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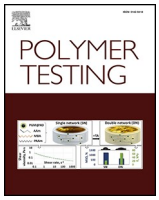

Efficient chemical recycling of poly(L-lactic acid) via either alcoholysis to alkyl lactate or thermal depolymerization to L-lactide promoted by Zn (II) catalysts

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A B S T R A C T

Poly(lactic acid) (PLA), a commercially fully bio-based and biodegradable polymer, stands out as a sustainable alternative to commodity plastics. Its current end-of-life management involves composting, but chemical recycling would be more appropriate for a circular economy model. Here we report two very efficient chemical recycling pathways for commercial high molar mass and highly crystalline PLA samples, both ones promoted by different imidazole[1,5-*a*]pyrid-3-yl)phenolate Zn(II) catalysts: (i) alcoholysis was easily achieved by simply treating the polymer samples in boiling methanol in the presence of 1 % Zn(II) catalyst, resulting in up to 99 % yield and selectivity in methyl lactate; and (ii) chemical recycling to the monomer was achieved by heating the polymer samples at 180 °C under vacuum or in a nitrogen flow in the presence of 0.1 % Zn(II) catalyst and a highly boiling alcohol, resulting in up to 99 % yield of L-lactide, having high chemical and steric purity, which could be repolymerized without any further purification.

1. Introduction

Poly(lactic acid) (PLA) is the most commercially relevant bio-based polymer [1] and one of the best candidates as a sustainable plastic material for a circular economy [2]. In fact, PLA assembles all the characteristics [3,4] ideally necessary for an environmentally sustainable material [5,6]: it is derived from bio-renewable sources, it is biodegradable, and it is well suited for a circular economy, owing to the possibility of both mechanical and chemical recycling [7]. Despite the green credentials of PLA, currently its recycling is not planned, as the end-of-life option for post-consumer PLA waste is the collection with the organic fraction for composting. In fact, the separate collection of plastics currently implemented for recycling involves only the polymers most widely used in packaging (PET, HDPE, LDPE, PP, PS, PVC), while all other plastics, although being collected as "others", are usually incinerated, mainly because recycling is not economically convenient for low volumes. However, if the worldwide industrial production of PLA will significantly increase (as expected based on the socio-economical and regulatory pressure toward the use of bio-renewable feedstocks) with respect to the current (probably underestimated) 600 ktons/year global installed capacity, the development of an efficient waste recycling management will be necessary. Even now the implementation of efficient procedures for removing PLA from a mixed plastic waste is of interest, since the presence of traces of PLA (as low as 1000 ppm) can drastically compromise well established recycling procedures, such as mechanical recycling of poly(ethylene terephthalate) [8]. Thus, the development of methods able to promote chemical depolymerization of PLA to the monomer or other value-added products under mild reaction conditions may be of fundamental importance to reduce the production costs and the environmental impact. In fact, recent LCA studies showed that the recovery of lactic acid from chemical depolymerization is more energetically favorable than the production by fermentation of glucose from biomass [9].

In this respect, the most investigated approach is the chemical depolymerization [10,11] of PLA by alcoholysis leading to valuable alkyl lactates (alkyl = ethyl or methyl), which are considered green solvents potentially able to substitute the traditional ones derived from fossil feedstocks, and which can be also used to produce the lactide monomer, closing the loop for a circular economy model for PLA [12, 13, 14]. Several studies have addressed the possible recycling of PLA by transesterification reactions with alcohols promoted by either simple metal salts [15] or organocatalysts [16–18] or, more recently, by properly designed metal complexes [19–21]. Concerning the latter class, Zn(II) complexes have emerged as the most promising catalysts for the depolymerization of PLA under mild conditions. E. g., an early study by Fliedel et al. [22] reported the controlled degradation of PLA by

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methanolysis promoted by dinuclear zinc-carbene complex in methylene chloride at room temperature, affording methyl lactate in 30 % yield after 24 h. Significant improvements in Zn catalyst design were reported by the group of Jones, including (i) monomeric and dimeric Zn (II) Schiff base complexes, with the best performing catalyst approaching 100 % Me-LA yield within 8 h at 80 °C in THF [23], and (ii) Zn(II) complexes based on ethylenediamine or propylenediamine Schiff bases, the latter providing up to 81 % yield of methyl lactate within 30 min at 50 °C in THF [24,25]. More recently, Mazzeo et al. [26] reported a heteroleptic pyridyl-imino-phenolate zinc complex promoting the methanolysis of commercial PLA samples in THF at room temperature with yields in methyl lactate up to 92 % in 1 h. Interestingly, the same catalyst was also tested for the methanolysis of PLA without solvent, resulting in good yields in methyl lactate, although after reactions prolonged several hours. Numerous studies in the literature also reported the alcoholysis of polyester under microwave irradiation [27–29].

Chemical recycling to monomer (CRM) has recently emerged as a highly desirable solution for a circular economy of plastics, offering the potential to convert post-consumer plastic waste back into its monomeric form for re-polymerization, thereby closing the loop and reducing dependence on virgin resources [30–32]. Of course, the polymerization thermodynamics [33] greatly affects the practicability of this approach, which is thus more or less challenging for different polymers: e.g., aliphatic polyesters produced by Ring Opening Polymerization (ROP) appear much more suitable for CRM than polyolefins [34]. However, until recently CRM was considered not viable for PLA [34,35], owing to undesired side reactions, such as epimerization leading to lactide racemization [36,37] or elimination giving acrylic acid [38]. In fact, this belief stimulated considerable research efforts in devising aliphatic polyesters with more favorable thermodynamic parameters for CRM via Ring Closing Depolymerization (RCD). In this respect, Chen [39] reported successful ROP of “non-polymerizable” ɣ-butyrolactone by performing the polymerization at sub-ambient temperature, to reduce the entropic penalty of the reaction, and by using reaction conditions such that the formed polymer precipitates, shifting the equilibrium toward the polymer, which then could be quantitatively subjected to CRM by heating at 220 °C. Subsequently, new monomers based on ɣ-butyrolactone with a trans-cyclohexyl fusion were synthesized and subjected to ROP at room temperature, affording high-molar mass polymers with “repeatable chemical recyclability” [40].

Recent reports have significantly changed the picture of PLA recyclability by CRM. Important advances include: (i) CRM of poly(L-lactic acid) (PLLA) in bulk at ≈ 200 °C using $Zn(acac)_2$ or $Sn(Oct)_2$ catalysts, affording 98 % yield and good turnover frequencies (TOF’s), but 12 % meso-lactide side product [41]; (ii) use of $Sn(Oct)_2$ catalyst and solvents that decrease the ceiling temperature of PLLA, allowing CRM at 140 °C, with ≈95 % conversion and up to 99 % selectivity, but low TOF’s [38]; (iii) use of $ZnCl_2$/poly(ethylene glycol) under vacuum for CRM of PLLA (and other polyesters and polycarbonates) in bulk at 160 °C (temperature for depolymerization optimized by isothermal TGA experiments), although with very low TOF’s [42,43]. Finally, CRM of PLLA films casted in the presence of $Sn(Oct)_2$ and glycerolethoxylate was evaluated and optimized using TGA analysis performed at 160 °C in nitrogen flow, resulting in up to 92 % yield and 99 % selectivity with extremely high TOF’s [44].

Although $Sn(Oct)_2$ is the catalyst commonly used in the industrial production of PLA, concern about its toxicity has spurred extensive research of catalysts based on safer metals. In connection to our continued interest in introducing new efficient ROP catalysts based on benign and earth-abundant metals [45–49], we have recently reported [50] a family of new Zn(II) complexes, bearing variously substituted monoanionic [N,O$^-$] (imidazole [1,5-*a*]pyrid-3-yl)phenol ligands, as catalysts for the ROP of L-LA under both mild (20 °C, solvent) and industrially relevant (190 °C, in the melt, technical grade unpurified monomer, very low catalyst loading) conditions. Interestingly, the best performing catalyst under mild conditions was the worst performing under harsh conditions, and, on the contrary, the less active catalysts under mild conditions competed well with $Sn(Oct)_2$ under industrially relevant conditions. We also reported a few preliminary PLA alcoholysis tests using some of the above-mentioned Zn(II) catalysts [50].

Herein, we report a detailed study of the chemical recycling of poly (L-lactic acid) (PLLA) commercial samples using heteroleptic or homoleptic (imidazole [1,5-*a*]pyrid-3-yl)phenolate Zn(II) catalysts (see Figs. 1 and 2), either by alcoholysis under mild conditions and without solvents, affording alkyl lactates, or by thermal depolymerization to L-lactide in bulk under vacuum in the presence of an alcohol. Both approaches resulted in very efficient chemical recycling, with conversions and selectivities up to 99 %.

2. Experimental

2.1. General

All manipulations involving air and/or moisture-sensitive compounds were performed under a nitrogen atmosphere in a Braun Labmaster glovebox or using Schlenk techniques. Glassware was dried in an oven at 120 °C overnight and exposed to vacuum–nitrogen cycles.

All solvents were dried as follows: dichloromethane was refluxed over CaH_2 and distilled under nitrogen before use, tetrahydrofuran and hexane were refluxed over sodium–benzophenone, and methanol was distilled under nitrogen. Deuterated solvents were purchased from Aldrich and stored in the glovebox over 3 Å molecular sieves before use. All other chemicals were commercially available and used as received unless otherwise stated.

NMR spectra were recorded using either a Bruker Advance 300, or 400 or a Bruker 600 MHz Ascend 3 HD spectrometer. Chemical shifts (δ) are expressed as parts per million and coupling constants (J) in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at δ 7.26 for $CDCl_3$, δ 5.32 for CD_2Cl_2, δ 7.16 for C_6D_6 and δ 3.58 for -CH_2 of THF-D_8 .^{13}C NMR spectra are referenced using the residual solvent peak at δ 77.22 for $CDCl_3$, δ 53.84 for CD_2Cl_2, 128.06 for C_6D_6 and δ 67.21 for -CH_2 of THF-D_8.

MALDI mass spectra were recorded using a Bruker solariX XR Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7 T refrigerated actively shielded superconducting magnet.

Thermogravimetric analysis (TGA) measurements were made using a TGA Q500 apparatus produced by TA Instruments (Waters/TA Instruments) in N_2 flow of 40.0 mL min^{-1}, placing the polymer samples in platinum crucibles.

2.2. Synthesis of Zn(II) complexes

2.2.1. Synthesis of complexes 1-3

Complexes 1–3 were synthesized with nearly quantitative yields through the reaction of equimolar amounts of proligands L1 (0.300 g, 1.04 mmol), L2 (0.265 g, 1.04 mmol) or L3 (0.315 g, 1.04 mmol) dissolved in 4 mL of CH_2Cl_2 and $Zn[(NSiMe_3)_2]_2$ (0.402 g, 1.04 mmol) in 2 mL of CH_2Cl_2 (Fig. 1) at 25 °C. The resulting mixtures were stirred at room temperature for 1 h. Then the mixtures were washed with hexane and the solvent was removed in vacuum. The complexes were characterized by multinuclear NMR spectroscopy, high resolution MALDI mass spectrometry, and X-ray diffraction studies, as reported in our previous work [50].

2.2.2. Synthesis of complex **4**

Proligand L4 was prepared as described in the Supplementary Material (see Figs. S1–S2). In a glovebox, a solution of L4 (0.200 g, 0.50 mmol) in dichloromethane (3 mL) was slowly added to a solution of Zn $[N(SiMe_3)_2]_2$ (0.110 g, 0.50 mmol) in dichloromethane (1 mL) (Fig. 2). The resulting mixture was stirred at room temperature for 1 h, resulting in the precipitation of an orange solid. The solvent was removed, and the

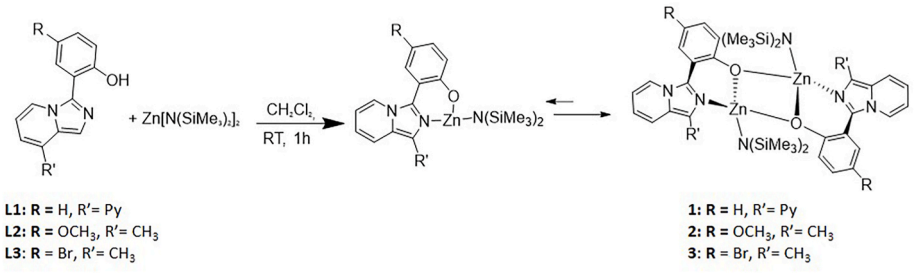

Fig. 1. Reaction scheme for the synthesis of catalysts **1**–**3**.

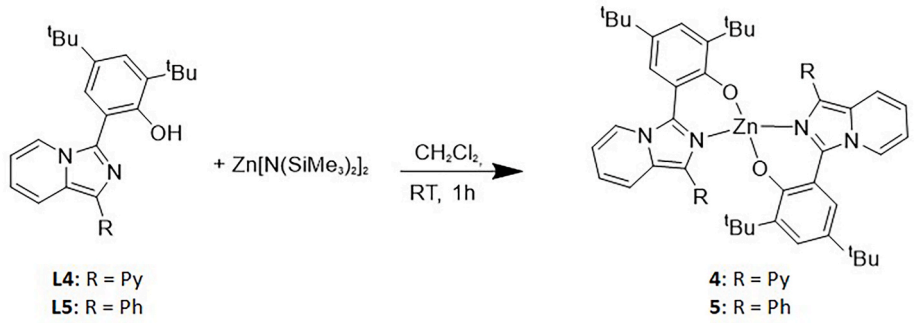

Fig. 2. Reaction scheme for the synthesis of catalysts **4**–**5**.

solid residue was washed using dry hexane. The solution was dried in vacuum to afford a light-yellow powder. ^{1}H NMR (600 MHz, CD_2Cl_2, 298K, Fig. S3) δ: 8.52 (d, J = 7.34 Hz, H_8, 2H), 8.15 (d, J = 9.24 Hz, H_{11}, 2H), 7.75 (d, J = 4.62 Hz, H_{18}, 2H), 7.70 (d, J = 8.0 Hz, H_{15}, 2H), 7.41 (d, J = 2.42 Hz, H_5, 2H), 7.22(m, H_3, H_{16}, 4H), 7.00 (m, H_{10}, 2H), 6.75 (m, H_9, 2H), 6.65(m, H_{17}, 2H), 1.38 (s, -C(CH_3)$_3$, 18H), 1.14(s, -C(CH_3)$_3$, 18H). ^{13}C NMR (150 MHz, CD_2Cl_2, 298 K, Fig. S4): δ 165.23 (C_q), 150.16 (C_q), 148.6 (C_{18}), 141.7 (C_q), 141.27 (C_q), 136.17 (C_{16}), 133.68 (C_q), 127.86 (C_q), 126.22 (C_q), 125.83 (C_3), 124.04 (C_8), 122.41 (C_{10}), 121.02 (C_5), 120.54 (C_{17}), 119.96 (C_{11}), 119.14 (C_{15}), 114.07 (C_9), 111.57 (C_q), 35.39 (C_q), 34.08 (C_q), 31.62 (-C(**C**H_3)$_3$), 29.00 (-C(**C**H_3)$_3$). Complex **4** was further characterized by DOSY NMR experiments (Fig. S5) and by MALDI-FT-ICR Mass Spectrometry (Fig. S6). The sample was prepared by dissolving the complex in CH_2Cl_2 at a concentration of 1.0 mg/mL and mixing it with the matrix, trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) and potassium tri-fluoroacetate (KTFA) as cationizing agent.

2.2.3. Synthesis of complex *5*

Proligand L5 was prepared as described in the Supplementary Material (Figs. S7–S8). In a glovebox, a solution of L5 (0.100 g, 0.25 mmol) in dichloromethane (3 mL) was slowly added to a solution of Zn[N($SiMe_3$)$_2$]$_2$ (0.110 g, 0.5 mmol) in dichloromethane (1 mL) (Fig. 2). The resulting mixture was stirred at room temperature for 1 h, resulting in precipitation of a dark yellow solid. The solvent was removed, and the solid residue was washed using dry hexane and dried in vacuum to afford a light-yellow powder.

^{1}H NMR (600 MHz, CD_2Cl_2, 298K, Fig. S9) δ: 8.06 (d, J = 7.42 Hz, H_1, 2H), 8.15 (d, J = 9.27 Hz, H_4, 2H), 7.45 (m, H_8, H_{12}, 4H), 7.38 (d, J = 2.66 Hz, H_{15}, 2H), 7.17 (d, J = 2.66 Hz, H_{17}, 2H), 6.82(m, H_9, H_{10}, H_{11}, 6H), 6.78 (m, H_3, 2H), 6.55 (m, H_2, 2H), 1.52 (s, -C(CH_3)$_3$, 18H), 1.35(s, -C(CH_3)$_3$, 18H). ^{13}C NMR (150 MHz, CD_2Cl_2, 298 K, Fig. S10): δ 163.77 (C_q), 141.54 (C_q), 141.18 (C_q), 134.65(C_q), 130.74 (C_q), 128.71 (C_7), 127.79 (C_{10}), 126.85 (C_8, C_9, C_{11}, C_{12}), 126.23 (C_q), 126.09 (C_{15}), 123.63 (C_1), 121.78 (C_{17}), 121.27 (C_3), 118.84 (C_4), 114.02 (C_2), 111.55 (C_q), 36.10 (C_q), 35.39 (C_q), 31.87 (-C(**C**H_3)$_3$), 29.63 (-C(**C**H_3)$_3$). Complex **5** was further characterized by DOSY NMR experiments (Fig. S11) and by MALDI-FT-ICR Mass Spectrometry (Fig. S12) The sample was prepared following a procedure analogous to that described above.

2.3. Alcoholysis of PLLA commercial samples

2.3.1. Methanolysis

The methanolysis reactions were carried out in magnetically stirred flasks under a nitrogen atmosphere. Commercial PLLA pellets were milled and sieved, resulting in particle size ranging between 150 and 180 μm. Samples (50 mg each) were treated in boiling methanol in the presence of catalysts **1**–**5** (1 mol % relative to ester linkages, see Table 1). After 1 h the reactions were stopped with $CHCl_3$ and the solvents were removed under reduced pressure. The relative amounts of the obtained products were determined by ^{1}H NMR analysis (see the Supplementary Material, Fig. S13). Methanolysis tests were also performed on films prepared by cast extrusion of different commercial PLLA pellets (see Table 2).

2.3.2. Kinetic studies for methanolysis

The kinetic studies for methanolysis were carried out for catalysts **1** and **2**, treating 50 mg of a commercial PLA with a M_n of 20 × 10^3 g

Table 1
PLLA depolymerization to methyl lactate in boiling methanol by Zn(II) catalysts **1**–**5**.[a]

Run	Catalyst	X_{int}[b] %	$S_{Me\text{-}LA}$[c] %	$Y_{Me\text{-}LA}$[d] %
1	**1**	>99	>99	>99
2	**2**	42 ± 2	>99	42 ± 2
3	**3**	33 ± 2	>99	33 ± 2
4	**4**	56 ± 3	>99	56 ± 3
5	**5**	6 ± 1	32 ± 1	2 ± 0.1

[a] **Conditions**: 0.050 g polymer (PLLA Sulzer L99L, M_n = 49 × 10^3 g mol^{-1}, 99 % L-LA, milled, diameter = 150–180 μm) were treated with 2.5 mL boiling methanol using 7 μmol catalyst (1 mol % relative to ester linkages); time = 1 h.
[b] X_{int} = conversion of internal methine groups, average errors were determined from duplicate tests.
[c] $S_{Me\text{-}LA}$ = selectivity in methyl lactate.
[d] $Y_{Me\text{-}LA}$ = yield in methyl lactate.

Table 2
Methanolysis of different PLA commercial samples by Zn catalyst **1**[a].

Entry	PLA	Molar mass[d] (g mol^{-1})	Crystallinity[e] (%)	Time (min)	X_{int}[f] (%)	$S_{Me\text{-}La}$[g] (%)	$Y_{Me\text{-}La}$[h] (%)
6	L99L[b]	49 × 10^3	40–45	60	>99	>99	>99
7	L99L[b]	49 × 10^3	40–45	30	72 ± 2	87 ± 1	62,5 ± 3
8	L98H[b]	63 × 10^3	35–40	30	>99	>99	>99
9	L98H[b]	63 × 10^3	35–40	15	74 ± 4	50 ± 2	37 ± 1
10	L96HH[b]	110 × 10^3	25–30	30	>99	>99	>99
11	L96HH[b]	110 × 10^3	25–30	15	59 ± 1	62 ± 2	36 ± 2
12	L95M[b]	50 × 10^3	20–25	30	>99	>99	>99
13	L95M[b]	50 × 10^3	20–25	15	80 ± 1	76 ± 2	61 ± 2
14	L96HH film[c]	110 × 10^3	25–30	60	88 ± 3	87 ± 2	77 ± 4
15	L98H film[c]	63 × 10^3	35–40	60	>99	>99	>99
16	L100HH film	92 × 10^3	45–55	60	55 ± 5	52 ± 3	29 ± 2

[a] **Conditions**: 0.050 g polymer were treated with 2.5 mL boiling methanol using 7 μmol Zn catalyst **1**.
[b] Sulzer PLA commercial samples were dissolved in CH_2Cl_2, reprecipitated as fine powders in *n*-hexane, and dried before depolymerization.
[c] Films (thickness 30–50 μm) were obtained by cast extrusion of commercial Sulzer PLA pellets.
[d] Molar mass were determined by GPC analysis in THF using polystyrene standards, the M_n were corrected using the Mark-Houwink factor of 0.58.
[e] % of crystallinity was calculated through DSC measurements.
[f] X_{int} = conversion of internal methine groups, average errors were determined from duplicate tests.
[g] $S_{Me\text{-}LA}$ = selectivity in methyl lactate.
[h] $Y_{Me\text{-}LA}$ = yield in methyl lactate.

mol^{-1} (previously dissolved in CH_2Cl_2 and reprecipitated as fine powders in *n*-hexane) in boiling methanol in the presence of 1 mol % of catalyst relative to ester linkages. For both catalysts, several methanolysis tests were carried out for different time intervals (See Fig. 4). After the prescribed time, the reaction mixtures were analyzed by ^{1}H NMR as reported above. Following a Reviewer's suggestion, we repeated a kinetic study of the methanolysis promoted by catalyst **1** under conditions like those described above: methanolysis reactions were carried out over different times and the reaction products were analyzed by both ^{1}H NMR and MALDI FT-ICR Mass Spectrometry. NMR analysis confirmed the progressive consumption of PLA and the progressive formation of oligomers and methyl lactate (the latter reaching 97 % after 30 min). On the other hand, using our FT-ICR mass spectrometer we were not able to detect in the mass spectra neither the starting high molar mass PLA, nor the formed methyl lactate, but only oligomers with molar masses in the range 200–10000 g mol^{-1}: the abundance of the latter seems to initially increase and then decreases at longer reaction times, in agreement with the NMR results (see Figs. S14–S15).

2.3.3. Ethanolysis

The ethanolysis reactions were carried out in magnetically stirred flasks under a nitrogen atmosphere. Samples prepared as above (50 mg each) were treated in boiling ethanol in the presence of catalysts **1**–**5** (1 mol % relative to ester linkages, see Table S1). The reactions were stopped with $CHCl_3$ after 6 h, the solvents were removed under reduced pressure and the relative amounts of the obtained products were determined as above (Fig. S16).

2.4. Depolymerization of PLLA to L-lactide

2.4.1. TGA experiments without alcohol

In the glovebox, solutions 0.02 M of **1** (31 mg in 3 mL of THF), **2** (19 mg in 2 mL of DCM), **3** (32 mg in 3 mL of DCM), **4** (34 mg in 2 mL of DCM), **5** (34.4 mg in 2 mL of DCM) and $Sn(Oct)_2$ (32 mg in 4 mL of THF) were prepared. Films were prepared by cast extrusion of commercial PLLA pellets (Sulzer L98H, molar mass 63 × 10^3 g mol^{-1}, M_w/M_n = 1.5, 98 % L-LA, crystallinity 40 %, T_m = 165.6 °C, melt flow index 14.0 g/10 min). Weighed film samples (3 mg each) were deposited onto the TGA crucible, and 0.1 mol% (relative to ester linkages) of one of Zn complexes **1**–**5** or $Sn(Oct)_2$ was added as a 0.02 M solution. The solvent was allowed to evaporate before the crucible was loaded into the TGA for monitoring the depolymerization (see Fig. S17 and Table S2). The TGA program used is as follows: jump from room temperature to 180 °C, isotherm for 100 min, ramp at 40 °C min^{-1} to 600 °C and jump to 30 °C.

2.4.2. TGA experiments with added alcohol

The TGA experiments were repeated under the same conditions described above but adding glycerolethoxylate (GEO) or polyglycerol-3 (PG-3) as solutions containing 20 equiv of OH groups relative to the catalyst (see Fig. 4, Table 3, and Table S3, for experiments in the presence of GEO, and Fig. S18 and Table S4 for experiments in the presence of PG-3).

2.4.3. Bulk depolymerization of PLLA to L-lactide

For each bulk depolymerization test, 200 mg of the same PLLA film used for TGA, 0.1 mol% (relative to ester linkages) of catalyst, and the alcohol (GEO or PG-3) in solution ([OH]:[cat.] = 20: 1) were introduced in a sublimator with magnetic stirring (Fig. S19). The tests were carried out at 180 °C for 100 min under vacuum (<1 torr). At the end of each test, the reactor was cooled at room temperature and all the contents were dissolved in $CHCl_3$. Then, the solvent was removed under reduced pressure and the solid residue was analyzed by ^{1}H NMR to determine its composition (Fig. S20).

A larger scale depolymerization run was carried out in a sublimator with magnetic stirring (Fig. S19) using 5 g of PLLA and 0.05 mol% (relative to ester linkages) of Zn complex **2** with a ratio [OH]: [**2**] of 20:1. The test was conducted at 180 °C for 24 h under reduced pressure (<1 torr), resulting in the recovery of 4.9 g (98 %) of L-lactide.

Table 3
Depolymerization of PLLA by Zn catalysts 1–5 and $Sn(Oct)_2$ with GEO, from TGA experiments[a].

Run	Catalyst	k [h^{-1}][b]
17	**$Sn(Oct)_2$**	73 ± 9
18	**1**	54 ± 12
19	**2**	115 ± 14
20	**3**	98 ± 10
21	**4**	65 ± 3
22	**5**	37 ± 5

[a] **Conditions**: 0.003 g polymer (PLLA Sulzer L98H film, molar mass = 63 × 10^3 g mol^{-1}, 98 % L-LA, thickness film 30–40 μm); 0.1 mol% (relative to ester linkages) of catalyst, ($[GEO]_{OH}$:[cat] = 20:1), T = 180 °C, isothermal time = 100 min.
[b] The rate constant is the gradient of the linear fits to the plots of %PLLA mass loss over the time estimated by TGA (Fig. 3), average errors are estimated from repeated trials (see Table S3).

2.4.4. Bulk depolymerization of PLLA to L-lactide: kinetic studies

50 mg of a PLLA in film was placed in a sublimator with magnetic stirring; then 0.1 mol% (relative to ester linkages) of catalyst (either **1**, or **2** or $Sn(Oct)_2$) and GEO ([OH]:[catalyst] = 20:1) were added. For each catalyst, several tests were carried out for different times (see Fig. S21) under vacuum (<1 torr) at 180 °C. At the end of the runs, the compositions of the reaction mixtures were analyzed by ^{1}H NMR as above.

3. Results and discussion

3.1. Synthesis of the Zn(II) complexes

Complexes **1**–**3** (Fig. 1) were synthesized allowing to react equimolar amounts of (imidazole [1,5-*a*]pyrid-3-yl)phenol proligands L1-L3 and $Zn[(NSiMe_3)_2]_2$ in methylene chloride at room temperature (see Fig. 1) as previously reported [50]. Detailed characterization using high-resolution MALDI-FT-ICR mass spectrometry, along with ^{1}H NMR and the ^{13}C NMR experiments and single crystal X-ray diffraction analysis indicated the formation of dinuclear heteroleptic species, having either unsymmetrical (complex **1**) or symmetrical (complexes **2** and **3**) structures [50].

The (imidazole [1,5-*a*]pyrid-3-yl)phenol ligands bearing bulky tert-butyl substituents in the ortho, para positions of the phenolic ring and either a 2-pyridine (L4) or a phenyl (L5) moiety in the position 1 of the imidazopyridine ring (Figs. S1, S2, S7, S8) were synthesized following a procedure similar to that reported in the literature [51]. In this case, reaction between the ligands and $Zn[N(SiMe_3)_2]_2$ under the above conditions did not afford the targeted heteroleptic species analogous to complexes **1**–**3**, but the homoleptic bis(chelate) complexes **4** and **5** (Fig. 2), as indicated by their NMR spectra (Figures S3-S5, S9-S11) and high-resolution MALDI-FT-ICR mass spectra (Figs. S6 and S12). The mass spectra of compounds **4** and **5** clearly showed lower masses than those expected for dinuclear species similar to those observed in the case of complexes **1**–**3** [50], but rather suggested homoleptic bis(chelate) mononuclear structures, as indicated for **4** by a peak at 861.41 *m/z*, corresponding to the molecular ion of the homoleptic species $C_{52}H_{56}N_6O_2Zn^+$, and for **5** by a peak at 858.38 *m/z*, corresponding to the molecular ion of the homoleptic species $C_{54}H_{58}N_4O_2Zn^+$.

Further evidence supporting the formation of homoleptic species is provided by the ^{1}H NMR spectra, which showed the number of peaks corresponding to two equivalent ligands bound to Zn, while no peak attributable to the -$N(SiMe_3)_2$ group, expected around −0.1 ppm, was observed. The distinct structural characteristics of complexes **4** and **5,** with the apparently counterintuitive preferential formation of bis (chelate) homoleptic complexes for ligands which bear bulkier substituents than those affording mono(chelate) heteroleptic complexes **1**–**3,** could be ascribed to the effect of steric bias making the formation of dimeric species for the former energetically less favorable with respect to the case of the latter [52].

3.2. Depolymerization of PLLA by alcoholysis

As mentioned in the Introduction, a variety of Zn(II) complexes have been reported to promote PLA depolymerization via transesterification with methanol or ethanol, affording alkyl lactates and lactide oligomers in variable relative amounts. Most of the depolymerization tests were carried out dissolving the polymer sample in a suitable solvent, usually THF or CH_2Cl_2. While this procedure allowed to study the mechanism and the kinetics of the reaction, and to define the most important operating parameters affecting the process [24], use of organic solvents is not recommended for a green industrial process.

Thus, we initially tested Zn(II) complexes **1**–**5** in the depolymerization of a commercial PLLA (Sulzer L99L, molar mass = 49×10^3 g mol^{-1}, 99 % L-LA) which was previously milled and sieved, and then treated with an excess of boiling methanol for 1 h. The reaction conditions and the results are reported in Table 1. The extent of depolymerization and the selectivity in the production of methyl lactate were evaluated by ^{1}H NMR analysis from the integrals of the resonances of the internal methine groups of PLLA, vs. those due to the oligomers and to methyl lactate (Fig. S13), according to the literature [24]. Under the above conditions, complex **1** allowed practically complete conversion of the PLLA sample to methyl lactate in 1 h, while the other complexes were less active. The apparent rate constants (k_{app}) of methanolysis were evaluated for complexes **1** and **2** by pseudo-first-order kinetic plots of ln ($[Int]_0/[Int]_t$) vs time (where $[Int]_t$ is the fraction of unconverted internal methine carbons at time t, see Fig. 3). The calculated k_{app}'s for methanolysis are 25.7 h^{-1} ± 1.5 for **1** and 4.4 h^{-1} ± 0.4 for **2**, respectively. It is worth mentioning that complex **1** was the best performing catalyst for the ROP of L-LA under mild temperature conditions [50].

Subsequently, powder samples were prepared by dissolving and precipitating different commercial grades of PLLA, differing for steric purity, crystallinity, and molar mass. The samples were treated in boiling methanol in the presence of complex **1** (1 mol % relative to ester linkages) for short times, to look for any influence of the polymer features on the depolymerization (see Table 2): as expected, polymer samples with higher crystallinity and molar mass showed slower depolymerization rate. The same trend was observed in the depolymerization of films obtained by cast extrusion of different grades of commercial PLA pellets. A real PLLA post-consumer waste film (a flexible packaging for biodegradable disposable cutlery taken from the cafeteria of the University of Salerno, see Figs. S22 and S23) was also successfully depolymerized to methyl lactate under the same conditions.

The Zn catalysts **1**–**5** were also tested in the depolymerization in boiling ethanol [53,54]. In this case the alcoholysis appears slower, as expected for the lower nucleophilicity of ethanol with respect to methanol: the best performing Zn catalyst **2** (which incidentally was the best performing in the ROP of L-lactide at high temperature) gives complete depolymerization to ethyl lactate with high selectivity in 6 h (see Table S1, Fig. S16).

3.3. Depolymerization of PLLA to L-lactide

As mentioned in Introduction, PLLA depolymerization to the monomer has been successfully optimized by following the polymer mass loss during isothermal TGA experiments under nitrogen flow [43–45]. We initially evaluated the performance of Zn complexes **1**–**5** by isothermal TGA experiments at 180 °C under a nitrogen flow of 40 mL/min using films obtained by cast extrusion of commercial PLLA pellets (Sulzer L98H, molar mass = 63×10^3 g mol^{-1}, M_w/M_n = 1.5, 98

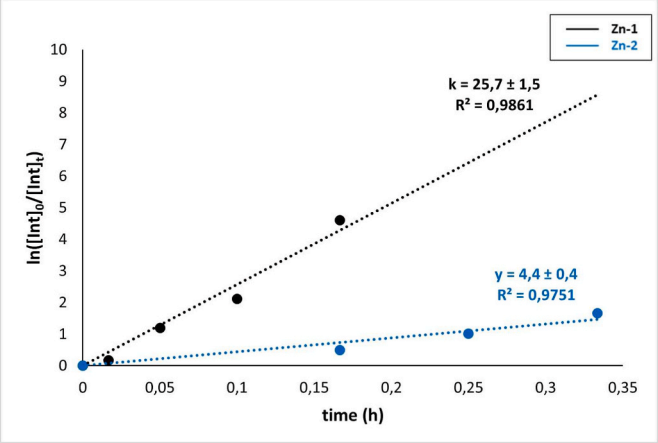

Fig. 3. Pseudo-first-order kinetic plots of ln($[Int]_0/[Int]_t$) vs. time for the methanolysis of a commercial PLA with a M_n of 20×10^3. The reactions were carried out with 0.050 g of PLA in presence of 2.5 mL boiling methanol and with 7 μmol of Zn catalyst (1 mol % relative to ester linkages).

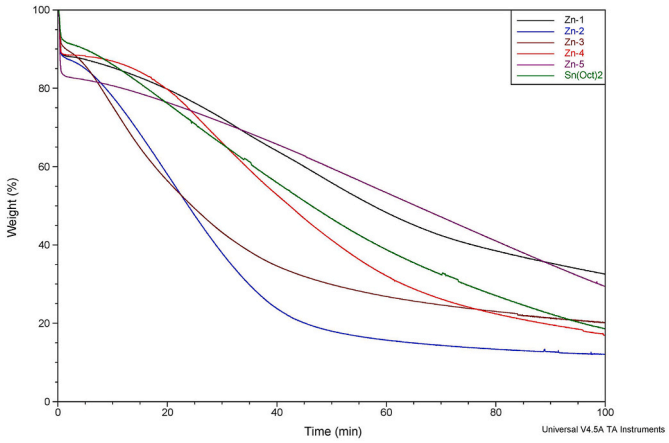

Fig. 4. Evolution of PLLA mass loss vs time from TGA experiments using different catalysts in presence of glycerolethoxylate (see Table 4).

% L-LA, crystallinity 40 %, T_m = 165.6 °C, melt flow index 14.0 g/10 min) to which 0.1 mol% (relative to ester linkages) of Zn complex as a 0.02 M solution was added onto the TGA crucible.

For comparison, the same experiment under identical conditions was performed using $Sn(Oct)_2$ as the catalyst. Evolution of polymer mass loss for the different catalysts was monitored over 100 min (see Fig. S17 and Table S2): under the above conditions, all the Zn complexes were poorly effective, with the best performing complex **1** promoting ≈20 % depolymerization, while $Sn(Oct)_2$ afforded ≈75 % depolymerization. We had previously found that Zn complexes of this class are poorly active also in the ROP of L-LA in the absence of alcohol co-initiator, while in the presence of alcohol they can compete with $Sn(Oct)_2$ under industrially relevant conditions (T = 190 °C, very low catalyst loading, excess of alcohol) [50]. Moreover, addition of a suitable alcohol (glycerolethoxylate, GEO) to $Sn(Oct)_2$ has been reported to result in increased depolymerization rates (by a factor of 2) [44]. We have thus repeated the TGA experiments under the same conditions described above but adding GEO (as a THF solution containing 20 equiv. in terms of OH groups with respect to the metal catalyst) onto the TGA crucible (see Fig. 4 and Table 3).

Gratifyingly, under these conditions Zn complexes **1**–**5** promote PLLA depolymerization with efficiencies similar or better than those of $Sn(Oct)_2$: complex **2** is the most active, promoting ≈92 % depolymerization in 100 min (cf. 82 % for $Sn(Oct)_2$). The difference is even larger at shorter times: e. g., after 40 min **2** promotes ≈75 % depolymerization, while $Sn(Oct)_2$ affords only ≈49 %.

The performances of Zn(II) catalyst **1, 2** and $Sn(Oct)_2$ were also compared by a kinetic study conducted in bulk using 0.1 mol% catalyst relative to ester linkages with a $[GEO]_{OH}$:[Cat] ratio of 20:1 at 180 °C under reduced pressure (see Fig. S19). The observed kinetic constants, comparable to those obtained from TGA tests, confirmed that **2** is the most active catalyst under these conditions, performing even better than $Sn(Oct)_2$. Noteworthy, we had previously observed that complex **2** was the best performing catalyst of this class in the ROP of L-LA at high temperature (190 °C) [50].

We have then performed bulk depolymerization tests, using 0.200 g of the same film of commercial PLLA, 0.1 mol% (relative to ester linkages) of Zn complex and GEO ([OH]: [Zn] = 20:1). The tests were carried out at 180 °C for 100 min in a sublimator (see Fig. S17) with magnetic stirring under vacuum (<1 torr). A test under identical conditions was also carried out using $Sn(Oct)_2$.

At the end of each test, the reactor was cooled at room temperature and all the content was dissolved in $CHCl_3$. Then, the solvent was removed under reduced pressure and the solid residue was analyzed by ^{1}H NMR (Fig. S18) to determine its composition: for all the tests the production of L-LA with excellent conversion was confirmed, with Zn complex **2** affording the highest yield (>99 %).

As a complementary investigation, we screened the performance of different high boiling alcohols both through TGA (see Fig. S18, Table S4) and bulk depolymerization of PLLA using either $Sn(Oct)_2$ or Zn complexes. Interestingly, polyglycerol-3 (PG-3), a low-cost commercial mixture of refined polyglycerols of vegetal origin, mainly composed of triglycerol, afforded excellent performance, comparable to that of GEO, when used together with catalysts **2** and **3** (See Table 4).

Thus, a larger scale depolymerization run was carried out using 5 g of PLLA and 0.05 mol% (relative to ester linkages) of Zn complex **2** and PG-3 with [OH]: [**2**] ratio of 20:1, resulting in the isolation of 4.90 g of pure L-LA (Fig. S22). ^{1}H NMR analysis also confirmed the absence of epimerization, since only 2 % of meso lactide was present, consistent with the starting polymer composition (98 % of L-lactide, see Fig. S23). The as recovered monomer could be successfully repolymerized without any further treatment using catalyst **2** under previously reported conditions [50]. Further evidence supporting the absence of epimerization was provided by the homo-decoupled spectrum of the resulting polymer (Fig. S24), which was identical to that of the starting polymer (Fig. S25). Following the suggestion of a reviewer, we also tried to repolymerize the as-recovered mixture of a depolymerization test, containing L-lactide, GEO, and catalyst **2**, without reintroducing additional catalyst or alcohol, by simply heating it at 190 °C under stirring, resulting in a monomer conversion of 62 % after 1 h and of 95 % after 3 h.

4. Conclusions

Three previously reported heteroleptic and two newly synthesized homoleptic (imidazole [1,5-*a*]pyrid-3-yl)phenolate Zn(II) complexes were tested in the chemical recycling of commercial poly(L-lactic acid) samples using two different pathways: (i) alcoholysis to alkyl lactates in boiling methanol or ethanol, and (ii) chemical recycling to monomer (CRM) in bulk under vacuum or in a nitrogen flow at 180 °C. The Zn(II) complexes were effective in promoting the alcoholysis of various PLLA samples, differing in molar mass and degree of crystallinity. Heteroleptic complex **1** emerged as the most efficient catalyst, enabling nearly complete and selective conversion of PLLA to methyl lactate using 1 mol % catalyst relative to ester linkages in boiling methanol in 1 h.

More interestingly, CRM of commercial PLLA film samples was studied by Thermogravimetric Analysis (TGA) using 0.1 mol-% catalyst (relative to ester linkages) and an excess of a highly boiling alcohol (glycerolethoxylate or polyglycerol-3) at 180 °C. Under the latter conditions, complex **2** showed the highest depolymerization rate constant of the tested Zn complexes and resulted more active than $Sn(Oct)_2$ tested under the same conditions. Bulk depolymerization tests carried out on different commercial PLLA samples, including post-consumer ones, scaled up to 5 g of treated polymer, confirmed the excellent performance

Table 4
Bulk depolymerization of PLLA by Zn catalysts **1**–**5** and **$Sn(Oct)_2$**[a].

Run	Catalyst	Alcohol	% depolymerization[b]
23	**$Sn(Oct)_2$**	GEO	94 ± 1
24	**$Sn(Oct)_2$**	PG-3	73 ± 2
25	**1**	GEO	90 ± 2
26	**1**	PG-3	57 ± 3
27	**2**	GEO	>99
28	**2**	PG-3	96 ± 1
29	**3**	GEO	83 ± 2
30	**3**	PG-3	81 ± 4
31	**4**	GEO	87 ± 2
32	**4**	PG-3	60 ± 1
33	**5**	GEO	67 ± 1
34	**5**	PG-3	14 ± 1

[a] **Conditions**: 0.200 g polymer (PLLA Sulzer L98H film, molar mass = 63 × 10^3 g mol^{-1}, 98 % L-LA, thickness film 30–40 μm); 0.1 mol% (relative to ester linkages) of catalyst, ([OH]:[cat] = 20:1), T = 180 °C, time 100 min, in vacuum.
[b] average errors are estimated from duplicate tests.

of the title Zn complexes, resulting in the recovery of high purity L-lactide, with yields and selectivity up to 99 %. The as recovered monomer could be repolymerized without any further purification, highlighting the potential of these catalysts for efficient and sustainable PLA recycling. Our results, complementing previous studies on the matter [12,20–26,34,42–44], support the idea that PLA could be the ideal candidate as a sustainable polymer in a circular economy model, capable of replacing conventional plastics for non-durable applications.

CRediT authorship contribution statement

Maria Gentile: Validation, Investigation, Conceptualization. **Licia Gaeta:** Investigation. **Stefano Brenna:** Investigation. **Claudio Pellecchia:** Writing – review & editing, Writing – original draft, 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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymertesting.2025.108727.

Data availability

Data will be made available on request.

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