Zinc Complexes for PLA Formation and Chemical Recycling: Towards a Circular Economy

Paul McKeown+,[a] Luis A. RomQn-Ram%rez+,[b] Samuel Bates,[a] Joseph Wood,*[b] and Matthew D. Jones*[a]

Wood School of Chemical Engineering
University of Birmingham Edgbaston,
Birmingham, B15 2TT (UK) E-mail:

j.wood@bham.ac.uk

[*] These authors contributed equally to this work.

A series of Zn^{II} complexes, based on propylenediamine Schiff bases, have been prepared and fully characterized. X-ray crystallography and NMR spectroscopy identified significant differences in the solid and solution state for the Zn^{II} species. All complexes have been applied to the ring-opening polymerization of l-lactide with emphasis on industrial conditions. High conversion and good molecular weight control were generally achievable for Zn(A–D)2, and high-molecular-weight poly(lactic acid) (PLA) was prepared in 1 min at a 10 000:1:33 [lactide]/

[Zn]/[BnOH] loading. The more active Zn^{II} catalysts were also applied to PLA degradation to alkyl lactate under mild conditions. Zn(A–B)2 demonstrated high activity and selectivity in this process with PLA being consumed within 1 h at 50 8C. Zn(C–D)2 were shown to be less active, and these observations can be related to the catalysts' structure and the degradation mechanism. Initial results for the degradation of poly(ethylene terephthalate) and mixed feeds are also presented, highlight-ing the broader applicability of the systems presented.

Owing to the inevitable depletion of fossil fuel resources, and inherent carbon emissions, alternatives to petrochemical plastics are desperately needed.[1] Poly(lactic acid) (PLA) is a po-tential replacement for fossil-fuel-derived plastics used for packaging applications.[2,3] PLA has the added advantage of being biocompatible and therefore suitable for biomedical applications.[4, 5] Because it is derived from annually harvested crops, PLA is biorenewable and has promising green credentials in terms of CO2 emissions and life-cycle assessment.[6, 7] High-molecular-weight PLA is preferentially prepared from the cyclic dimer of lactic acid, lactide (LA), through ring-opening polymerization (ROP).[8] Current PLA research seeks to reduce energy/material input of LA monomer synthesis,[9–12] demon-strate and elucidate stereoselective initiation[13–29] and prepare

[a] Dr. P. McKeown,+ S. Bates, Prof. M. D. Jones Department of Chemistry

University of Bath
Claverton Down, Bath, BA2 7AY
(UK) E-mail: mj205@bath.ac.uk

[b] Dr. L. A. RomQn-Ram%rez,+ Prof. J.

robust initiators to compete with Sn(Oct)2 under industrial conditions.[30–34]

Plastic waste and pollution are a further 21st century challenge for both academia and industry. Although PLA is biodegradable under high-temperature industrial conditions, it will not readily degrade in the natural environment and there-fore will contribute to the millions of tonnes of waste in landfill and in oceans.[35–37] End-of-life plastic waste management is key to tackling this issue, and it is imperative this is addressed for all aspiring materials such as PLA. For PLA, chemical recy-cling is a particularly attractive route because it can produce valueadded products such as alkyl lactates, lactic acid and acrylic acid.[38, 39] These can be useful in their own right or used to reform LA, and therefore PLA, to facilitate a circular-econo-my approach. Lactic acid, for example, is regarded as a plat-form chemical, and alkyl lactates are considered green sol-vents.[40– 44] The conversion of PLA back to lactic acid is highly desirable because the traditional fermentation route is costly and wasteful, producing gypsum as a byproduct.[42] Compared to other waste management strategies such as incineration and biodegradation, chemical recycling offers the greatest value with potential to reduce the cost of PLA and increase market uptake.[45] Previous examples of PLA recycling process-es include hydrolysis,[46–53] alcoholysis,[54–63] hydrogenation[64, 65] and hydrosilylation.[66]

Commercially available metal salts and precursors have been shown to facilitate the transesterification of PLA to alkyl lactates, typically methyl lactate (Me-La).[55, 58, 67] Sobota and coworkers have also shown the use of metallic precursors at relatively high temperatures, demonstrating a range of alcohols for transesterification.[55] There are also examples of organocatalyzed degradation with triazabicyclodecene (TBD) and 4-dimethylaminopyridine (DMAP).[59, 63] The use of metal complexes for this purpose is rare despite the amount of complexes re-ported for LA polymerization.[60, 61, 68] Recently,

we have report-ed the use of a discrete homoleptic Zn^{II} complex [$Zn(A^{ethyl})_2$] (ethyl denotes the length of the N@N backbone with the same substituents as in Scheme 1) for PLA degradation to Me-La.[62] To demonstrate the versatile nature of the process, a range of PLA grades were degraded in a controlled manner; experimental design and kinetic modelling were used to further elucidate key experimental factors and reaction mechanism.[62]

Herein, we report the rapid polymerization of LA, under industrially relevant conditions, competitive with $Sn(Oct)_2$, and the fast and selective chemical degradation of PLA. The effect of ligand and metal on these processes is highlighted and discussed.

AH, R^1 = tBu, R^2 = N(H)Me
BH, R^1 = tBu, R^2 = NMe_2
CH, R^1 = Cl, R^2 = NMe_2
DH, R^1 = tBu, R^2 = H
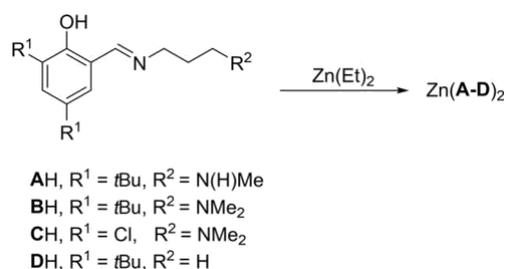
Scheme 1. Synthesis of metal complexes.

Ligands (A–DH) were prepared through a simple Schiff-base condensation in MeOH. All ligands were dried prior to complexation and characterized by multinuclear NMR spectroscopy and high-resolution MS. AH exists as two isomers in solution, having two distinct series of resonances. This results from ligand cyclization owing to intramolecular attack of the secondary amine (see the Supporting Information). Complexes were prepared by using diethylzinc, with the homoleptic com-plex, Zn(A–D)2, targeted (Scheme 1, Figure 1). Successful for-mation of Zn(A–D)2 was confirmed by multinuclear NMR spec-troscopy, X-ray crystallography and elemental analysis for all complexes.

A range of different coordination numbers and motifs were observed in the solid state (Figure 1, Table 1). Zn(A)2 tended to-wards a dimeric species whereas the remaining structures were monomeric. The ^{1}H NMR spectra of all complexes were consistent with a symmetrical monomeric structure in solution. Diffusion-ordered spectroscopy (DOSY) NMR spectroscopy was used to further analyse the solution-state structure of these complexes (Table 1).The decrease in diffusion coefficients relative to the ethylenediamine analogues, Zn(A–C^{ethyl})2, is suggested to be owing to a lower coordination number and unbound amine moieties.

Initial studies were performed to demonstrate the activities of these complexes towards ROP of l-lactide (Table 2). Singly recrystallized lactide was used to align with industrial practices and demonstrate the robust nature of the complexes. Polymerization reactions were exclusively performed under solvent-free conditions and at high temperatures (180 8C) with low metal loading ([LA]/[Zn]/[BnOH] =10 000:1:100) to increase in-dustrial relevance. The ratio of metal complex to alcohol is consistent with an immortal polymerization. The complexes
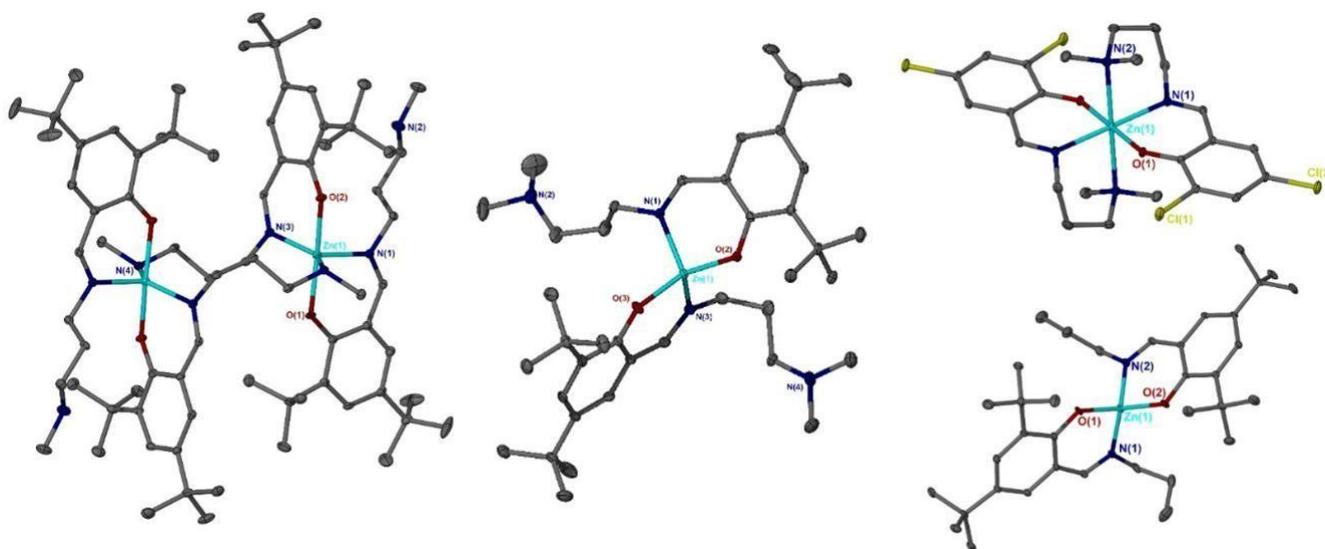
Figure 1. Solid-state structure of, from left to right, [Zn(A)2]2, Zn(B)2, Zn(C)2 (top) and Zn(D)2 (bottom) ; ellipsoids are shown at 30 % probability level and all hydrogen atoms have been omitted for clarity.

Table 1. Solid-state and solution structural information for Zn(A–D)$_2$. Corresponding data ethylenediamine complexes, Zn(A–C^{ethyl})$_2$.[31]

| Complex | Solid-state | | | Solution | |
	CN[a]	t$_{(4/5)}$[b]	(Pseudo) structure	D[c] [0 10@10 m^2 s@1]	Predicted coordination
Zn(A)$_2$	5 (dimer)	0.54	trigonal bipyramidal	5.89	4/5
Zn(B)$_2$	4	0.80	tetrahedral	5.94	4
Zn(C)$_2$	6	–	octahedral	8.12	6
Zn(D)$_2$	4	0.87	tetrahedral	6.70	4
Zn(A^{ethyl})$_2$	6	–	octahedral	7.38	6
Zn(B^{ethyl})$_2$	5	0.01	square-based pyramidal	7.11	5/6
Zn(C^{ethyl})$_2$	–	–	–	8.16	6

[a] CN =coordination number. [b] t$_4$ =1 for a perfect tetrahedron; t$_5$ =1 for a perfect trigonal bipyramid or 0 for a perfect square-based pyramidal structure. [c] Diffusion coefficients calculated from DOSY NMR spectroscopy (CDCl$_3$).

is also possible that these amine moieties allow the formation of dimeric zinc structures, in which there is a cooperative effect between metal centers.

Differential scanning calorimetry (DSC) analysis of the PLA produced by Zn(A–D)$_2$ revealed melting temperatures of 160–167 8C (see the Supporting Information). This indicates high polymer crystallinity and a lack of stereocenter epimeriza-tion.

The potential to control molecular weight by varying the ratio of benzyl alcohol has also been demonstrated with Zn(A)$_2$. Higher-molecular-weight PLA was achieved through the reduction of alcohol amount ([LA]/[Zn]/[BnOH] = 10 000:1:33, where [Zn] =concentration of Zn complex). The rapidity of the polymerization remains unchanged, with high conversion achieved within 1 min. However, molecular-weight control is slightly reduced (M$_n$ =53 750 g mol@1, M$_{n,theo}$ = 42 000 g mol@1; Đ =1.95). This catalyst was further tested by re-ducing the catalyst loading ([LA]/[Zn]/[BnOH] =20 000:1:200). Reaction time is greatly lengthened to 30 min; however, rea-sonable conversion is still achieved. There is also a decrease in molecular-weight control (Đ =1.54), and this is likely related to the extended reaction time.

Table 2. Polymerization of l-lactide.

| Catalyst | t | X$_{L-LA}$[d] | M$_{n,theo}$[e] | M$_{n}$[f] | Đ[f] |
	[min]	[%]	[g mol@1]	[g mol@1]	
Zn(A)$_2$[a]	1	98	14 100	14 400	1.27
Zn(A)$_2$[b]	1	97	42 000	53 750	1.95
Zn(A)$_2$[c]	303	7794	1113 200 650	119400 500	1.541.45
Zn(C)$_2$[a]	30	69	10 050	10 150	1.11
Zn(D)$_2$[a]	12	89	12 900	13 350	1.21

Conditions: l-LA, 180 8C, solvent-free ; [a] [LA]/[Zn]/[BnOH] =10 000:1:100; [b] [LA]/[Zn]/[BnOH] =10 000:1:33; [c] [LA]/[Zn]/[BnOH] =20 000:1:200. [d] Determined by ^{1}H NMR spectroscopy. [e] Theoretical molecular weight calculated from conversion and [LA]/[BnOH]. [f] Measured by GPC (RI =re-fractive index); a correction factor of 0.58 has been applied to M$_n$.

were tolerant to air/moisture in the solid state, allowing for storage under ambient conditions. However, the complexes had no polymerization activity in air, signifying complex de-composition under the reaction conditions. Therefore, all reac-tions were performed under argon. Under these conditions, Zn(A/B)$_2$ demonstrated the highest activity, achieving high conversion within 3 min. Excellent molecular-weight control was achieved despite the challenging conditions. There is good agreement between the theoretical molecular weight, based on conversion, and that measured by gel-permeation chromatography (GPC) [for Zn(A)$_2$: M$_n$ =14 400 g mol@1, M$_{n,theo}$ =14 100 g mol@1]. In addition, a relatively narrow disper-sity is observed (Đ =1.24–1.45). The relative activities of Zn(A/B)$_2$ agree with the previous ethylene diamine-based system,[31] but the complexes herein are twice as active. The activities of Zn(A/B)$_2$ are comparable to Sn(Oct)$_2$ under identical conditions

Initial degradation studies were performed by using com-mercially available PLA (0.25 g, VegWare^{TM}, PLA cup, M$_n$ = 45 150 g mol@1). Degradation progress was monitored by regu-lar sampling and ^{1}H NMR spectroscopic analysis. This technique quantified the relative concentrations of methine groups, which are defined as internal (Int), chain end (CE) and alkyl lac-tate (A-La). We have previously shown the production of Me-La is a two-step process with the intermediate formation of CE groups (see the Supporting Information).[62] For comparison, internal methine conversion (X$_{Int}$), alkyl lactate selectivity (S$_{A-La}$)

[for Sn(Oct)$_2$: 3 min, 95 %, M_n =16 100 Da, $Đ$ =1.54].[31] required considerably more time (15–30 min) to achieve a conversion similar to that of Zn(A/B)$_2$. Despite the extended reaction time, good control over molecular weight was maintained. All catalysts furnished white polymer under these conditions (see the Supporting Information). The slower reaction for Zn(C)$_2$ is likely related to the more sterically hindered octahedral metal center, and this is likely a reason for improved molecular-weight control ($Đ$ =1.11). Matrix-assisted laser desorption ionization-time of flight (MALDI-ToF) analysis of polymer derived from Zn(C)$_2$ revealed a symmetrical distribution with the expected BnO@/@H end groups. A peak spacing of 144 g mol^{-1} demonstrates the absence of undesired transesterification reactions. Similar to Zn(A/B)$_2$, Zn(C)$_2$ is more active than the analogous ethylene diamine complex, Zn(C^{ethyl})$_{2,}$ attaining a similar conversion in half the time.[31] The reduction in activity for Zn(D)$_2$ could be related to the mechanistic pathway. It is suggested that all initiators follow an activated monomer mechanism,[69] with molecular-weight control suggesting immortal characteristics. However, the pendant amine groups of Zn(A–C)$_2$ are suggested to participate in the reaction, potentially assisting in the proton-transfer steps, leading to a ligand-assisted activated monomer mechanism.[70] In the case of Zn(D)$_2$, there are no amine groups to facilitate this step, leading to the difference in activity when compared to Zn(A–C)$_2$. It

Our previous studies demonstrated the use of THF/MeOH at 50 8C to be reasonable conditions for the transesterification reaction, and these conditions were used to perform a catalyst screening for PLA degradation activity. The amount of catalyst was reduced from 8 to 4 wt % in an attempt to improve the viability of the process. Under these conditions, Zn(A)$_2$ was shown to be highly active, with PLA being completely consumed within 30 min, with 20 % of CE methine groups remaining (Table 3). For Zn(B)$_2$, complete PLA consumption was generally achieved after 1 h. In contrast, Zn(C/D)$_2$ were less active towards PLA degradation under the same conditions, with PLA still being present after 20 h with a low Me-La selectivity. Zn(C)$_2$ and Zn(A^{ethyl})$_2$, which has an ethylenediamine backbone, had rates and selectivities on the same order of magnitude. The activity of these complexes can be related to the geometry: those with a higher coordination demonstrated a lower activity. For Zn(D)$_2$, the reduced activity may suggest the presence of the pendant amine groups to be important, perhaps assisting in the degradation mechanism through hydrogen-bonding interactions as suggested for the polymerization studies. In comparison, commercially available ZnCl$_2$ was found to be inactive for degradation under these conditions, and we have previously shown Zn(OAc)$_2$ to be much less active than Zn(A$_{ethyl}$)$_2$.[62]

Table 3. PLA degradation at 50 8C.[a]

Catalyst	t	X_{Int}	$S_{A\text{-}La}$	$Y_{A\text{-}La}$	k_{app}
	[h]	[%]	[%]	[%]	[min^{-1}]
Zn(A)$_2$	0.5	100	81	81	0.20
Zn(B)$_2$	1	100	84	84	0.094
Zn(C)$_2$	3	51	20	10	3.8 × 10^{-3}
Zn(D)$_2$	3	29	17	5	1.7 × 10^{-3}
Zn(A$_{ethyl}$)$_2$[b]	3	66	29	19	5.9 × 10^{-3}
Zn(A)$_2$[c]	0.5	100	89	89	0.14
Zn(A)$_2$[d]	0.5	100	63	63	0.12
Zn(B)$_2$[c]	1	99	81	80	0.066
Zn(B)$_2$[d]	1	99	71	70	0.064
Zn(A)$_2$[e]	1.5	93	55	53	0.029
Zn(B)$_2$[e]	1.5	95	60	57	0.028
Zn(B)$_2$[f]	1	100	87	87	0.087
Zn(B)$_2$[g]	1	100	80	80	0.094

[a] Conditions: 50 8C, 4 wt % catalyst loading, 0.42–0.48 mol % relative to ester linkages, solvent =THF, alcohol =MeOH, THF/MeOH =4:1, n_{MeOH}/ n_{ester} =7:1. X_{Int}, $S_{A\text{-}La}$ and $Y_{A\text{-}La}$ obtained by ^{1}H NMR spectroscopy. [b] Ethyl- ene diamine complex. [c] solvent =toluene. [d] solvent =acetonitrile. [e] alcohol =EtOH; n_{EtOH}/n_{ester} =7:1. [f] PET (100 mg) added. [g] PET (250 mg) added.

The active catalyst species was investigated by removal of volatile components, with the residue being analysed by ^{1}H NMR spectroscopy. For Zn(A,B,D)$_2$, there is evidence of ligand dissociation, as well as the formation of a new species. This new species is suggested to be a heteroleptic complex, ZnXL, formed with concomitant loss of one ligand. The ancillary ligand could be methoxy, lactyl or higher oligomers. For Zn(C)$_2$ and our previous Zn(A^{ethyl})$_2$ catalyst, there is no evidence of ligand dissociation, despite the extended reaction time. Instead, there is only broadening of the Zn^{II}-complex NMR spectroscopic resonances, suggesting the coordination of reaction components only.

These complexes were six-coordinate in the solid state, and it is likely that the propensity for a higher coordination prevents dissociation. Equally, the dissociation of ligand for Zn(A/B)$_2$ (5- and 4-coordinate, respectively) likely leads to the enhanced activity. Based on this result, a control experiment was performed with ligand BH (12 wt %). No degradation was observed after 24 h, indicating dissociated ligand was not the active species.

For Zn(C)$_2$, time-dependent GPC kinetics studies were performed (see the Supporting Information). An exponential decrease in molecular weight was observed, with M_n being less than 10 % of the original value after 30 min. This suggests that the chain scission is random and not localized at chain ends. The rapid decrease in molecular weight precludes similar analysis for other catalysts.

The scope of solvents was expanded to include toluene and acetonitrile with Zn(A/B)$_2$. For both complexes there was a slight reduction in the rate of degradation, but the selectivity and yield remained high after 30 min. The ability to produce ethyl lactate is arguably more desirable, with this compound having wider applications than Me-La.[43, 44] Using EtOH instead of MeOH

reduced the rate of degradation for both catalysts; however, high conversion of [Int] units was still achievable

within 90 min, showing the viability of producing other alkyl lactates.

Zn(A/B)$_2$ were also tested in the absence of solvent at 130 °C (Table 4). Catalyst loading was decreased further to 1 wt %. Under these conditions, full PLA consumption was generally achieved after 1 h. As for the solution degradation reactions, Zn(A)$_2$ was more efficient, giving a higher selectivity towards Me-La.

Table 4. PLA degradation at 130 °C.[a]	X	S	Y
Catalyst	$X_{Int A-La}$ [%]	S_{A-La} [%]	Y_{A-La} [%]
Zn(A)$_2$	100	98	98
Zn(B)$_2$	98	76	74

[a] Conditions: 130 °C, 1 h, 1 wt % catalyst loading, 0.105–0.110 mol % rela-tive to ester linkages, MeOH (2 mL), n_{MeOH}/n_{ester} =14:1. X_{Int}, S_{A-La} and Y_{A-La} obtained by ^{1}H NMR spectroscopy.

Initial investigations were made into the degradation of other polyesters. With Zn(B)$_2$, the degradation of poly(ethylene terephthalate) (PET, Coca-Cola bottle) was demonstrated at 150 °C with benzyl alcohol (5 wt %, 30 min). Complete solubilization and subsequent analysis by ^{1}H NMR spectroscopy demonstrated the complete degradation of PET under these conditions. On cooling, the benzyl alcohol di-ester crystallized from solution the structure was confirmed by single-crystal XRD (see the Supporting Information).

The contamination of plastic waste streams with different polymers can severely impact the recycling procedure and re-sultant material quality.[67, 71] For Zn(B)$_2$, the rate of degradation of PLA, in solution with a PLA/PET mixed feed, was not im-paired by addition of PET (100–250 mg). Subsequent removal of Me-La by distillation and addition of benzyl alcohol then al-lowed for the selective degradation of PET at 150 °C. Crystalli-zation of the terephthalic di-ester allowed for the removal of trace amounts of benzyl lactate.

The scalability of the PLA degradation process was also tested on the Zn(B)$_2$ catalyst, with reactions being performed at 50 °C in a 300 mL SS316 bench-top stirred reactor (see the Supporting Information). In a typical experiment, commercial

PLA (12.5 g, NatureWorks Ingeo 6202D, M_n =44 350 g mol^{-1}) reacted with MeOH (50 mL) in the presence of THF (250 mL) as solvent and 4 wt % catalyst loading. The progress of the reac-tions was followed by measuring the A-La concentration by GC-FID (flame ionization detector) with further analysis by ^{1}H NMR spectroscopy to identify the CE intermediates. For GC analysis, 0.07 g mL^{-1} is the maximum Me-La concentration achieved (maximum theoretical is 0.072 g mL^{-1}), suggesting a similar reaction mechanism with both catalysts (Figure 2, and Figures

S31 and S39 in the Supporting Information). Zn(B)$_2$ was clearly higher in activity than Zn(A^{ethyl})$_2$ (Figure 2). The calculat- ed X_{Int}, S_{A-La}, Y_{A-La} and rate coefficient for the degradation step (k$_1$, Table 5) are in good agreement with the values obtained in the small-scale studies (Table 3), demonstrating the scale-up potential of the process. Rate coefficients k$_2$ and k$_{-2}$ correspond

Figure 2. A-La concentration profiles at 50 °C with Zn(B)$_2$ and Zn(A^{ethyl})$_2$ (maximum theoretical Me-La concentration is 0.072 g mL^{-1}).

Table 5. Scale-up studies of PLA degradation at 50 °C.[a]		X	S	Y	K	K	k
Catalyst	t	X_{Int}	S_{A-La}	Y_{A-La}	k_1	k_2	k_{-2}
	[h]	[%]	[%]	[%]	[min^{-1}]	[min^{-1}]	[min^{-1}]
Zn(B)$_2$	1	97	79	77	6.9 0 10^{-2}	5.5 0 10^{-2}	6.3 0 10^{-2}
Zn(A^{ethyl})$_2$	1	30	17	5	0.4 0 10^{-2}	0.2 0 10^{-2}	0.5 0 10^{-2}

[a] Conditions: 50 °C, 1 h, PLA (12.5 g), 4 wt % catalyst loading, 0.40–0.43 mol % relative to ester linkages, THF/MeOH =4 :1, n_{MeOH}/n_{ester} =7:1. X_{Int}, S_{A-La} and Y_{A-La} obtained by ^{1}H NMR spectroscopy.

to the reversible reaction for A-La formation from CE groups (Figures S31 and S39 in the Supporting Information), calculated from the kinetic model presented in [62].

In conclusion, four new and fully characterized zinc complexes have been applied to the catalytic ROP of l-lactide under industrially relevant conditions and the transesterifica-tion of PLA into alkyl lactates. Various degradation parameters (solvent, solvent-free, temperature, alcohol) were assessed, and the difference in the activities of the complexes was found to be related to the differences in their structure. The degradation process has also been scaled up for the more active catalyst, and kinetic parameters have been calculated demonstrating the fast

degradation at mild conditions. As a proof of concept, the selective degradation of PET has also been demonstrated.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

[1] S. Shafiee, E. Topal , Energy Policy 2009, 37, 181 – 189.
[2] M. Rabnawaz, I. Wyman, R. Auras, S. Cheng , Green Chem. 2017, 19, 4737 – 4753.
[3] R. Auras, B. Harte, S. Selke, Macromol. Biosci. 2004, 4, 835 – 864.
[4] K. Madhavan Nampoothiri, N. J. Nair, R. P. John, Bioresour. Technol. 2010, 101, 8493 – 8501.
[5] A. J. R. Lasprilla, G. A. R. Martinez, B. H. Lunelli, A. L. Jardini, R. M. Filho, Biotechnol. Adv. 2012, 30, 321 – 328.
[6] E. T. H. Vink, S. Davies, Ind. Biotechnol. 2015, 11, 167 – 180.
[7] W. J. Groot, T. Bor n, Int. J. Life Cycle Assess. 2010, 15, 970 – 984.
[8] O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, Chem. Rev. 2004, 104, 6147 – 6176.
[9] R. De Clercq, M. Dusselier, C. Poleunis, D. P. Debecker, L. Giebeler, S. Oswald, E. Makshina, B. F. Sels, ACS Catal. 2018, 8, 8130 – 8139.
[10] M. Dusselier, P. V. Wouwe, A. Dewaele, P. A. Jacobs, B. F. Sels, Science 2015, 349, 78 – 80.
[11] M. Ghadamyari, S. Chaemchuen, K. Zhou, M. Dusselier, B. F. Sels, B. Mousavi, F. Verpoort, Catal. Commun. 2018, 114, 33 – 36.
[12] P. Van Wouwe, M. Dusselier, E. Vanleeuw, B. Sels, ChemSusChem 2016, 9, 907 – 921.
[13] M. J. Stanford, A. P. Dove, Chem. Soc. Rev. 2010, 39, 486 – 494.
[14] C. M. Thomas, Chem. Soc. Rev. 2010, 39, 165 – 173.
[15] N. Spassky, M. Wisniewski, C. Pluta, A. LeBorgne, Macromol. Chem. Phys. 1996, 197, 2627 – 2637.
[16] Z. Zhong, P. J. Dijkstra, J. Feijen, J. Am. Chem. Soc. 2003, 125, 11291 – 11298.
[17] N. Nomura, R. Ishii, Y. Yamamoto, T. Kondo, Chem. Eur. J. 2007, 13, 4433 – 4451.
[18] M. D. Jones, L. Brady, P. McKeown, A. Buchard, P. M. Sch fer, L. H. Thomas, M. F. Mahon, T. J. Woodman, J. P. Lowe, Chem. Sci. 2015, 6, 5034 – 5039.
[19] P. McKeown, M. G. Davidson, G. Kociok-Kohn, M. D. Jones, Chem. Commun. 2016, 52, 10431 – 10434.
[20] A. J. Chmura, M. G. Davidson, C. J. Frankis, M. D. Jones, M. D. Lunn, Chem. Commun. 2008, 1293 – 1295.
[21] A. Pilone, K. Press, I. Goldberg, M. Kol, M. Mazzeo, M. Lamberti, J. Am. Chem. Soc. 2014, 136, 2940 – 2943.
[22] M. Cheng, A. B. Attygalle, E. B. Lobkovsky, G. W. Coates, J. Am. Chem. Soc. 1999, 121, 11583 – 11584.
[23] Z. Dai, Y. Sun, J. Xiong, X. Pan, N. Tang, J. Wu, Catal. Sci. Technol. 2016, 6, 515 – 520.
[24] P. Hormnirun, E. L. Marshall, V. C. Gibson, A. J. P. White, D. J. Williams, J. Am. Chem. Soc. 2004, 126, 2688 – 2689. [25] C. Bakewell, A. J. P. White, N. J. Long, C. K. Williams, Angew. Chem. Int. Ed. 2014, 53, 9226 – 9230; Angew. Chem. 2014, 126, 9380 – 9384.
[26] P. Marin, M. J.-L. Tschan, F. Isnard, C. Robert, P. Haquette, X. Trivelli, L.-M. Chamoreau, V. Gu rineau, I. del Rosal, L. Maron, V. Venditto, C. M. Thomas, Angew. Chem. Int. Ed. 2019, 58, 12585 – 12589.
[27] D. Myers, A. J. P. White, C. M. Forsyth, M. Bown, C. K. Williams, Angew. Chem. Int. Ed. 2017, 56, 5277 – 5282; Angew. Chem. 2017, 129, 5361 – 5366.
[28] C. Robert, T. E. Schmid, V. Richard, P. Haquette, S. K. Raman, M. N. Rager, R. M. Gauvin, Y. Morin, X. Trivelli, V. Gu rineau, I. del Rosal, L. Maron, C. M. Thomas, J. Am. Chem. Soc. 2017, 139, 6217 – 6225.
[29] J. A. Stewart, P. Mckeown, O. J. Driscoll, M. F. Mahon, B. D. Ward, M. D. Jones, Macromolecules 2019, 52, 5977 – 5984.
[30] P. M. Sch fer, M. Fuchs, A. Ohligschl ger, R. Rittinghaus, P. McKeown, E. Akin, M. Schmidt, A. Hoffmann, M. A. Liauw, M. D. Jones, S. Herres-Pawlis, ChemSusChem 2017, 10, 3547 – 3556.
[31] P. McKeown, S. N. McCormick, M. F. Mahon, M. D. Jones, Polym. Chem. 2018, 9, 5339 – 5347.
[32] J. Bçrner, I. Dos Santos Vieira, A. Pawlis, A. Dçring, D. Kuckling, S. Herres-Pawlis, Chem. Eur. J. 2011, 17, 4507 – 4512.
[33] J. Bçrner, U. Florke, K. Huber, A. Doring, D. Kuckling, S. HerresPawlis, Chem. Eur. J. 2009, 15, 2362 – 2376.

[34]   T. Ebrahimi, D. C. Aluthge, B. O. Patrick, S. G. Hatzikiriakos, P. Mehrkhoda- vandi, ACS Catal. 2017, 7, 6413 – 6418.

[35]   S. Lambert, M. Wagner, Chem. Soc. Rev. 2017, 46, 6855 – 6871.

[36] R. Geyer, J. R. Jambeck, K. L. Law, Sci. Adv. 2017, 3, e1700782. [37] J. R. Jambeck, R. Geyer, C. Wilcox, T. R. Siegler, M. Perryman, A. Andrady, R. Narayan, K. L. Law, Science 2015, 347, 768 – 771.

[38]   J. Payne, P. McKeown, M. D. Jones, Polym. Degrad. Stab. 2019, 165, 170 – 181.

[39]   M. Hong, E. X.-Y. Chen, Green Chem. 2017, 19, 3692 – 3706.

[40] J. J. Bozell, G. R. Petersen, Green Chem. 2010, 12, 539 – 554.

[41]   Y. Fan, C. Zhou, X. Zhu, Catal. Rev. Sci. Eng. 2009, 51, 293 – 324.

[42]   M. Dusselier, P. V. Wouwe, A. Dewaele, E. Makshina, B. F. Sels, Energy En- viron. Sci. 2013, 6, 1415 – 1442.

[43]   C. S. M. Pereira, V. M. T. M. Silva, A. E. Rodrigues, Green Chem. 2011, 13, 2658 – 2671.

[44]   S. Aparicio, R. Alcalde, Green Chem. 2009, 11, 65 – 78.

[45]   V. Piemonte, S. Sabatini, F. Gironi, J. Polym. Environ. 2013, 21, 640 – 647. [46] P. Coszach, J.-C. Bogaert, J. Wilocq (Futerro SA, Escanaffles, Belgium), US8431683B2, 2013.

[47]   H. Tsuji, T. Saeki, T. Tsukegi, H. Daimon, K. Fujie, Polym. Degrad. Stab. 2008, 93, 1956 – 1963.

[48]   V. Piemonte, F. Gironi, J. Polym. Environ. 2013, 21, 313 – 318.

[49] C. F. Van Nostrum, T. F. J. Veldhuis, G. W. Bos, W. E. Hennink, Polymer 2004, 45, 6779 – 6787.

[50] H. Tsuji, H. Daimon, K. Fujie, Biomacromolecules 2003, 4, 835 – 840.

[51] F. Codari, S. Lazzari, M. Soos, G. Storti, M. Morbidelli, D. Moscatelli, Polym. Degrad. Stab. 2012, 97, 2460 – 2466.

[52]   S. Lazzari, F. Codari, G. Storti, M. Morbidelli, D. Moscatelli, Polym. Degrad. Stab. 2014, 110, 80 – 90.

[53]   K. Odelius, A. Hçglund, S. Kumar, M. Hakkarainen, A. K. Ghosh, N. Bhat nagar, A. C. Albertsson, Biomacromolecules 2011, 12, 1250 – 1258.

[54]   K. Hirao, Y. Nakatsuchi, H. Ohara, Polym. Degrad. Stab. 2010, 95, 925 – 928.

[55] R. Petrus, D. Bykowski, P. Sobota, ACS Catal. 2016, 6, 5222 – 5235.

[56] L. D. Brake (Nature Works LLC, Minnetonka, MN), US5264617A, 1993.

[57] X. Song, X. Zhang, H. Wang, F. Liu, S. Yu, S. Liu, Polym. Degrad. Stab. 2013, 98, 2760 – 2764.

[58] H. Liu, X. Song, F. Liu, S. Liu, S. Yu, J. Polym. Res. 2015, 22, 135.

[59] F. A. Leibfarth, N. Moreno, A. P. Hawker, J. D. Shand, J. Polym. Sci. Part A 2012, 50, 4814 – 4822.

[60] C. Fliedel, D. Vila-ViÅosa, M. J. Calhorda, S. Dagorne, T. Avil s, Chem- CatChem 2014, 6, 1357 – 1367.

[61] E. L. Whitelaw, M. G. Davidson, M. D. Jones, Chem. Commun. 2011, 47, 10004 – 10006.

[62] L. A. RomQn-Ram%rez, P. Mckeown, M. D. Jones, J. Wood, ACS Catal. 2019, 9, 409 – 416.

[63] F. Nederberg, E. F. Connor, T. Glausser, J. L. Hedrick, Chem. Commun. 2001, 47, 2066 – 2067.

[64] S. Westhues, J. Idel, J. Klankermayer, Sci. Adv. 2018, 4, eaat9669.

[65] E. M. Krall, T. W. Klein, R. J. Andersen, A. J. Nett, R. W. Glasgow, D. S. Reader, B. C. Dauphinais, S. P. Mc Ilrath, A. A. Fischer, M. J. Carney, D. J. Hudson, N. J. Robertson, Chem. Commun. 2014, 50, 4884 – 4887.

[66] L. Monsigny, J.-C. Berthet, T. Cantat, ACS Sustainable Chem. Eng. 2018, 6, 10481 – 10488.

[67] A. Carn SQnchez, R. S. Collinson, Eur. Polym. J. 2011, 47, 1970 – 1976.

[68] D. Je̢ drzkiewicz, I. Czelus´niak, M. Wierzejewska, S. Szafert, J. Ejfler, J. Mol. Catal. A 2015, 396, 155 – 163.

[69] S. C. Roșca, D. A. Roșca, V. Dorcet, C. M. Kozak, F. M. Kerton, J. F. Carpent- ier, Y. Sarazin, Dalton Trans. 2013, 42, 9361 – 9375.

[70] B. Liu, T. Roisnel, L. Maron, J. F. Carpentier, Y. Sarazin, Chem. Eur. J. 2013, 19, 3986 – 3994.

[71] F. P. La Mantia, L. Botta, M. Morreale, R. Scaffaro, Polym. Degrad. Stab. 2012, 97, 21 – 24.