOH}:n_{ester} = 7:1 Y_{Me-LA}, S_{Me-LA} and X_{int} determined by ¹H NMR upon solvent removal. [b] 8 wt% cat. loading (0.49–1.1 mol% relative to ester linkages) [c] 4 wt% cat. loading (0.44 – 0.54 mol% relative to ester linkages).

Table 6Alcoholysis of PLA with Zn(4)₂ at 80 °C with varying alcohols and in air. [a].

Cat.	Time [h]	Cat. Loading [wt %]	Alcohol	Y _{A-LA} [%]	S _{A-LA} [h]	X _{int} [h]
Zn(4) ₂ ^[c]	8	8	MeOH	30	38	78
Zn(4) ₂	8	8	EtOH	23	34	69
Zn(4) ₂	8	8	nBuOH	12	25	49

[a] Reaction conditions: V_{THF}:V_{MeOH} = 4:1, 0.25 g of PLLA cup (M_n = 45 510 g mol⁻¹), n_{MeOH}:n_{ester} = 14:1 Y_{Me-LA}, S_{Me-LA} and X_{int} determined by ¹H NMR [b] 8 wt% cat. loading (1.3–2.1 mol% relative to ester linkages) [c] Reaction performed in air.

%) = 93 – 100 %) alongside a more significant drop in Me-LA yield [Y_{Me-LA}(8 wt%) = 82 – 93 %, Y_{Me-LA}(4 wt%) = 44 – 78 %]. Chlorinated analogues, Zn(6,9)₂ followed the same trend, however, Zn(3)₂ slightly improved when catalyst loading was reduced [8 wt%: X_{int} = 90 %, S_{Me-LA} = 60 %, Y_{Me-LA} = 54 %; 4 wt%: X_{int} = 100 %, S_{Me-LA} = 66 %, Y_{Me-LA} = 65 %]. This could be evidence for catalyst agglomeration, and there may have been more active, monomeric species in solution at the lower concentration, explaining this result. From the reaction profiles of PLA degradation with Zn(3)₂ at 4 wt% and 8 wt%, clear differences can be observed (Figure S37). After three hours the composition of the reaction mixtures were very similar (8 wt%: [int] = 35 %, [CE] = 45 %, [Me-LA] = 20 %; 4 wt%: [int] = 34 %, [CE] = 49 %, [Me-LA] = 17 %). However, at 8 wt%, conversion tailed off significantly after this point and the final reaction mixture still contained 20 % internal methine. By contrast, the 4 wt% experiment consumed PLA consistently up to 100 %. This suggests that the catalyst saw significant deactivation around this point, disrupting the conversion of PLA to oligomers.

A selection of catalysts were tested for PLA methanolysis at 50 °C over 18 hours (Table 5). At 8 wt%, Zn(4)₂ performed reasonably well, converting 89 % of internal methine units to give a Me-LA yield of 49 %. This outperformed all of the thioether analogues that were tested under these conditions [43]. At 4 wt%, a predictable drop in activity was observed in line with the higher temperature experiments. Two experiments at different catalyst loadings were also performed with Zn(3)₂ to see if activity could again be improved through reduced catalyst loading. A small drop in activity was observed at 4 wt% suggesting that the deactivation observed at higher temperature is not relevant under these conditions. For the remaining complexes, Zn₄(1)₄ and Zn(7,8)₂, results were similar (X_{int} = 42 – 65 %, S_{Me-LA} = 16 – 29 %, Y_{Me-LA} = 7 – 19 %); these are all significantly lower than the 80 °C reactions.

The best performing catalyst, Zn(4)₂, was subjected to further testing to further explore the alcoholysis reaction scope (Table 6). When the reaction was performed in a round-bottom flask open to air, conversion and yield were significantly reduced [Argon: X_{int} = 100 %, Y_{Me-LA} = 93 %; Air: X_{int} = 78 %, Y_{Me-LA} = 30 %]. This suggests that moisture in the air interferes with the active catalytic species and, as the conversion remains high, this is likely to mainly affect the conversion of oligomers

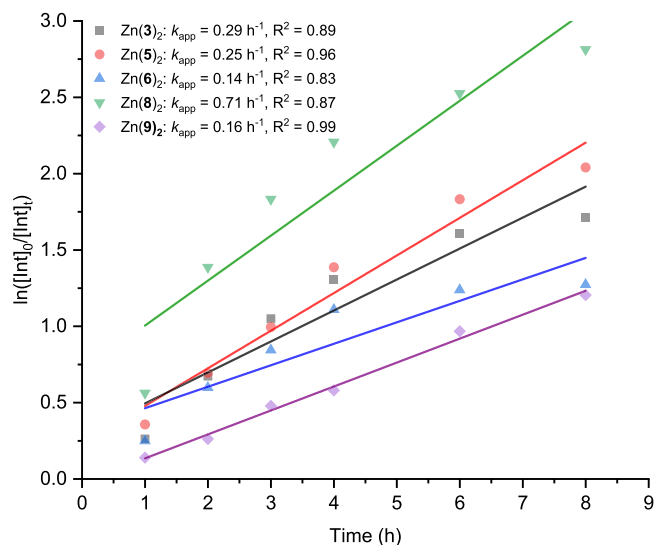


Fig. 4. Semi logarithmic plot for PLA degradation at 8 wt% catalyst loading with Zn(3,5,6,8,9)₂.

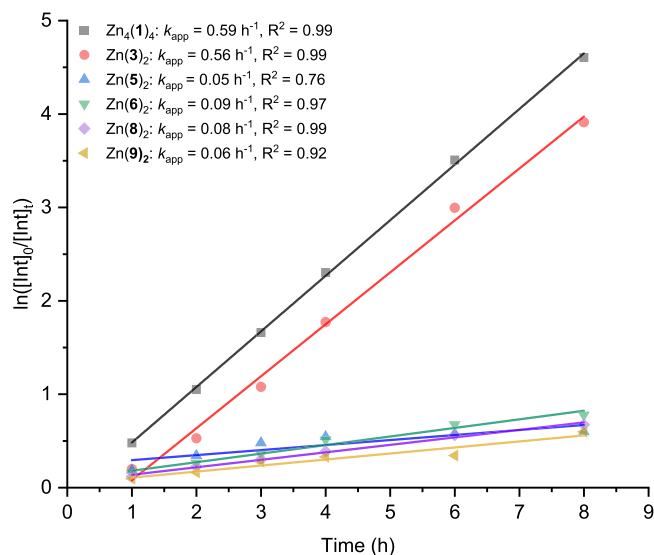


Fig. 5. Semi logarithmic plot for PLA degradation at 4 wt% catalyst loading with Zn₄(1)₄ & Zn(3,5,6,8,9)₂.

to Me-LA in the final step. Zn(4)₂ was also tested with different alcohols, ethanol and *n*-butanol, to give the industrially relevant lactate esters, ethyl lactate (Et-LA) and *n*-butyl lactate (nBu-LA). As expected, reactivity decreased with increasing alcohol size (MeOH > EtOH > nBuOH), although the catalyst produced a reasonable yield of all three over 8 hours ($Y_{\text{Me-LA}} = 93\%$, $Y_{\text{Et-LA}} = 34\%$, $Y_{\text{nBu-LA}} = 12\%$).

4.3. Kinetics of PLA methanolysis

Apparent rate constants (k_{app}) were calculated for a selection of catalysts using a semi-logarithmic plot and assuming first order kinetics as have been previously observed for this reaction [39–43]. At 8 wt%, five complexes, Zn(3,5,6,8,9)₂, yielded useful data (Fig. 4). The remaining complexes, Zn₄(1)₄ and Zn(2,4,7)₂, were too quick to provide comparable kinetic data. Zn(8)₂ was the most active catalyst ($k_{\text{app}} = 0.71\text{ h}^{-1}$, $R^2 = 0.87$), which is comparable to other literature examples but significantly less than the most active examples in the literature, such as the propylenediamine-based complexes reported by McKeown *et*

Table 7
Degradation of PET to BHET. [a].

Cat.	Time [h]	T [°C]	Cat. Loading [wt%]	Y _{BHET} [g (%)]
Zn ₄ (1) ₄	4	180	8	0.12 (36 %)
Zn(3) ₂	3.5	180	8	0.14 (42 %)
Zn(4) ₂	2	180	8	0.14 (42 %)
Zn(5) ₂	2.5	180	8	0.22 (66 %)
Zn(7) ₂	4	180	8	0.04 (12 %)

[a] Reaction conditions: 0.25 g of carbonated drinks bottle (Mn ~ 40 000 g mol⁻¹), 27.5 equivalents of EG (relative to ester linkages), 8 wt% cat. loading (20 mg, 1.3–3.4 mol% relative to ester linkages).

al. ($k_{\text{app}} = 12\text{ h}^{-1}$) [40]. Zn(5)₂ is interesting as it provides a direct comparison to analogous {ONN} and {ONS} complexes with the same substitution pattern [41,43]. Zn(5)₂ ($k_{\text{app}} = 0.25\text{ h}^{-1}$) is the least active of these examples whilst there is no significant difference between the {ONN} and {ONS} complexes. This suggests that, in this case, the pendant donor atom has little effect on reactivity. The remaining complexes, Zn(3,6,8)₂, had a range of activities and Zn(9)₂ was the least active ($k_{\text{app}} = 0.16\text{ h}^{-1}$). A conversion vs. time plot of the 8 wt% reactions can be seen in Figure S37 where the same trend in reactivity can be observed.

Further kinetic data was obtained at 4 wt% catalyst loading, and Zn(5,6,8,9)₂ were all relatively inactive under these conditions ($k_{\text{app}} = 0.05 - 0.09\text{ h}^{-1}$). Zn₄(1)₄ and Zn(3)₂ were much more active, giving apparent rate constants of $k_{\text{app}} = 0.59$ & 0.56 h^{-1} respectively. This can also be seen in the conversion vs. time plot (Figure S38). The rate constant for Zn(3)₂ is almost doubled at reduced catalyst loading, again suggesting an agglomeration effect hampering activity at high loading. Fig. 5

4.4. Chemical recycling of PET

A selection of the most active catalysts, Zn₄(1)₄ & Zn(3,4,7,8)₂, were tested for the glycolysis of PET to BHET, which can be used in the production of virgin PET or unsaturated polymer resins (Table 7) [63,64]. The glycolysis was performed with 17.5 equivalents of ethylene glycol under solvent-free conditions at 180 °C. The reaction was stopped when full disappearance of PET was observed. Despite the absence of visible PET, only 12 % yield was observed with Zn(7)₂, suggesting the formation of soluble oligomers. Zn(5)₂ (R = H, Y = -CH₂CH₂-, X = OMe) gave the highest isolated yield of BHET (66 %), in 2.5 hours. Interestingly, the direct thioether analogue (R = H, Y = -CH₂CH₂-, X = SMe) was the most active complex in its series [43]. This could suggest that a lack of steric hindrance is important for this reaction. Hydroxyethyl complexes, Zn₄(1)₄ (R = tBu) and Zn(3)₂ (R = Cl), were relatively slow taking 4 and 3.5 hours to achieve 36 % and 42 % respectively. Zn(4)₂ (R = tBu, Y = -CH₂CH₂-, X = OMe) was the quickest to consume PET and gave a 42 % isolated yield of BHET.

4.5. Mixed polymer degradation

A series of experiments were conducted to assess the suitability of zinc {ONO} catalysts to the chemical recycling of mixed polymer waste, including PLA and PET (Table 7). Zn(4)₂ was selected as the most active catalyst for PLA and PET degradation. Initially, the PET reaction was repeated and gave an isolated BHET yield of 44 % after 1.5 h (Table 7, entry 1). There are obvious drawbacks to reporting isolated yield in this way as the method relies on a recrystallisation step during which product could easily be lost. This likely explains the low yields reported in previous literature [43]. To obtain a more accurate measurement of BHET, a spectroscopic method was developed using an internal standard. This gave a yield of 95 %, suggesting that around half of the product was lost during the subsequent recrystallisation.

For mixed polymer studies, a PLA cup and a carbonated drinks bottle were selected as a model of a realistic waste stream. PET degradation

Table 8
Mixed-plastic recycling experiments with Zn(4)₂.

Entry	Polymer 1	Polymer 2	Conditions		BHET Yield		Alkyl Lactate		
			T [°C]	t [h]	¹ H NMR [%] ^[a]	Isolated [%]	X _{int} [%] ^[b]	S _{Me-LA} [%] ^[b]	Y _{Me-LA} [%] ^[b]
1 ^[c]	PET	-	180	1.5	95	44	-	-	-
2 ^[d]	PLA	-	80	8	-	-	100	93	93
3 ^{[c][e]}	PET	HDPE	180	5	97	57	-	-	-
4 ^{[c][f]}	PET	PVC	180	2.5	99	55	-	-	-
5 ^{[c][g]}	PET	PLA	180	5	79	50	100 ^[j]	-	-
6 ^{[d][h]}	PLA	PET	80	8	0	-	97	69	67
7 ^{[c][d][i]}	PLA	PET	A) 80 B) 180	8 2.5	92	36	96	55	53

[a] Determined by ¹H NMR spectroscopy using trimethoxy benzene as an internal standard. [b] Determined by ¹H NMR analysis of methine protons. [c] 0.25 g of carbonated drinks bottle (M_n ~ 40 000 g mol⁻¹), 27.5 equivalents of EG (relative to ester linkages), 8 wt% cat. loading (20 mg, 2.4 mol% relative to ester linkages). [d] 0.25 g of PLLA cup (M_n = 45 510 g mol⁻¹), V_{THF}: V_{MeOH} = 4:1, n_{MeOH}: n_{ester} = 7:1, 8 wt% cat. loading (0.9 mol% relative to ester linkages). [e] 0.25 g of HDPE bottle cap added. [f] 0.125 g of PVC label added. [g] 0.25 g of PLA cup added. [h] 0.25 g of PET bottle added. [i] Reaction was run under standard PLA methanolysis conditions ([d]) for 8 hours. Volatiles were removed, ethylene glycol was added and PET glycolysis conditions ([c]) were applied. [j] No PLA methine resonance observed at end of reaction. Product and intermediate methine peaks were obscured.

was repeated in the presence of the HDPE bottle cap and PVC label from the same bottle (Table 7, entry 3 – 4). Both polyolefin contaminants slowed the reaction down and the addition of HDPE more than tripled the reaction time. After disappearance of the PET pieces, a similar BHET yield was observed using the ¹H NMR (97 – 99 %) and isolated yield (55 – 57 %) methods for both reactions. HDPE melted during the reaction, but no mass loss was observed. The PVC label fragmented during the reaction and the reaction mixture went brown, however no mass was lost. These results demonstrate the stability of these polyolefins under PET degradation conditions, and, by extension, the conditions used for PLA degradation.

An equal mixture of PLA and PET were subjected to PET glycolysis conditions (Table 7, entry 5) and PLA methanolysis conditions (Table 7, entry 6). Under glycolysis conditions, both PLA and PET were degraded and a spectroscopic BHET yield of 79 % was measured. Characteristic methine protons for PLA degradation products were obscured but there was clearly no PLA resonance remaining at ca. 5.2 ppm so 100 % conversion (X_{int}) was assumed. It was expected that the harsh glycolysis would quickly degrade PLA, as observed, and its presence reduced the effective catalyst concentration available for PET glycolysis, explaining the low yield and extended reaction time. When PLA methanolysis conditions were applied in the presence of PET, nearly full conversion of PLA was observed after 8 hours, although the selectivity and yield of Me-LA was reduced. The PET remained unchanged both spectroscopically and in terms of mass loss. Table 8

Finally, a sequential degradation of PLA and PET was attempted (Table 7, entry 7). PLA methanolysis was conducted in THF at 80 °C for 8 hours, resulting in 96 % PLA conversion and no conversion of PET. The solvent and excess methanol were removed *in vacuo* before ethylene glycol was added and the reaction heated to 180 °C. No fresh catalyst was added to the reaction. After 2.5 h, disappearance of PET was observed and ¹H NMR and isolated yields of 92 % and 36 % were calculated. The low isolated yield could be the result of lactate esters disrupting the crystallisation of BHET. This demonstrates the feasibility of selective PLA/PET sequential recycling using zinc catalysis. Furthermore, this result shows that Zn(4)₂ is not significantly deactivated under PLA methanolysis conditions, and that the glycolysis reaction is not affected by the presence of methyl lactate and small PLA oligomers.

5. Conclusion

Nine Zn(II) {ONO} complexes were prepared and characterised in solution and in the solid state. The polymerisation of *rac*-lactide was demonstrated but was limited to a relatively high catalyst loading. PLA was degraded to methyl lactate and the temperature, catalyst loading and reaction times were varied. The most active catalyst was capable of producing other small lactate esters and showed some activity in air.

PET degradation was demonstrated, and full consumption of PET was observed after 2 hours with Zn(4)₂. PET glycolysis was shown to be tolerant to the presence of polyolefin impurities and the selective and sequential depolymerisation of PLA and PET was reported.

CRedit authorship contribution statement

Joseph I. Pearce: Investigation. **Matthew J. Cullen:** Writing – review & editing, Investigation. **Gabriele Kociok-Köhn:** Formal analysis. **Benjamin D. Ward:** Supervision. **Jack A. Stewart:** Writing – review & editing, Writing – original draft, Supervision, Investigation, Conceptualization. **Matthew Davidson:** Supervision, Resources. **Matthew D. Jones:** Writing – review & editing, Writing – original draft, Validation, Supervision, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2024.115037.

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