ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
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Chemical recycling of polylactide by microwave-assisted processes†

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The chemical recycling of post-consumer polylactic acid by microwave-assisted alcoholysis promoted by a phenoxy-imine pyridine zinc is investigated. Different alcohols and diols are used to achieve, in all cases, outstanding activity and selectivity toward the targeted products. Thanks to the robustness of the catalyst the reactions can be performed in the air, with technical grade reagents and without the use of additional solvents, thus ensuring the full sustainability of the procedure.

Introduction

Oil derived synthetic plastics are the largest synthetic consumer products in the world; from their introduction into the market to nowadays the cumulative global plastic production has exceeded 9 billion tons.[1] Unfortunately, the waste management strategies and recycling technologies of post-consumer plastics have not advanced at a rate comparable to their production and, currently, more than 9 billion tons of plastic waste are accumulated in landfills or dispersed into the environment.[2]

The dramatic consequences of plastic pollution and the progressive depletion of fossil-based resources are growing issues that require concrete corrective actions finalized to a transition from a linear to a circular model for plastic materials flows.[3] Currently, only 9% of the total plastic waste is recycled, almost exclusively through mechanical processes, inevitably leading to material down-cycling and eventual disposal after a limited number of cycles with the irreversible loss of intrinsic values of original feedstock.[4]

An alternative way to valorize post consumer plastic is chemical recycling; this is emerging as a promising strategy to convert plastic waste into value-added

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chemicals or original monomers. The latter, commonly known as chemical recycling to monomer, allows re-obtaining the original polymer with potentially enabling "infinite" loops, thereby diminishing the need for virgin feedstocks.[5,6]

This method expresses its highest potential in the case of polymers containing functional groups that can be chemically attacked such as polyesters,[7–10] polyurethanes[11,12] and polycarbonates.[7,13,14]

A complementary approach for a sustainable productive model for plastics is the replacement of oil derived plastics with biodegradable materials produced by renewable resources.[15]

In this context, aliphatic polyesters, as bioderived and chemically recyclable materials, may represent the point of convergence of the two strategies. They are thermoplastic polymers, typically easy to process, and show a large variety of mechanical and chemical properties that make them very versatile materials for a large range of applications.[16]

Within this class, poly-L-lactic acid (PLLA) is the most representative material since it offers advantages including renewable feedstocks, biocompatibility, and mechanical properties comparable to those of polystyrene. In addition, the ester bonds along the polymer chains can be used for chemical and biological degradation. However, its disposal still present some challenges in terms of sustainability.[17]

Polylactic acid generally shows moderate thermal stability which causes extra constraints for mechanical recycling. In addition, its biodegradation occurs only under industrial conditions, while in soil at 30 °C, it requires a minimum of one year for complete degradation.[18] In addition, the raw materials for the production of its monomer, lactide (LA), mainly come from corn and sugar beets and mass production will pose a risk to food security.

The development of chemical recycling methods for end-of-life PLLA has attracted great attention to make its production more sustainable even from an economical point of view, since the LA production accounts for approximately 50% of the total production costs of polylactic acid.[8,19–22]

Chemical recycling by alcoholysis is a very promising strategy to convert PLLA to value-added lactate esters that can be used as environmentally friendly solvents or as feedstocks for the synthesis of lactide, opening the chance for a circular economy for PLLA.[8,20,23]

In chemical recycling by transesterification, catalysts play an important role leading to increased reaction rate, high yield and selectivity. Different organic catalysts, ionic liquids[24] and metal species, predominantly Zn-based complexes,[25,26] have been revealed as able to promote this process.

In previous studies we demonstrated that homoleptic and heteroleptic phenoxy-imine pyridine zinc complexes efficiently promote the polymerization of lactide and cyclic esters, with high activity and excellent control, even under industrially relevant conditions. The same complexes were also successfully employed in the chemical recycling, by alcoholysis, of PLLA, several aliphatic polyesters, polyethylene terephthalate and polycarbonates.[27–32]

In this work we explored the potential of this class of catalysts in chemical recycling of PLLA *via* microwave-assisted processes. Generally, microwave-assisted reactions are based on the ability of microwave radiation to excite polar molecules and force them to align with the oscillating electric field. Heating of the reaction mixture is generated by rotation and the collision of molecules
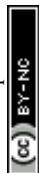
within the reaction mixture thus reaction rate is generally higher than that obtained under conventional heating.[33]

Alcoholysis of polyesters under microwave irradiation was first reported by Ohara *et al.*, in which its products were compared with those from conventional heating methods.[34] Achilias described the PLLA degradation by using alkali solution (10% w/v NaOH concentration) and a phase transfer catalyst to achieve complete degradation after 10 min at 100 °C.[35]

More recently, Enthaler described the methanolysis of PLLA by alkali metal-halides, tin,[36] zinc compounds[37] and 4-dimethylaminopyridine[38] as catalysts and utilizing microwave heating with excellent conversions and yields (>99%) in less than 20 min.[37] The lactate yield was significantly affected by parameters such as reaction time, catalyst concentration and temperature. However, the highest turnover frequencies, up to 39 600 h^{-1}, were achieved with tin catalysts.

In this study, we investigated the alcoholysis of PLLA by phenoxy-imine pyridine zinc catalyst under microwave irradiation in comparison with conventional heating. To further investigate the efficiency and selectivity of the process, multifunctional alcohols have been employed. The effects of the types of diols and PLLA/diol feeding ratios on the structures and properties of the resulting alcoholized products were examined.

Results and discussion

For the studies of microwave-assisted alcoholysis reactions, a zinc homoleptic complex was selected that was stable at high temperature and in the presence of high concentrations of protic species allowing its use with unpurified solvents and monomers. Additional advantages of this system are the cost-effective synthesis and its recyclability after use in PLLA alcoholysis experiments.

Zinc complex **1** was obtained by direct reaction between ZnEt$_2$ and two equivalents of the tridentate proligand in toluene solution (Scheme 1). The proligand and complex **1** were fully characterized by NMR spectroscopy, as detailed in Fig. S1–S5.†

All alcoholysis reactions were performed on commercial PLLA cups. The PLLA samples were characterized by GPC to determinate the molecular mass ($M_n = 51$ kDa, $D = 1.9$) and by ^{1}H NMR spectroscopy and thermal analysis (TGA) to verify
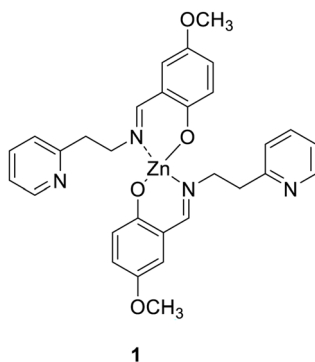
Scheme 1 Structure of the phenoxy-imine pyridine zinc catalyst **1** used for this study.
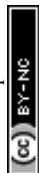
the presence of impurities. TGA established that the residual after thermal decomposition up to 340 °C was around 5%.

The reactions were performed in the air, without the addition of solvent and with unpurified technical grade alcohols that are considerably cheaper than the analytical grade ones.

Initial tests of degradation by methanolysis were performed by using an excess of alcohol (30 equivalents with respect to the lactyl repeating monomer unit) and low catalytic amounts of **1** (0.5 mol% with respect to the repeating units) at 65 °C. The heating was interrupted when the PLLA was completely dissolved resulting in the formation of a homogeneous solution in which $CHCl_3$ was added to solubilize eventual residues. To a small aliquot of the resulting solution the opportune amount of $CDCl_3$ was added for ^1H NMR analysis.

All parameters for monitoring of the degradation reaction, namely conversion, selectivity, and yield of methyl lactate (X_{Int}, S_{Me-La}, Y_{Me-La}, respectively) were evaluated by integration of the diagnostic signals of the methine region (*ca.* $\delta = 4.2$–5.2 ppm) of the ^1H NMR spectra.

When conventional heating was used (entry 1, Table 1), the degradation reaction in neat alcohol selectively produced Me-La after 30 minutes.

The correctness of the NMR estimations was confirmed by performing the same experiment in deuterated methanol and in the presence of tetrakis(trimethylsilyl)silane (TMSS) as the internal standard (see Experimental section) from which the same results were obtained.

As reported in previous studies, in these conditions the reaction proceeds by an unzipping mechanism that occurs from the chain end groups with the exclusive formation of methyl lactate (Scheme 2).[27–29] In the proposed mechanism the Zn center should be coordinated by the two oxygen atoms of the lactyl end group, thus activating the carbonyl atom for the nucleophilic attack by the alcohol. At the same time, the H bond interaction between the pyridine and the hydroxyl group of methanol could make the alcohol more nucleophilic, favoring the reaction. The synergic action of the metal centre and of the peripheral

Table 1 Alcoholysis reactions of a PLLA sample with complex **1**

Entry[a]	[PLA]:[ROH]	ROH	MW (W)	T (°C)	Time (min)	X_{Int}^b (%)	S_{RLa}^b (%)	Y_{RLa}^b (%)
1	1:30	MeOH	—	65	30	100	100	100
2	1:30	MeOH	6	65	9	100	100	100
3	1:30	MeOH	35	120	1	100	100	100
4[c]	1:3	MeOH	35	120	3	100	100	100
5[c,d]	1:3	MeOH	35	120	3	0	0	0
6[c]	1:3	EtOH	35	120	20	54	30	16
7[c]	1:3	EtOH	35	120	40	93	56	52
8[c]	1:3	EtOH	35	120	60	97	65	63
9[c]	1:3	EtOH	35	120	90	100	100	100
10[c]	1:3	BuOH	40	120	60	98	67	66
11[c]	1:3	BuOH	40	120	90	100	88	88

[a] All reactions were carried out in air by using 10 μmol of **1** (0.6 mol% relative to ester linkages), 0.116 g of transparent PLLA cup with 2 mL of MeOH (30 equiv. with respect to the lactyl units). For entries 2–4, reaction times were not optimized. [b] Determined by ^1H NMR spectroscopy. [c] Volume of ROH ~0.2 mL (3 equiv. with respect to the lactyl units). [d] Without catalyst.
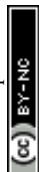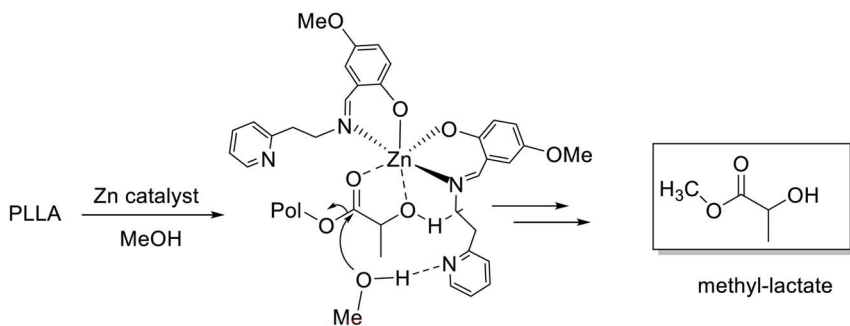
Scheme 2   Solvent-free methanolysis of PLA by complex **1**.

pyridine could be the reason for the higher activity observed for this class of catalysts in comparison to the simple zinc amide.

Subsequently, analogous degradation tests were performed by applying microwave heating (MW) in the range of temperature from 65 to 120 °C (entries 2 and 3, Table 1). All reagents were added to a microwave glass vial and the reaction was performed for the time necessary to achieve a complete dissolution of the PLLA sample. At 65 °C, the quantitative conversion of the PLLA into MeLa was achieved only after 9 minutes (entry 2, Table 1); increasing the temperature to 120 °C (entry 3, Table 1) the process was complete after only 1 min reaching a turnover frequency (TOF) of $\approx 12\,000\ h^{-1}$, which is among the highest TOFs reported so far. In all cases, even when the conversion of the polymer was not complete, the reaction proceeded in a selective way producing exclusively methyl lactate (Fig. 1). Interestingly, when reducing the amount of alcohol to three equivalents with respect to the repeating units, the quantitative production of
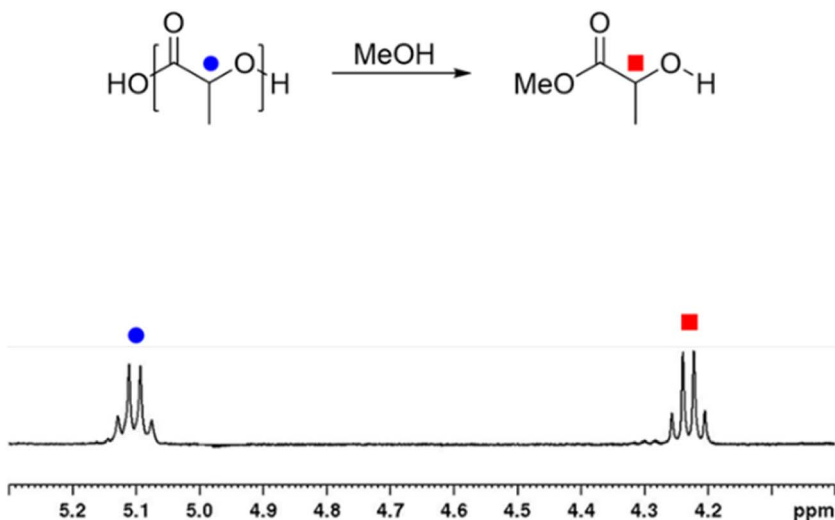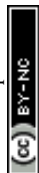

Fig. 1 ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 298 K) with methine group assignments for a PLLA methanolysis (NMR monitoring of entry 2 of Table 1 at 58% of conversion).

methyl lactate was still achieved after only 3 minutes (entry 4, Table 1). Since several studies demonstrated that the amount of nucleophile alcohol affects the yield of methyl lactate,[39,40] a drastic reduction in the amount of alcohol used represents value-added in this process since this allows reduction of tedious and expensive procedures for the purification of the final product. As a control experiment, in the absence of catalyst no formation of methyl lactate was detected by NMR (entry 5, Table 1).

Subsequently, the ethanolysis reactions were performed under the same reaction conditions optimized for methanolysis: at 120 °C with an alcohol/repeating units ratio = 3 : 1. The final product ethyl lactate (EtLa) is a biodegradable solvent that, thanks to its low toxicity, finds large application in pharmaceutical and cosmetic fields.[41]

As expected, ethanol as the nucleophile is less reactive than methanol and the degradation reactions were slower, probably because of the higher steric encumbrance of the alkyl groups that disfavors the attack at the carbonyl group (entries 6–9, Table 1). However, the complete conversion of the PLLA sample to ethyl lactate was achieved after 1.5 hours (entry 9, Table 1) as evident by the ^{1}H NMR spectrum (Fig. 2). Coherently with the previous comment, lower activity was observed with *n*-butanol; full conversion of the polymer was achieved after 1.5 hours but, in this case, the presence of oligomers persisted.

Contrary to what was observed in the methanolysis experiments, the alcoholysis reactions performed with higher alcohols were not selective (entries 6–10, Table 1), a two-step mechanism was active in which the polymer was first degraded into oligomeric fragments that were progressively converted to alkyl lactates. Probably, primary alcohols with longer alkyl portions favor the polymer swelling, facilitating the sorption of the alcohol itself in the polymer bulk.

From the ^{1}H NMR spectra of the reaction mixtures were evaluated the amounts of internal (Int, 5.0–5.1 ppm), chain-end (CE, 4.9–5.0 ppm and 4.1–4.2 ppm) and
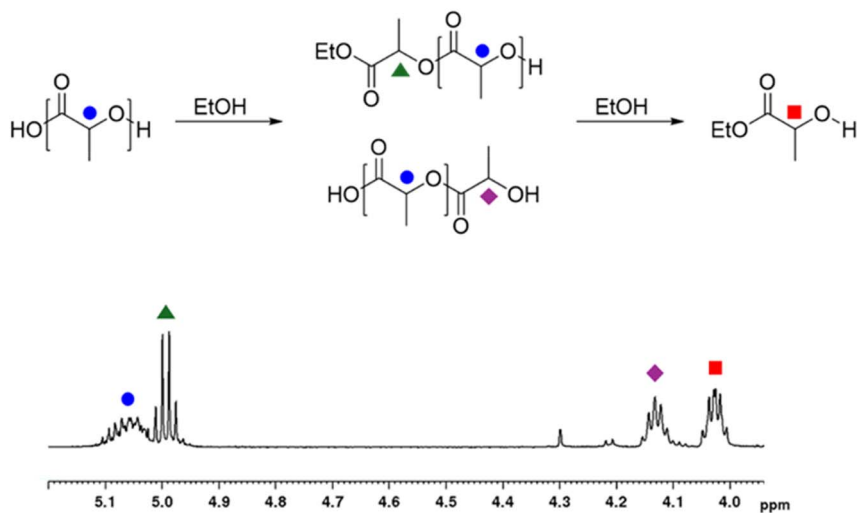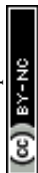

Fig. 2 ^{1}H NMR spectrum (600 MHz, CDCl₃, 298 K) with methine group assignments for a PLLA ethanolysis.

EtLa (4.0–4.1 ppm) methine groups, related to the amounts of PLLA fragments,[42] intermediates and the final product ethyl lactate as reported in Fig. 2.

Ethanolysis tests previously performed with the same complex, or with zinc bis [bis(trimethylsilyl)amide] ($Zn(HMDS)_2$), by using conventional heating revealed lower activities, in fact 24 hours were necessary for the quantitative production of ethyl lactate. Alcoholysis processes by primary alcohols yield monohydric alcohol derivatives; thus, we extended our tests to diols to convert PLLA into various bifunctional value-added products. Ethylene glycol (EG) is a diol commonly applied in the alcoholysis of polyesters and as a bi-functional molecule it can lead to the formation of two possible products, as a consequence of a single or double esterification of the hydroxyl groups (Scheme 3).

All the tests have been carried out introducing the PLLA sample, the catalyst and ethylene glycol (a specific amount related to the ester linkages of the polymer) into a 10 mL vessel in the air and then brought to the microwave reactor.

As expected, the efficiency and selectivity of the process were strongly influenced by parameters like temperature and time of reaction. At 120 °C, the quantitative conversion of PLLA was achieved after 30 minutes (entry 1, Table 2). The products obtained were glycolyl lactate with a yield of 77% while the residual amount was oligomeric species.

Extending the reaction time to one hour (entry 2, Table 2), glycolyl lactate was produced selectively as shown by the ^1H NMR spectrum in which the presence of a single species was evident, that was fully characterized by mono and bi-dimensional NMR experiments (Fig. 3 and S12–S14†). Although EG was used in small excess (3 equivalents per ester unit) no product of double esterification was observed. Increasing the temperature up to 200 °C, the degradation time was
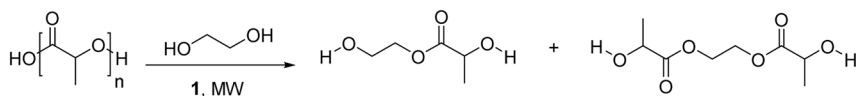

Scheme 3 Alcoholysis reaction of PLA with ethylene glycol.

Table 2 Degradation of PLA by ethylene glycol (EG) and diols

Entry[a]	$[PLA]:[R(OH)_2]$	$R(OH)_2$	T (°C)	Time (min)	X_{Int}^{b} (%)	$S_{RLa}^{b,c}$ (%)	$Y_{RLa}^{b,c}$ (%)
1	1 : 3	EG	120	30	100	77	77
2	1 : 3	EG	120	60	100	100	100
3	1 : 3	EG	200	20	100	100	100
4	1 : 1	EG	120	60	89	54	48
5	1 : 1	EG	200	20	96	56	55
6	1 : 3	BDO	120	60	16	80	15
7	1 : 3	BDO	200	60	100	100	100
8	1 : 3	cis-BDO	200	60	100	100	100

[a] All reactions were carried out in air by using 10 μmol of catalyst (0.6 mol% relative to ester linkages), 0.116 g of transparent PLLA cup. [b] Determined by ^1H NMR spectroscopy. [c] The yield of the desired product is calculated by considering all the species found after the reaction; the selectivity specifically refers to the product of alkyl mono substitution, which gives the mono substituted species as compared to oligomer PLLA fragments.
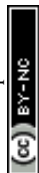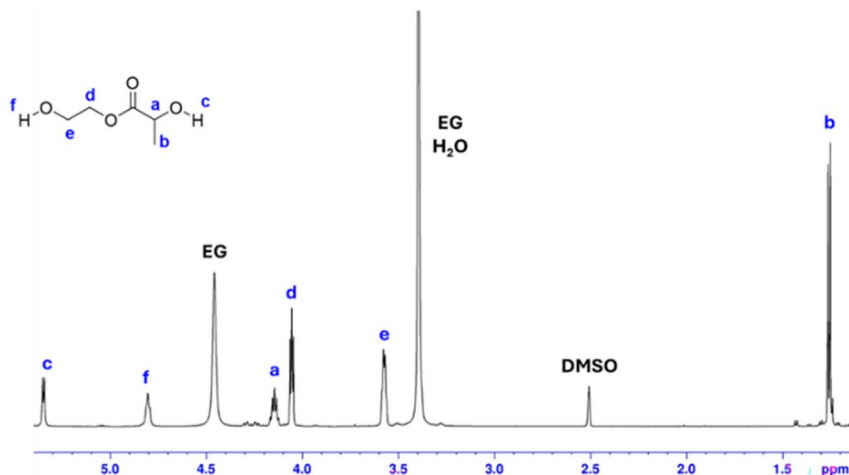
Fig. 3 ^{1}H NMR spectrum (600 MHz, DMSO-d$_6$, 298 K) of glycolyl lactate (entry 2, Table 2).

significantly reduced and the complete conversion of PLA into glycolyl lactate was observed after only 20 minutes (entry 3, Table 2). When the amount of alcohol was reduced to a single equivalent (entry 4, Table 2), the conversion of about 90% was reached after one hour at 120 °C producing about 50% of glycolyl lactate. Similar results were obtained after 20 minutes when the reaction was performed at 200 °C (entry 5, Table 2).

Additional experiments were performed using 1,4-butanediol (BDO) which resulted in complete degradation of PLLA into a single target product within 1 hour at 200 °C (entry 7, Table 2, Fig. 4 and S15–S17†).

Finally, with the aim of producing new monomers containing additional functional groups, a degradation experiment was performed using *cis*-2-butene-
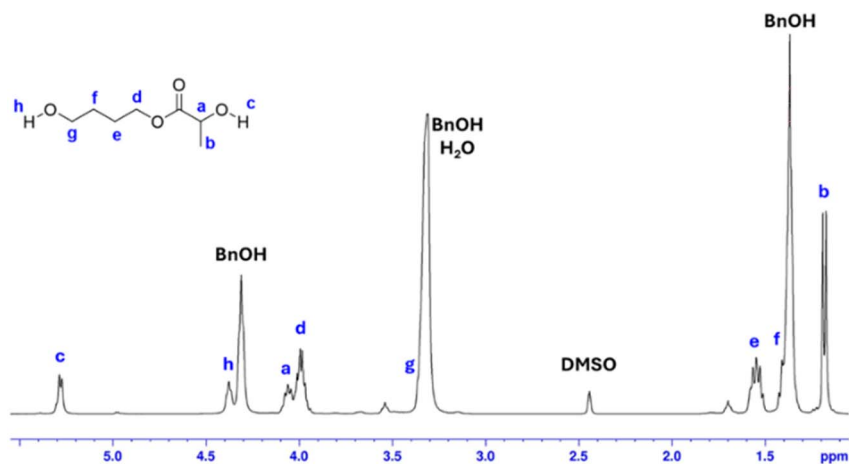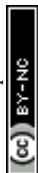

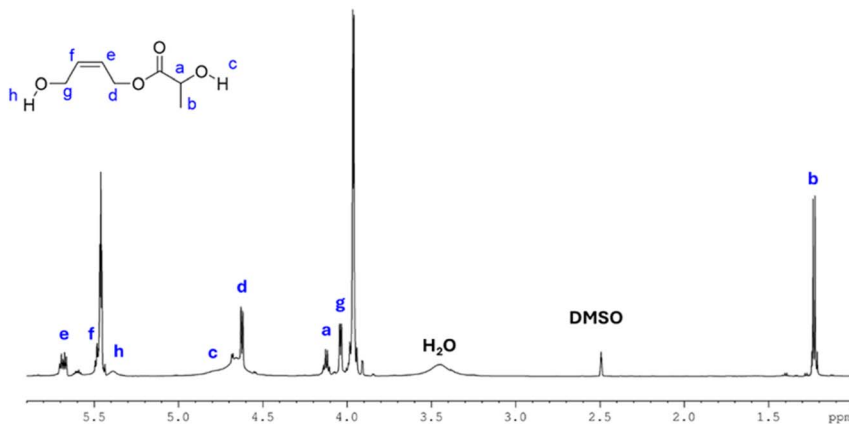Fig. 4 ^{1}H NMR spectrum (600 MHz, DMSO-d$_6$, 298 K) assignments of 4-hydroxybutyl 2-hydroxypropanoate.

Fig. 5 ^{1}H NMR spectrum (600 MHz, DMSO-d$_6$, 298 K) of PLA degradation product with *cis*-2-butene-1,4-diol (entry 8, Table 2).

1,4-diol (*cis*-BDO) as the nucleophile (entry 8, Table 2 and Fig. 5). Also in this case, the procedure resulted in efficiently and selectively achieving the target product that could be used as a comonomer in the production of polyesters or polyurethanes with unsaturation along the polymer chains.

Experimental

Materials and methods

All manipulations of air- and/or water-sensitive compounds were carried out under a dry nitrogen atmosphere using an MBraun Labmaster glove box or standard Schlenk-line techniques. Glassware and vials used in the degradation were dried in an oven at 120 °C overnight and exposed three times to vacuum–nitrogen cycles.

Reagents and solvents

PLLA waste cups (Natura Bio, from the companies Aristea or Selex) were used as received. A sample of PLLA was analyzed by ^{1}H and ^{13}C NMR spectroscopy, GPC and TGA (Fig. S19–S21 of the ESI†). The PLLA samples were reduced to small fragments about 1 cm^2. Technical grade methanol, ethanol, butanol, ethylene glycol, 1,4-butanediol and *cis*-2-butene-1,4-diol were purchased from Merck or Carlo Erba and used without further purification.

Instruments and measurements

NMR analysis. NMR spectra were recorded on Bruker Avance 300, 400 and 600 MHz spectrometers at 25 °C. Chemical shift (δ) are reported as parts per million (ppm) and coupling constants (J) in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at $\delta = 7.16$ for C$_6$D$_6$, $\delta = 7.26$ for CDCl$_3$, and $\delta = 2.50$ for DMSO. ^{13}C NMR spectra are referenced using the residual solvent peak at $\delta = 128.06$ for C$_6$D$_6$.

Microwave reactor. All the microwave-assisted reactions have been performed using the CEM reactor model Discover 2.0. The reactor can work with 10
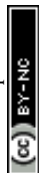
and 35 mL glass pressurized vessels and is equipped with an IR temperature sensor and a touchscreen interface from which it is possible to program the parameters of the reaction such as temperature, time, stirring power, power limit that the instrument can reach and max pressure that the reactor can handle before activating the safety control of pressure and release all the excess gasses.

MALDI – FT ICR MS analysis. Mass spectra were acquired using a Bruker solariX XR Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7 T refrigerated actively-shielded superconducting magnet (Bruker Biospin, Wissembourg, France). The polymer samples were ionized in positive ion mode using the MALDI ion source. The mass range was set to m/z 200–8000. The laser power was 12% and 18 laser shots were used for each scan. Mass spectra were calibrated externally using a mix of peptide clusters in MALDI ionization positive ion mode. Linear calibration was applied. The polymer samples were dissolved in THF at a concentration of 1 mg mL^{-1}. The cationization agent used was potassium trifluoroacetate (Fluka, >99%) dissolved in THF at a concentration of 1 mg mL^{-1}. The matrix used was *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (Fluka) and was dissolved in THF at a concentration of 10 mg mL^{-1}. Solutions of matrix, salt and polymer were mixed in an equal volume. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry.

Synthesis of ligand LH

In a 50 mL round-bottom flask 2-(2-pyridyl)ethylamine (0.122 mg, 1 mmol), 2-hydroxy-5-methoxybenzaldehyde (0.152 mg, 1 mmol) and 25 mL of ethanol were introduced. The reaction medium was magnetically stirred at reflux temperature for the night. The solvent was eliminated by evaporation at reduced pressure, and the resulting solid was dried under vacuum. ^{1}H NMR (600 MHz, C$_6$D$_6$, 298 K): δ 13.04 (br, 1H, –OH), 8.46 (d, J = 4.2 Hz, 1H, Ar), 7.65 (s, 1H, CH=N), 7.00 (m, 2H, Ar), 6.73 (m, 2H, Ar), 6.57 (t, J = 5.4 Hz, 1H, Ar), 6.45 (d, J = 3.0 Hz, 1H, Ar), 3.72 (t, J = 7.2 Hz, 2H, N–CH$_2$), 3.10 (s, 3H, O–CH$_3$), 2.89 (t, J = 7.2 Hz, 2H, N–CH$_2$–CH$_2$). ^{13}C NMR (150 MHz, C$_6$D$_6$, 298 K): δ 165.01, 159.35, 155.74, 151.99, 149.43, 135.50, 123.25, 120.95, 118.89, 117.75, 115.05, 59.00, 55.03, 39.22.

Synthesis of zinc complex 1

The synthesis was carried out under inert conditions in an MBraun Labmaster glovebox. In a 20 mL vial, the ligand LH (1.350 g, 5.27 mmol, 2 eq.) was weighed and was dissolved in 5 mL of dry benzene. In another vial, the metal precursor ZnEt$_2$ (0.333 g, 2.64 mmol, 1 eq.) was weighed and was dissolved in 2 mL of dry benzene. The ZnEt$_2$ solution was added drop by drop to the ligand solution. Once the addition was complete, the reaction mixture was left to stir for 2 h at room temperature. The solvent was removed under vacuum and the obtained solid was washed three times with *n*-hexane. The formation of the desired species was confirmed by NMR analysis. ^{1}H NMR (600 MHz, C$_6$D$_6$, 298 K): δ 8.46 (br, 2H, Ar), 7.45 (s, 2H, CH=N), 7.08 (d, J = 8.8 Hz, 2H, Ar), 6.95 (d, J = 7.2, 2H, Ar), 6.83 (m, 4H, Ar), 6.42 (br, 2H, Ar), 6.20 (s, 2H, Ar), 3.67 (br, 4H, N–CH$_2$), 3.31 (s, 6H, O–CH$_3$),
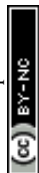
3.00 (br, 4H, N–CH$_2$–CH$_2$). ^{13}C NMR (150 MHz, C$_6$D$_6$, 298 K): δ 171.36, 163.13, 158.62, 149.00, 135.81, 124.32, 120.93, 118.01, 116.34, 112.67, 60.07, 55.94, 38.04.

Degradation reaction of PLLA by alcohol

PLLA plastic cups (0.116 g, 1.6 mmol, 160 eq.), the catalyst (10 μmol, 1 eq.) and the alcohol were added to a 10 mL MW vessel with a magnetic stirrer. The reaction was conducted at the required temperature under magnetic stirring for the designated time. The conversion of PLLA and the percentages of alkyl lactate and oligomers were calculated *via* ^{1}H NMR spectroscopy, using the following equations:

$$X_{\text{Int}} = 1 - \frac{[\text{Int}]}{[\text{Int}]_0} \times 100$$

$$S_{\text{A-La}}(\%) = \frac{[\text{A-La}]}{[\text{Int}] - [\text{Int}]_0} \times 100$$

$$Y_{\text{A-La}}(\%) = X_{\text{Int}} \times S_{\text{A-La}}$$

Methanolysis of PLLA with standard tetrakis(trimethylsilyl)silane (TMSS)

PLA plastic cups (41 mg, 0.58 mmol, 160 eq.), the catalyst (2.0 mg, 3.5 μmol, 1 eq.), the standard tetrakis(trimethylsilyl)silane (TMSS, 15 mg, 48 μmol, 12 eq. with respect to the lactyl units) and the CD$_3$OD (0.7 mL, 30 eq. with respect to the lactyl units) were added to a J-Young NMR tube. The reaction was conducted at 65 °C and monitored by ^{1}H NMR spectroscopy after 5 and 30 minutes (Fig. S6 and S7†). The yield of MeLa was calculated using the following equation:

$$Y_{\text{Me-La}}(\%) = \frac{[\text{Me-La}]}{\dfrac{[\text{TMSS}]}{36} \times 12} \times 100$$

where:

• [Me-La] is the integral of the methine group of methyl lactate at $\delta \approx 4.3$ ppm (1 proton);

• $\dfrac{[\text{TMSS}]}{36}$ is the integral of the methyl group of TMSS at $\delta = 0.25$ ppm normalized to 1 proton;

• 12 represents the ratio of repeating units to TMSS (12 : 1).

Degradation reaction of PLLA by diol

PLLA plastic cups (0.116 g, 1.6 mmol, 160 eq.), the catalyst (10 μmol, 1 eq.) and the diol were added to a 10 mL MW vessel with a magnetic stirrer. The reaction was conducted at the required temperature under magnetic stirring for the designated time. The conversion of PLLA, the percentage of alkyl lactate and oligomers were calculated *via* ^{1}H NMR spectroscopy as described in the previous paragraph.
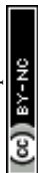
Conclusions

A chemical recycling process of post-consumer PLLA has been successfully developed by employing microwave-assisted alcoholysis reactions promoted by a phenoxy-imine pyridine zinc catalyst. The structures of the resulting products were strongly dependent on the type of alcohol/diol used and the corresponding PLLA/alcohol ratio. The catalyst showed excellent efficiency in degrading PLLA by methanolysis even when only three equivalents alcohol for each lactyl repeating unit were used. The polymer was converted selectively into methyl lactate after 3 min at 65 °C. This activity is among the highest reported in the literature although very mild reaction conditions were selected. When higher alcohols or diols were used as transesterifying agents, the complete conversion into the corresponding lactates occurred effectively and selectively, although longer times were required. When diols were used, new bifunctional molecules suitable as monomers have been selectively obtained.

In conclusion, in solvent-free conditions and by using different technical grade alcohols in quantities just above the stoichiometric ones, the non-toxic zinc catalyst showed high efficiency and selectivity in the degradation of PLLA samples. A fundamental role was played by microwaves, which accelerated the degradation process, significantly reducing the reaction times.

Data availability

The data supporting this article are included as part of the supplementary information.†
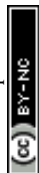
Author contributions

M. M. designed the study. F. S., M. F., and C. C. performed all the research. All authors contributed to the analysis of the data.

# Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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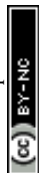
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