



Cite this: *Polym. Chem.*, 2018, **9**, 5339

Highly active Mg(II) and Zn(II) complexes for the ring opening polymerisation of lactide†

Paul McKeown,^a Strachan N. McCormick,^b Mary F. Mahon^a and Matthew D. Jones *^a

A range of simple ethylenediamine based Zn(II) and Mg(II) complexes have been prepared and their structures determined via NMR spectroscopy and X-ray crystallography. Preparation of these complexes was also demonstrated to be scalable, with 25 g of Zn(1)₂ being readily produced. These complexes were trialed for the ring opening polymerisation (ROP) of lactide under industrially relevant conditions. Their reactivity has been related to their structure in solution. Incredibly high activity is achieved in the majority of cases including low catalytic loading and high temperatures, under industrially relevant conditions (180 °C 10 000 : 1 : 100 [LA] : [Zn] : [BnOH]), with high conversion achieved within 10 minutes and TOFs in excess of 100 000 h⁻¹ achieved. The performance of these initiators for polymer production is supported by GPC, DSC and IR spectroscopy which all highlight the excellent control achieved.

Received 20th September 2018,
Accepted 16th October 2018

DOI: 10.1039/c8py01369a

rsc.li/polymers

Introduction

The production of bioplastics is currently a hot topic in light of the environmental burden associated with petrochemically derived materials. Polymers, such as poly(lactic acid) (PLA), are widely researched as a viable commodity plastic, being both renewably sourced and biodegradable. PLA is suitable for a range of applications, including use in food packaging and for *in vitro* surgical tools.^{1–7} The production of PLA, from ring opening polymerisation (ROP) of the lactic acid dimer, lactide (LA), has received considerable interest both industrially and in academia.⁸ Current research is generally motivated by a desire to improve the initiators used for production of PLA, maintaining high activity, and control while avoiding the use of toxic heavy metals. A diverse library of metal complexes has been explored, particularly with the aim of controlling polymer microstructure.^{9–13} Aluminium has received considerable attention in the literature.^{14–23} In particular, {ONNO}Al(III) complexes have been shown to be stereoselective in the ROP of *rac*-LA, albeit often with poor activity and subject to severe air/moisture sensitivity. For the ROP of *rac*-LA, strong isotactic bias has often been demonstrated by such complexes, the

most notable examples from Spassky,^{24,25} Feijen^{26,27} and Nomura.^{28,29} In(III) analogues have been explored as initiators for ROP.^{17,30–36} Typically, greater activity is achieved at the cost of reduced stereocontrol as a consequence of a larger metal cation. Mehrkhodavandi and co-workers have investigated a range of amino/iminophenolate systems.^{37–41} Recently, this group has reported an air and moisture stable indium salan system.⁴² A range of lanthanide initiators have also been applied to the ROP of *rac*-LA;^{43–53} in particular Williams and co-workers have demonstrated highly active Y(III) and Lu(III) systems amenable to the preparation of isotactic and heterotactic PLA.^{43,44,47} Group IV metal complexes have also garnered interest, due to their high activity and robustness,^{54–63} with both isotactic and heterotactic PLA being achieved with Zr(IV).^{64,65} Whilst the majority of these are solution based studies there is a need for catalysts with earth abundant and benign metals that work under challenging melt conditions as these are the industrial conditions.

Zinc complexes have also been successfully applied to the ROP of lactide, generally being highly active under solution conditions.^{66–83} Early work by Coates and co-workers employed a β -diiminate based Zn(II) complex which demonstrated a high degree of heterotacticity in solution.⁸⁴ Highly active zinc catalysts in solution have been examined by Williams and co-workers.^{85,86} The most recent work utilises dinuclear macrocyclic zinc complexes which show high TOFs (up to 60 000 h⁻¹) at room temperature, in solution, as well as immortal polymerisation characteristics. Currently, the most isoselective Zn(II) complex has been reported by Ma and co-workers in solution at -40 °C.⁸⁷ These aminophenolate complexes were also found to be suitable for solvent-free polymerisation under

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

^bCentre for Doctoral Training in Sustainable Chemical Technologies, University of Bath, Claverton Down, Bath, BA2 7AY, UK

† Electronic supplementary information (ESI) available: Full experimental data, including ligand, complex, and polymer characterisation data. CCDC 1844404–1844413. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8py01369a



immortal conditions. Magnesium complexes have also attracted attention for the ROP of LA.^{88–100} Often, such complexes are isostructural to their Zn(II) analogues. In the case of the β -diiminato Mg(II) complex, the heteroselectivity observed with the Zn(II) analogue was not replicated.⁶⁶ However, Chisholm and co-workers have demonstrated several Mg(II) complexes for the production of heterotactic PLA.^{67,101–103} Ma and co-workers have shown chiral aminophenolate Mg(II) complexes whose heterotactic preference perfectly contrasts the isotactic bias of the Zn(II) analogue.⁷⁶ Kol and co-workers have exploited a Mg(II) complex for the facile preparation of stereoblock PLA under solution conditions *via* an activated monomer mechanism.¹⁰⁴ Such metals are of interest since they are abundant and biocompatible, making PLA derived from Zn(II) and Mg(II) amenable for *in vitro* applications.

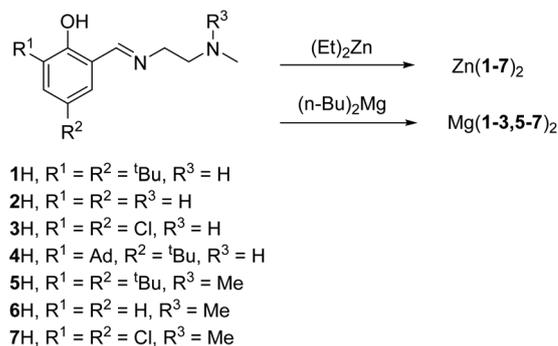
Whilst there are numerous examples of initiators detailing changes in tacticity, there remains a desire to develop new initiators that are active under industrial conditions. There is a gap in the literature for simple complexes that are able to polymerise lactide approaching industrial conditions with temperature around 180 °C with M_n being controlled by BnOH. Herein we report the preparation of simple ethylenediamine based Zn(II) and Mg(II) complexes and their application to the ROP of lactide under highly industrially relevant conditions. Polymerisation kinetics have been assessed under melt conditions by *in situ* IR spectroscopic measurements. The production of PLA stereoblocks under solvent-free conditions is also demonstrated.

Results and discussion

Synthesis

All ligands were prepared *via* a simple condensation to afford the respective Schiff base, which were characterised by multinuclear NMR spectroscopy and mass spectrometry. For 2H and 3H, the ¹H NMR spectra is observed to be broad and suggestive of multiple species in solution. This could be explained by an intramolecular ligand cyclisation reaction, which has been reported for similar types of systems in the literature.^{105,106}

Complexes of Zn(II) and Mg(II) were prepared in toluene and purified by hexane recrystallisation or *via* washing (Scheme 1). In each case, the bis-ligated complex, M(L)₂ was targeted and isolated. Chen *et al.* have previously prepared the alkoxide complexes Zn(5/6)OBn and [Ca(6)₂]₂.^{68,107} The Zn complexes were dimers in the solid state and shown to efficiently polymerise *rac*-LA in solution *via* a coordination insertion mechanism.⁶⁸ The preparation of Zn(1)₂ was successfully scaled up to 25 g, with good yield (73%) and high purity of the isolated complex in less than 48 h. In the solid state, with the exception of Zn(5/6)₂, the metal centres were observed to have an octahedral coordination. For the octahedral complexes, the ligands wrap around the metal centres in a *mer-mer* manner {Zn(1)₂, Fig. 1}. The phenoxy group is situated axially to the corresponding amine of the same ligand with a deviation from the ideal axial angle {Zn(1)₂: O(1)–Zn(1)–N(2) = 164.74(5)°}.



Scheme 1 Ligands and their complexation to Zn(II) and Mg(II).

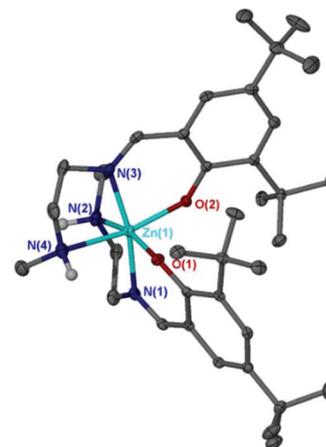


Fig. 1 Solid-state structure of Zn(1)₂. Ellipsoids shown at 30% probability level and all hydrogen atoms, except those bound to nitrogen have been omitted for clarity.

The imine groups of both ligands also share a pseudo axial arrangement {Zn(1)₂: N(1)–Zn(1)–N(3) = 167.66(5)°}. Of the Zn–N bonds, the imine has a shorter bond length compared to the secondary amine {Zn(1)₂: Zn(1)–N(1) = 2.0841(14) Å; Zn(1)–N(2) = 2.3117(15) Å}. On coordination of 1–4H, new chiral centres are formed on the nitrogen atom of the secondary amine. For Zn(1)₂, only one configuration is observable in the unit cell, with the nitrogen centres of each ligand having opposing chirality (*S,R/R,S*). The solid-state structure of Zn(4)₂ and Mg(1)₂ are also represented by one configuration in which each ligand has the same chirality (*S,S/R,R*). The observed configurations of these complexes is suggestive of the presence of enantiomers. However, the other analyzed solid-state structures, Zn(2/3)₂, are observed to have both opposing and matching ligand chirality (*S,R/S,S*) within the unit cell suggesting the potential for diastereoisomers. For Mg(2)₂, the crystal structure revealed a phenoxy bridged dimeric complex with cyclisation of one ligand to form a 5 membered ring. This is likely related to the fluxionality observed for the ligand *via* ¹H NMR spectroscopy. The magnesium centres displayed a distorted octahedral geo-



metry in this structure $\{\text{Mg}(2)_2: \text{O}(1)\text{-Mg}(1)\text{-N}(3) = 168.40(6)^\circ\}$ (see ESI†).

Complexes based upon ligands 5–7H have no chiral centres. $\text{Zn}(5)_2$ is observed to be five coordinate in the solid-state, with one amine group being directed at the zinc centre but sufficiently separated as to not be considered as a formal bonding interaction $\{\text{Zn}(1)\text{-N}(4) = 2.744 \text{ \AA}\}$. Due to this, the geometry at the metal centre has a strong preference for square based pyramidal ($\tau_5 = 0.01$). $\text{Zn}(6)_2$ also shows preference for a five coordinate complex in the solid-state. In this instance, the pendant arm and amine centre is rotated away from the metal centre. This is likely achieved due to the absence of phenyl substituents, which would otherwise hinder this movement. $\text{Zn}(6)_2$ also shows a strong preference for a square based pyramidal geometry ($\tau_5 = 0.05$). Chen *et al.* report the *para*-only bromo substituted $\text{Zn}(\text{II})$ complex.⁶⁸ This structure is four coordinate with the pendant amine groups directed towards the metal centre but this cannot be considered a formal bonding interaction $\{\text{Zn}(1)\text{-N}(3) = 2.573 \text{ \AA}\}$. The geometry and bond lengths at the metal centre are similar to $\text{Zn}(5)_2$. $\text{Mg}(5/7)_2$ are observed to have a pseudo octahedral geometry despite the methylation of the amine. For $\text{Zn}(1)_2$ and $\text{Mg}(1)_2$, the $-\text{CH}_2-$ resonances are observed as four discrete multiplets and a broad quartet is also observable for the NH proton. In contrast, $\text{Zn}(2/3)_2$ yield ^1H NMR spectra in which the $-\text{CH}_2-$ resonances appear as two broad resonances at room temperature in CDCl_3 . This observation could be an indication of greater fluxionality in solution caused by the lability of the pendant amine. At 233 K, the spectrum of $\text{Zn}(2)_2$ is more resolved, having four discrete resonances for the CH_2 protons, suggesting the “locking” of geometry under these conditions (see ESI†). Both ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for $\text{Mg}(2)_2$ indicates the two ligands are equivalent at the metal centre suggesting the presence of the homoleptic imino complex in solution rather than the dimeric cyclised structure observed in the solid-state. It is anticipated that the tridentate imino coordination mode would be favored over the bidentate cyclised system. For $\text{Mg}(2/3)_2$, the ^1H NMR spectra consist of 5 broad resonances for the $-\text{CH}_2-$ and NH protons while the aromatic and methyl resonances are sharp. The ^1H NMR spectrum for $\text{Zn}(5)_2$ shows the greatest resolution, with splitting

patterns of the $-\text{CH}_2-$ groups observable at room temperature. The signals due to the methylene group attached to the amine are split into two discrete resonances suggesting inequivalence of these protons on coordination. This spectrum implies the two ligands around the metal are equivalent and locked in their coordination suggesting a different coordination mode to the solid-state (presumably 6 coordinate). The appearance of the ^1H NMR spectra for $\text{Zn}(6/7)_2$ is comparable to the analogous $\text{Zn}(2/3)_2$ spectra. However, for each methylated complex, there is resolution of one of the methylene groups to indicate a broad triplet at room temperature. This resolution could imply a lesser degree of fluxionality compared to $\text{Zn}(2/3)_2$. Diffusion ordered spectroscopy (DOSY) NMR was performed on the zinc complexes. For each sample, there is one main species as indicated by the diffusional correlation peaks. The magnitude of the diffusion coefficients correlates with the bulk of the aryl and nitrogen substituents (see ESI†).

Polymerisation

All polymerisations were carried out under industrially preferred conditions, without solvent at elevated temperatures. The lactide monomers were not rigorously purified but used after a single recrystallisation. Benzyl alcohol was added as a co-initiator in the majority of cases. For all initiators, the polymerisation of *rac*-LA afforded atactic PLA ($P_r \sim 0.50$) with the exception of $\text{Zn}(5)_2$ which demonstrated a slight heterotactic preference ($P_r = 0.66$). With *L*- or *D*-LA, no epimerisation was observable, even at high temperatures, as shown by the $^1\text{H}\{^1\text{H}\}$ NMR spectra of the methine region which yields a single iii resonance (see ESI†). At 130 °C, polymerisation is observed to be very rapid for $\text{Zn}(1,4,5,7)_2$ with high conversion being achieved within minutes $\{[\text{LA}]:[\text{Init}]:[\text{BnOH}] = 300:1:1\}$ (Table 1). In contrast, for $\text{Zn}(2,3,6)_2$, polymerisation performance is observed to be much poorer with 30–60 minutes being required to achieve high conversion. The reduction in activity for $\text{Zn}(5/6)_2$ compared to $\text{Zn}(1/2)_2$, which have the same aryl substituents is likely due to the increased steric bulk of the methylated amine. For this subseries increasing aryl sterics increase rate and the addition of a methyl group to the amine centre reduces the rate.

Table 1 Polymerisation of *rac*-lactide at 130 °C with $\text{Zn}(\text{II})$ complexes

Init.	$[\text{LA}]:[\text{I}]:[\text{BnOH}]$	Time/min	Conv. ^a %	$M_{n/\text{theo}}^b$	M_n^c	D^c
$\text{Zn}(1)_2$	300 : 1 : 1	1	92	39 850	22 750	1.42
$\text{Zn}(1)_2$	300 : 1	1	81	— ^d	21 100	1.86
$\text{Zn}(2)_2$	300 : 1 : 1	36	77	33 350	8050	1.63
$\text{Zn}(3)_2$	300 : 1 : 1	60	67	29 050	12 400	1.49
$\text{Zn}(4)_2$	300 : 1 : 1	4	83	35 950	22 350	1.28
$\text{Zn}(5)_2$	300 : 1 : 1	3	56	24 300	38 750	1.21
$\text{Zn}(6)_2$	300 : 1 : 1	50	75	32 500	13 100	1.13
$\text{Zn}(7)_2$	300 : 1 : 1	8	76	37 750	14 700	1.05

Conditions: *rac*-LA, solvent free (130 °C). ^a Determined *via* ^1H NMR spectroscopy. ^b Theoretical molecular weight based on conversion and co-initiator added $\{(M_{r,\text{LA}} \times 3 \times \%_{\text{conv}}) + M_{n,\text{BnOH}}\}$. ^c Molecular weight *via* GPC analysis (in THF). A correction factor of 0.58 has been applied.¹⁰⁸ ^d As no initiating group it is not possible to calculate a theoretical M_n .



Table 2 Polymerisation of *rac*-lactide at 130 °C with Mg(II) complexes

Init.	[LA] : [I] : [BnOH]	Time/min	Conv. ^a %	$M_{n/theo}$ ^b	M_n ^c	\bar{D} ^c
Mg(1) ₂	300 : 1 : 1	1	89	38 550	36 850	1.80
Mg(2) ₂	300 : 1 : 1	32	64	27 750	19 550	1.38
Mg(3) ₂	300 : 1 : 1	45	77	33 350	10 350	1.57
Mg(5) ₂	300 : 1 : 1	1	79	34 250	12 850	1.37
Mg(6) ₂	300 : 1 : 1	60	67	29 050	13 350	1.47
Mg(7) ₂	300 : 1 : 1	10	71	30 800	13 150	1.27

Conditions: *rac*-LA, solvent free (130 °C). ^a Determined *via* ¹H NMR spectroscopy. ^b Theoretical molecular weight based on conversion and co-initiator added $\{(M_{r,LA} \times 3 \times \%_{conv}) + M_{n,BnOH}\}$. ^c Molecular weight *via* GPC analysis (in THF). A correction factor of 0.58 has been applied.¹⁰⁸

In contrast, Zn(7)₂ is observed to be more active than the secondary amine analogue Zn(3)₂ (R¹ = R² = Cl). In this case, the combination of both aryl substituents and methylated amine likely cause a change of coordination around the metal centre. Similar relationships of activity are observed for polymerisation with the Mg(II) complexes under these conditions (Table 2); both Mg(1,5)₂ achieve a high conversion of LA in one minute compared to Mg(2,3,6)₂ which require significantly more time. Mg(7)₂ is observed to be more active compared to Mg(3)₂ requiring 10 minutes to reach high conversion. The difference in activity displayed by these complexes is contrary to what would be expected based purely on the steric contribution of the substituents. While a six coordinate metal centre is indicated in the solid-state structure {with the exception of Zn(5/7)₂}, the coordination in solution is fluxional. There is, however, a correlation between the distinct nature of the methylene resonances and activity towards polymerisation; the more active complexes {M(1,4,5)₂} have a greater number of -CH₂- resonances with discrete splitting patterns being observed. For the less active complexes {M(2,3,6)₂} these resonances appear as two broad signals at room temperature. It is suggested that this broadness is due to fluxionality at the metal centre due to the lability of the pendant amine which hinders polymerisation. In essence activity is superior for the systems where the ligands are “locked” in solution.

For the majority of initiators, under these conditions, the molecular weight control is observed to be moderate, with broad dispersities (\bar{D} = 1.05–1.86). These complexes were also capable of polymer degradation through transesterification reactions and this may be responsible for the poor molecular weight control. For Zn(1,4,5)₂, the reduced control could also be due to the short reaction time in which polymerisation con-

ditions were not homogenous leading to sub-optimal initiation.

For Zn(1)₂, similar results are achievable without the use of benzyl alcohol albeit with an increase of dispersity (\bar{D} = 1.86). Initiation in this case could either be due to impurities in the monomer or initiation by the ligand. Zn(6/7)₂ provide the narrowest dispersity, however, the molecular weights are much lower than expected. MALDI-ToF analysis of the polymer derived from both initiators show a series consistent with the molecular weight from GPC (however the data is weak/poor likely due to the high molecular weight). In both cases BnO- and -H are indicated as the polymer end groups (see ESI†).

An improvement in molecular weight control can be achieved by decreasing the concentration of initiator, which is also favourable for industrial PLA production. At 10 000 : 1 : 100, the polymerisation of L-LA reaches high conversion after just 5 minutes for Zn(1)₂ (TOF = 99 600 h⁻¹, Table 3). Excellent molecular weight control is demonstrated under these conditions, (M_n = 12 050 Da; $M_{n,theo}$ = 12 850 Da). The distribution of polymer chain lengths is also observed to be narrowed (\bar{D} = 1.09). MALDI-ToF analysis of this polymer revealed one series (M_p = 10362.9 Da) with a peak spacing of 144 Da indicating the complete absence of transesterification side reactions. The expected end groups of BnO- and H- are also confirmed. These improvements are undoubtedly due to a decrease in initiator concentration which increases reaction time allowing for a more homogenous polymerisation and reduces the extent of side reactions. A further consequence of the reduced metal content is the isolation of colourless polymer prior to purification (see ESI†). Zn(4/5)₂ are also active under these conditions, achieving moderate conversions within 10 and 8 minutes respectively. The slight reduction in

Table 3 Immortal polymerisation of L-lactide at 130 °C with Zn/Mg(II) complexes

Init.	[LA] : [I] : [BnOH]	Time/min	Conv. ^a %	$M_{n/theo}$ ^b	M_n ^c	\bar{D} ^c
Zn(1) ₂	10 000 : 1 : 100	5	83	12 050	12 850	1.09
Zn(4) ₂	10 000 : 1 : 100	10	67	9750	11 250	1.05
Zn(5) ₂	10 000 : 1 : 100	8	69	10 050	9900	1.04
Mg(1) ₂	10 000 : 1 : 100	20	45	6600	5000	1.14
Mg(5) ₂	10 000 : 1 : 100	20	23	3400	2700	1.06

Conditions: L-LA, solvent free (130 °C). ^a Determined *via* ¹H NMR spectroscopy. ^b Theoretical molecular weight based on conversion and co-initiator added $\{(M_{r,LA} \times \%_{conv}) + M_{n,BnOH}\}$. ^c Molecular weight *via* GPC analysis (in THF). A correction factor of 0.58 has been applied.¹⁰⁸



activity relative to Zn(1)₂ is most likely related to the increase in steric bulk of 4H and 5H. Good control of molecular weight and dispersity is maintained by these complexes ($\mathcal{D} = 1.04\text{--}1.05$). MALDI-ToF analysis of polymer from Zn(4)₂ and Zn(5)₂ reveals one symmetrical series with a peak spacing of 144 Da indicating the absence of side reactions. There is a good agreement between measured molecular weight with the theoretical value {for Zn(4)₂, $M_p = 9930$ Da; $M_{n,theo} = 9750$ Da} and the residual peak mass is consistent with BnO- and H-end groups. The magnesium analogues, Mg(1/5)₂, display a much reduced activity under analogous conditions, requiring 20 minutes to achieve 45 and 23% conversion respectively. A good agreement of theoretical and measured molecular weight is observed for both initiators. MALDI-ToF of polymer derived from Mg(1/5)₂ identifies the end groups as BnO- and H-. However there is a minor series which has a separation of 72 Da indicative of transesterification side reactions.

Zn(1,4,5,7)₂ and Mg(1,5)₂ were also tested for polymerisation activity at higher temperatures (180 °C) (Table 4). Under these conditions, reduced metal loading was necessary due to the high activity of the initiators. For Zn(1/4)₂, high conversion is achieved within 4 minutes {[LA]:[Init]:[BnOH] = 10 000:1:100}. For these polymers, there is a reasonable agreement between molecular weight with the theoretical value {for Zn(1)₂, $M_n = 16\ 100$ Da; $M_{n,theo} = 13\ 050$ Da, TOF = 180 000 h⁻¹}. However, the GPC trace has a shoulder towards high molecular weight. As a consequence, the chain dispersity is increased relative to 130 °C {for Zn(1)₂, $\mathcal{D} = 1.47$ }. For comparison, commercially available Sn(Oct)₂ and Zn(OAc)₂·2H₂O were also tested under these conditions. Polymerisation of L-LA with Sn(II) was observed to be comparable to Zn(1)₂ (3 minutes, 95%, $M_n = 16\ 100$ Da, $\mathcal{D} = 1.54$). Zn(OAc)₂·2H₂O performed less well, (10 minutes, 27%) demonstrating the need for ligated complexes. The production of higher molecular weight was also demonstrated with Zn(1)₂ {[LA]:[Init]:[BnOH] = 10 000:1:33} within the same timeframe ($M_n = 42\ 500$ Da; $M_{n,theo} = 40\ 700$ Da, TOF = 188 000 h⁻¹). Reasonable conversion

and high molecular weight is also achieved at 10 000:1:15 after 5 minutes (63%; $M_n = 66\ 400$ Da, $\mathcal{D} = 1.47$). There is good agreement of measured and theoretical molecular weight ($M_{n,theo} = 60\ 600$ Da). The molecular weight achieved is comparable to that of commercially available PLA (NatureWorks, 6202D: $M_n = 44\ 350$ Da, $\mathcal{D} = 2.00$, see ESI†).¹⁰⁹ This system was also found to achieve relatively high molecular weight in the absence of co-initiator (3 minutes, 38%; $M_n = 48\ 950$ Da, $\mathcal{D} = 1.29$). In this case the dispersity is found to be lower and it is suggested that the polymerisation pathway without benzyl alcohol leads the observed shoulder in the GPC trace. Conversion can be increased by extension of the polymerisation time (15 minutes, 73%), however this is achieved with a broadening of the dispersity due to increased viscosity and poor mixing. The molecular weight achieved is industrially applicable ($M_n = 82\ 400$ Da, $\mathcal{D} = 1.64$), being comparable to that of commercial PLA samples (NatureWorks, 4043D: $M_n = 61\ 900$ Da, $\mathcal{D} = 1.98$ /NatureWorks, 2500HP: $M_n = 71\ 900$ Da, $\mathcal{D} = 1.62$).¹⁰⁹ A similar result is observed for Zn(4)₂ in the absence of benzyl alcohol. Zn(5)₂ requires more time to reach higher conversion, which is consistent with the previous experimental conditions. However, this initiator facilitates a more controlled ROP with excellent agreement between experimental and theoretical molecular weight values and a narrow dispersity ($M_n = 11\ 550$ Da, $M_{n,theo} = 11\ 350$ Da; $\mathcal{D} = 1.08$). Polymerisation without co-initiator affords negligible conversion within the same timeframe and this is undoubtedly the reason for enhanced control. Zn(5)₂ is therefore more resistant to lactide impurities or stable towards insertion of the complex-ligand bonds into the lactide carbonyl. Zn(7)₂ also facilitated polymerisation under these conditions with good control being maintained despite 1 hour at high temperature ($M_n = 11\ 650$ Da, $M_{n,theo} = 8600$ Da; $\mathcal{D} = 1.06$). In the absence of co-initiator, the polymerisation activity is suppressed, similar to Zn(5)₂.

The magnesium complexes activity is not enhanced at 180 °C with similar conversions being achieved in the same time frame. However, reasonable molecular weight control is

Table 4 Immortal polymerisation of L-lactide at 180 °C with Zn/Mg(II) complexes

Init.	[LA]:[I]:[BnOH]	Time/min	Conv. ^a %	$M_{n,theo}$ ^b	M_n ^c	\mathcal{D}^c
Zn(1) ₂	10 000:1:100	3	90	13 050	16 100	1.47
Zn(1) ₂	10 000:1:33	3	94	40 700	42 500	1.41
Zn(1) ₂	10 000:1:15	5	63	60 600	66 400	1.47
Zn(1) ₂	10 000:1	3	38	— ^d	48 950	1.29
Zn(1) ₂	10 000:1	15	72	— ^d	82 400	1.64
Zn(4) ₂	10 000:1:100	4	94	13 650	14 150	1.40
Zn(4) ₂	10 000:1	4	28	— ^d	33 000	1.17
Zn(5) ₂	10 000:1:100	8	78	11 350	11 550	1.08
Zn(5) ₂	10 000:1	8	2	—	—	—
Zn(7) ₂	10 000:1:100	60	59	8600	11 650	1.06
Zn(7) ₂	10 000:1	60	4	—	—	—
Mg(1) ₂	10 000:1:100	20	47	6850	7000	1.17
Mg(5) ₂	10 000:1:100	20	25	3700	4000	1.17

Conditions: L-LA, solvent free (180 °C). ^a Determined via ¹H NMR spectroscopy. ^b Theoretical molecular weight based on conversion and co-initiator added $\{(M_{r,LA} \times \%_{conv}) + M_{n,BnOH}\}$. ^c Molecular weight via GPC analysis (in THF). A correction factor of 0.58 has been applied.¹⁰⁸ ^d As no initiating group it is not possible to calculate a theoretical M_n .



maintained. MALDI-ToF analysis of these polymers confirms the expected benzyl alcohol groups. A greater degree of transesterification reactions is also indicated and this is more pronounced for polymer derived from Mg(1)₂.

Mechanistic studies

The stability of these complexes, with respect to lactide, has been investigated on an NMR scale at room temperature in CDCl₃ (see ESI†). The addition of L-LA to Zn(4/5)₂ caused no change of the resonances originating from the complexes. From these NMR spectra, there is also evidence of lactide coordination through an upfield shift of methine resonances. Further to this, conversion of the lactide is observed over the course of a week to give oligomers without the addition of an exogenous alcohol. As the complexes appear to be unchanged by addition of the LA or PLA, it is likely that an activated monomer mechanism is in operation facilitated by impurities in the monomer.^{110,111} Stability was also assessed under melt conditions: 5 equivalents of L-LA were added to Zn(1)₂ at 180 °C and stirred for 1 minute. The resultant material was analyzed by ¹H NMR to reveal complete conversion of lactide (see ESI†). The majority of the complex is shown to be intact, albeit with broadened resonances. There are new resonances in the aromatic region suggesting some decomposition, although the resonances are minor (~5%); the material was also analyzed by ESI-MS which showed the presence of oligomers. The mass of which was consistent with lactide being ring-opened by the ligand rather than lactic acid or water. It was observed that Zn(1)₂ was capable of initiating the ROP of lactide in the absence of a co-initiator and this evidence suggests this is achieved through insertion of the ligand. This would generate a new species which is capable of facilitating the coordination–insertion ROP. With the loss of a ligand, the lower coordinate zinc centre could be predicted to be more active. The operation of a second active species would also explain the high molecular weight shoulder in the GPC trace. It is hypothesised that it is the amine group which inserts into the lactide rather than the phenoxide as this explains the inactivity of Zn(5,7)₂ in the absence of co-initiator. In the presence of co-initiator the predominant ROP pathway is presumably an activated monomer mechanism.

Kinetics

An investigation into the kinetics of the most active initiators was carried out *via in situ* IR spectroscopy measurements.

These experiments were conducted on a 15 g scale (L-LA) to immerse the IR probe fully in the lactide melt. For each initiator {Zn(1,4,5)₂}, the observed activity on this scale is consistent with the smaller scale polymerisation in a sealed tube (Table 5). Rate data is extracted from the first 2–3 minutes of reaction. After this period, the increased viscosity leads to a second linear regime with a reduced rate. Zn(1)₂ was shown to have the highest rate constant { $k_{app} = (6.86 \pm 0.36) \times 10^{-3} \text{ s}^{-1}$, TOF = 114 000 h⁻¹} Zn(4)₂ and Zn(5)₂ were shown to have slightly reduced rates of polymerisation { $k_{app} = (6.28 \pm 0.31) \times 10^{-3} \text{ s}^{-1}$ and $(6.05 \pm 0.26) \times 10^{-3} \text{ s}^{-1}$ with TOFs 112 800 and 54 000 h⁻¹ respectively}, although within experimental error. Under these conditions, polymerisation with Zn(1/4)₂ leads to polymer with a relatively broad dispersity and this is once again attributed ligand initiated polymerisation. However, Zn(5)₂ maintains the excellent control previously seen ($D = 1.05$). All molecular weights observed are slightly higher than expected and this could be due to loss of benzyl alcohol from the molten mixture. All isolated polymer from these studies were colourless powders prior to purification (see ESI†). DSC analysis was carried out on the PLLA derived from Zn(1)₂ under these challenging large scale conditions to determine the extent of epimerisation. For this sample, a melt temperature of 171 °C was observed highlighting once again the excellent control of this initiator (see ESI†).

Stereocomplexation

The ability to control the polymerisation of L-LA, with the absence of epimerization or transesterification at 180 °C massively widens the applications of these initiators. The production of isotactic stereoblock PLA is an important goal, improving material properties. A particular challenge is to achieve this under industrial conditions, in the absence of solvent. Using Zn(1)₂, this has been achieved through an initial polymerisation of L-LA at 180 °C with a ratio of 1500 : 1 : 10 followed by the addition of an equivalent amount of D-LA (total ratio 3000 : 1 : 10). Best results were achieved using overhead stirring to ensure the polymerisation remained mobile. High conversion was achieved after 5 minutes and a clear film like material was isolated (see ESI†). Conversion and molecular weight are both consistent with the sequential polymerisation of the two monomers (95%; $M_n = 33\,400 \text{ Da}$, $M_{n,theo} = 42\,000 \text{ Da}$, $D = 1.62$). Analysis by homonuclear decoupled ¹H NMR spectra showed the main polymer linkage to be isotactic ($P_m = 0.80$). However, other tetrad relationships were observa-

Table 5 IR kinetics for polymerisation of L-lactide at 180 °C with Zn(II) complexes

Init.	Time/min	Conv. ^a %	$M_{n,theo}$ ^b	M_n ^c	D^c	$k_{app}/\times 10^{-3} \text{ s}^{-1}$
Zn(1) ₂	5	95	13 700	14 500	1.63	6.86 ± 0.36
Zn(4) ₂	5	94	13 650	16 100	1.41	6.28 ± 0.31
Zn(5) ₂	8	72	10 450	12 750	1.05	6.05 ± 0.26

Conditions: L-LA (15 g), [LA] : [I] : [BnOH] = 10 000 : 1 : 100, solvent free (180 °C). ^a Determined *via* ¹H NMR spectroscopy. ^b Theoretical molecular weight based on conversion and co-initiator added { $(M_{r,LA} \times \%_{conv}) + M_{n,BnOH}$ }. ^c Molecular weight *via* GPC analysis (in THF). A correction factor of 0.58 has been applied.¹⁰⁸



ble suggesting defects in the polymer microstructure. This is most likely due to tapering between the L- and D-blocks. Significantly, DSC analysis shows successful formation of a stereocomplex ($T_m = 190\text{ }^\circ\text{C}$).

Conclusions

Simple ethylenediamine complexes have been prepared and applied to the ROP of lactide with benign and earth abundant metals. These consist of Zn(II) and Mg(II) metal centres and therefore represent attractive complexes for the production of biocompatible PLA. In the solid-state, a tendency towards octahedral coordination was observed in most cases. Rapid polymerisation was observed for the least fluxional complexes. Excellent control and activity was achieved under industrially relevant conditions of high temperature and low catalyst loading, with the resultant PLA having no colouration. Kinetic data under these conditions was recorded *via* IR spectroscopy, further demonstrating and quantifying the activity of these complexes, with TOFs in excess of $100\,000\text{ h}^{-1}$, which are undoubtedly at the forefront of the field. Due to a lack of epimerisation, solvent-free stereoblock formation was also achieved through sequential monomer addition.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful to the EPSRC for funding (EP/P016405). We would also like to thank PURAC/CORBION for generous donation of D-Lactide. NatureWorks are also thanked for generous donation of commercial PLA samples. We also acknowledge the EPSRC (EP/L027267/1) for analysis facilities at the University of Bath.

Notes and references

- M. Jamshidian, E. A. Tehrani, M. Imran, M. Jacquot and S. Desobry, *Compr. Rev. Food Sci. Food Saf.*, 2010, **9**, 552.
- R. Auras, B. Harte and S. Selke, *Macromol. Biosci.*, 2004, **4**, 835.
- I. S. M. A. Tawakkal, M. J. Cran, J. Miltz and S. W. Bigger, *J. Food Sci.*, 2014, **79**, R1477.
- A. J. R. Lasprilla, G. A. R. Martinez, B. H. Lunelli, A. L. Jardim and R. M. Filho, *Biotechnol. Adv.*, 2012, **30**, 321.
- V. Siracusa, P. Rocculi, S. Romani and M. D. Rosa, *Trends Food Sci. Technol.*, 2008, **19**, 634.
- S. Farah, D. G. Anderson and R. Langer, *Adv. Drug Delivery Rev.*, 2016, **107**, 367.
- M. I. Sabir, X. Xu and L. Li, *J. Mater. Sci.*, 2009, **44**, 5713.
- R. E. Drumright, P. R. Gruber and D. E. Henton, *Adv. Mater.*, 2000, **12**, 1841.
- O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147.
- R. H. Platel, L. M. Hodgson and C. K. Williams, *Polym. Rev.*, 2008, **48**, 11.
- M. J. Stanford and A. P. Dove, *Chem. Soc. Rev.*, 2010, **39**, 486.
- J.-C. Buffet and J. Okuda, *Polym. Chem.*, 2011, **2**, 2758.
- J. Wu, T.-L. Yu, C.-T. Chen and C.-C. Lin, *Coord. Chem. Rev.*, 2006, **250**, 602.
- P. Hormnirun, E. L. Marshall, V. C. Gibson, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 2004, **126**, 2688.
- P. Hormnirun, E. L. Marshall, V. C. Gibson, R. I. Pugh and A. J. P. White, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15343.
- H. Du, A. H. Velders, P. J. Dijkstra, J. Sun, Z. Zhong, X. Chen and J. Feijen, *Chem. – Eur. J.*, 2009, **15**, 9836.
- N. Maudoux, T. Roisnel, V. Dorcet, J.-F. Carpentier and Y. Sarazin, *Chem. – Eur. J.*, 2014, **20**, 6131.
- A. Pilone, K. Press, I. Goldberg, M. Kol, M. Mazzeo and M. Lamberti, *J. Am. Chem. Soc.*, 2014, **136**, 2940.
- L. Chen, W. Li, D. Yuan, Y. Zhang, Q. Shen and Y. Yao, *Inorg. Chem.*, 2015, 4699.
- K. Press, I. Goldberg and M. Kol, *Angew. Chem., Int. Ed.*, 2015, **54**, 14858.
- S. Tabthong, T. Nanok, P. Sumrit, P. Kongsaree, S. Prabpai, P. Chuawong and P. Hormnirun, *Macromolecules*, 2015, **48**, 6846.
- S. M. Kirk, H. C. Quilter, A. Buchard, L. H. Thomas, G. Kociok-Kohn and M. D. Jones, *Dalton Trans.*, 2016, **45**, 13846.
- P. McKeown, M. G. Davidson, G. Kociok-Kohn and M. D. Jones, *Chem. Commun.*, 2016, **52**, 10431.
- N. Spassky, M. Wisniewski, C. Pluta and A. LeBorgne, *Macromol. Chem. Phys.*, 1996, **197**, 2627.
- M. Wisniewski, A. LeBorgne and N. Spassky, *Macromol. Chem. Phys.*, 1997, **198**, 1227.
- Z. Zhong, P. J. Dijkstra and J. Feijen, *J. Am. Chem. Soc.*, 2003, **125**, 11291.
- Z. Y. Zhong, P. J. Dijkstra and J. Feijen, *Angew. Chem., Int. Ed.*, 2002, **41**, 4510.
- N. Nomura, R. Ishii, M. Akakura and K. Aoi, *J. Am. Chem. Soc.*, 2002, **124**, 5938.
- N. Nomura, R. Ishii, Y. Yamamoto and T. Kondo, *Chem. – Eur. J.*, 2007, **13**, 4433.
- I. Peckermann, A. Kapelski, T. P. Spaniol and J. Okuda, *Inorg. Chem.*, 2009, **48**, 5526.
- A. Pietrangelo, M. A. Hillmyer and W. B. Tolman, *Chem. Commun.*, 2009, 2736.
- J.-C. Buffet, J. Okuda and P. L. Arnold, *Inorg. Chem.*, 2010, **49**, 419.
- A. Pietrangelo, S. C. Knight, A. K. Gupta, L. J. Yao, M. A. Hillmyer and W. B. Tolman, *J. Am. Chem. Soc.*, 2010, **132**, 11649.



- 34 A. Kapelski and J. Okuda, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 4983.
- 35 M. Normand, V. Dorcet, E. Kirillov and J.-F. Carpentier, *Organometallics*, 2013, **32**, 1694.
- 36 P. Horeglad, M. Cybularczyk, A. Litwinska, A. M. Dabrowska, M. Dranka, G. Z. Zukowska, M. Urbanczyk and M. Michalak, *Polym. Chem.*, 2016, **7**, 2022.
- 37 D. C. Aluthge, J. M. Ahn and P. Mehrkhodavandi, *Chem. Sci.*, 2015, **6**, 5284.
- 38 D. C. Aluthge, B. O. Patrick and P. Mehrkhodavandi, *Chem. Commun.*, 2013, **49**, 4295.
- 39 D. C. Aluthge, E. X. Yan, J. M. Ahn and P. Mehrkhodavandi, *Inorg. Chem.*, 2014, **53**, 6628.
- 40 A. F. Douglas, B. O. Patrick and P. Mehrkhodavandi, *Angew. Chem., Int. Ed.*, 2008, **120**, 2322.
- 41 I. Yu, A. Acosta-Ramírez and P. Mehrkhodavandi, *J. Am. Chem. Soc.*, 2012, **134**, 12758.
- 42 T. Ebrahimi, D. C. Aluthge, B. O. Patrick, S. G. Hatzikiriakos and P. Mehrkhodavandi, *ACS Catal.*, 2017, **7**, 6413.
- 43 C. Bakewell, A. J. P. White, N. J. Long and C. K. Williams, *Angew. Chem., Int. Ed.*, 2014, **53**, 9226.
- 44 C. Bakewell, T.-P.-A. Cao, N. Long, X. F. Le Goff, A. Auffrant and C. K. Williams, *J. Am. Chem. Soc.*, 2012, **134**, 20577.
- 45 C. Bakewell, T.-P.-A. Cao, X. F. Le Goff, N. J. Long, A. Auffrant and C. K. Williams, *Organometallics*, 2013, **32**, 1475.
- 46 A. Amgoune, C. M. Thomas, S. Ilinca, T. Roisnel and J.-F. Carpentier, *Angew. Chem., Int. Ed.*, 2006, **45**, 2782.
- 47 C. Bakewell, A. J. P. White, N. J. Long and C. K. Williams, *Inorg. Chem.*, 2015, **54**, 2204.
- 48 C.-X. Cai, A. Amgoune, C. W. Lehmann and J.-F. Carpentier, *Chem. Commun.*, 2004, 330.
- 49 H. Ma, T. P. Spaniol and J. Okuda, *Angew. Chem., Int. Ed.*, 2006, **45**, 7818.
- 50 T.-P.-A. Cao, A. Buchard, X. F. Le Goff, A. Auffrant and C. K. Williams, *Inorg. Chem.*, 2012, **51**, 2157.
- 51 R. H. Platel, A. J. P. White and C. K. Williams, *Chem. Commun.*, 2009, 4115.
- 52 A. Amgoune, C. M. Thomas and J.-F. Carpentier, *Macromol. Rapid Commun.*, 2007, **28**, 693.
- 53 R. H. Platel, A. J. P. White and C. K. Williams, *Inorg. Chem.*, 2011, **50**, 7718.
- 54 S. Gendler, S. Segal, I. Goldberg, Z. Goldschmidt and M. Kol, *Inorg. Chem.*, 2006, **45**, 4783.
- 55 A. J. Chmura, D. M. Cousins, M. G. Davidson, M. D. Jones, M. D. Lunn and M. F. Mahon, *Dalton Trans.*, 2008, 1437.
- 56 A. L. Zelikoff, J. Kopilov, I. Goldberg, G. W. Coates and M. Kol, *Chem. Commun.*, 2009, 6804.
- 57 T. K. Saha, V. Ramkumar and D. Chakraborty, *Inorg. Chem.*, 2011, **50**, 2720.
- 58 C. Romain, B. Heinrich, S. B. Laponnaz and S. Dagorne, *Chem. Commun.*, 2012, **48**, 2213.
- 59 A. Stopper, J. Okuda and M. Kol, *Macromolecules*, 2012, **45**, 698.
- 60 A. Sauer, A. Kapelski, C. Fliedel, S. Dagorne, M. Kol and J. Okuda, *Dalton Trans.*, 2013, **42**, 9007.
- 61 A. Stopper, K. Press, J. Okuda, I. Goldberg and M. Kol, *Inorg. Chem.*, 2014, **53**, 9140.
- 62 M. D. Jones, L. Brady, P. McKeown, A. Buchard, P. M. Schafer, L. H. Thomas, M. F. Mahon, T. J. Woodman and J. P. Lowe, *Chem. Sci.*, 2015, **6**, 5034.
- 63 S. M. Kirk, G. Kociok-Köhn and M. D. Jones, *Organometallics*, 2016, **35**, 3837.
- 64 A. J. Chmura, M. G. Davidson, C. J. Frankis, M. D. Jones and M. D. Lunn, *Chem. Commun.*, 2008, 1293.
- 65 M. D. Jones, S. L. Hancock, P. McKeown, P. M. Schafer, A. Buchard, L. H. Thomas, M. F. Mahon and J. P. Lowe, *Chem. Commun.*, 2014, **50**, 15967.
- 66 B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 3229.
- 67 M. H. Chisholm, J. C. Gallucci and K. Phomphrai, *Inorg. Chem.*, 2005, **44**, 8004.
- 68 H.-Y. Chen, H.-Y. Tang and C.-C. Lin, *Macromolecules*, 2006, **39**, 3745.
- 69 J. Börner, U. Florke, K. Huber, A. Döring, D. Kuckling and S. Herres-Pawlis, *Chem. – Eur. J.*, 2009, **15**, 2362.
- 70 D. J. Darensbourg and O. Karroonnirun, *Inorg. Chem.*, 2010, **49**, 2360.
- 71 J. Börner, I. dos Santos Vieira, A. Pawlis, A. Döring, D. Kuckling and S. Herres-Pawlis, *Chem. – Eur. J.*, 2011, **17**, 4507.
- 72 I. dos Santos Vieira and S. Herres-Pawlis, *Eur. J. Inorg. Chem.*, 2012, **2012**, 765.
- 73 H. Wang and H. Ma, *Chem. Commun.*, 2013, **49**, 8686.
- 74 C. Fliedel, D. Vila-Viçosa, M. J. Calhorda, S. Dagorne and T. Avilés, *ChemCatChem*, 2014, **6**, 1357.
- 75 Z. Mou, B. Liu, M. Wang, H. Xie, P. Li, L. Li, S. Li and D. Cui, *Chem. Commun.*, 2014, **50**, 11411.
- 76 H. Wang, Y. Yang and H. Ma, *Macromolecules*, 2014, **47**, 7750.
- 77 Y. Chapurina, T. Roisnel, J.-F. Carpentier and E. Kirillov, *Inorg. Chim. Acta*, 2015, **431**, 161.
- 78 Y. Yang, H. Wang and H. Ma, *Inorg. Chem.*, 2015, **54**, 5839.
- 79 T. Rosen, Y. Popowski, I. Goldberg and M. Kol, *Chem. – Eur. J.*, 2016, **22**, 11533.
- 80 P. M. Schäfer, M. Fuchs, A. Ohligschläger, R. Rittinghaus, P. McKeown, E. Akin, M. Schmidt, A. Hoffmann, M. A. Liauw, M. D. Jones and S. Herres-Pawlis, *ChemSusChem*, 2017, **10**, 3547.
- 81 D. E. Stasiw, A. M. Luke, T. Rosen, A. B. League, M. Mandal, B. D. Neisen, C. J. Cramer, M. Kol and W. B. Tolman, *Inorg. Chem.*, 2017, **56**, 14366.
- 82 D. Jędrzkiewicz, G. Adamus, M. Kwiecień, Ł. John and J. Ejfler, *Inorg. Chem.*, 2017, **56**, 1349.
- 83 S. Abbina and G. Du, *ACS Macro Lett.*, 2014, **3**, 689.



- 84 M. Cheng, A. B. Attygalle, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 1999, **121**, 11583.
- 85 A. Thevenon, C. Romain, M. S. Bennington, A. J. P. White, H. J. Davidson, S. Brooker and C. K. Williams, *Angew. Chem., Int. Ed.*, 2016, **55**, 8680.
- 86 C. K. Williams, L. E. Breyfogle, S. K. Choi, W. Nam, V. G. Young, M. A. Hillmyer and W. B. Tolman, *J. Am. Chem. Soc.*, 2003, **125**, 11350.
- 87 C. Kan, J. Hu, Y. Huang, H. Wang and H. Ma, *Macromolecules*, 2017, **50**, 7911.
- 88 J. Kasperczyk and M. Bero, *Polymer*, 2000, **41**, 391.
- 89 L. F. Sánchez-Barba, A. Garcés, M. Fajardo, C. Alonso-Moreno, J. Fernández-Baeza, A. Otero, A. Antiñolo, J. Tejada, A. Lara-Sánchez and M. I. López-Solera, *Organometallics*, 2007, **26**, 6403.
- 90 V. Poirier, T. Roisnel, J.-F. Carpentier and Y. Sarazin, *Dalton Trans.*, 2009, 9820.
- 91 C. A. Wheaton, P. G. Hayes and B. J. Ireland, *Dalton Trans.*, 2009, 4832.
- 92 L. Wang and H. Ma, *Macromolecules*, 2010, **43**, 6535.
- 93 L. F. Sánchez-Barba, A. Garcés, J. Fernández-Baeza, A. Otero, C. Alonso-Moreno, A. Lara-Sánchez and A. M. Rodríguez, *Organometallics*, 2011, **30**, 2775.
- 94 H.-J. Chuang, H.-L. Chen, J.-L. Ye, Z.-Y. Chen, P.-L. Huang, T.-T. Liao, T.-E. Tsai and C.-C. Lin, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 696.
- 95 A. Garcés, L. F. Sánchez-Barba, J. Fernández-Baeza, A. Otero, M. Honrado, A. Lara-Sánchez and A. M. Rodríguez, *Inorg. Chem.*, 2013, **52**, 12691.
- 96 W. Yi and H. Ma, *Inorg. Chem.*, 2013, **52**, 11821.
- 97 M. J. Walton, S. J. Lancaster and C. Redshaw, *ChemCatChem*, 2014, **6**, 1892.
- 98 K. Devaine-Pressing, J. H. Lehr, M. E. Pratt, L. N. Dawe, A. A. Sarjeant and C. M. Kozak, *Dalton Trans.*, 2015, **44**, 12365.
- 99 H. Wang, J. Guo, Y. Yang and H. Ma, *Dalton Trans.*, 2016, **45**, 10942.
- 100 P. McKeown, J. Brown-Humes, M. G. Davidson, M. F. Mahon, T. J. Woodman and M. D. Jones, *Dalton Trans.*, 2017, **46**, 5048.
- 101 M. H. Chisholm, K. Choojun, A. S. Chow, G. Fraenkel and J. C. Gallucci, *Inorg. Chem.*, 2013, **52**, 11302.
- 102 M. H. Chisholm, K. Choojun, J. C. Gallucci and P. M. Wambua, *Chem. Sci.*, 2012, **3**, 3445.
- 103 M. H. Chisholm, J. Gallucci and K. Phomphrai, *Inorg. Chem.*, 2002, **41**, 2785.
- 104 T. Rosen, I. Goldberg, V. Venditto and M. Kol, *J. Am. Chem. Soc.*, 2016, **138**, 12041.
- 105 H. J. Beim and A. R. Day, *J. Heterocycl. Chem.*, 1970, **7**, 355.
- 106 P. McKeown, M. G. Davidson, J. P. Lowe, M. F. Mahon, L. H. Thomas, T. J. Woodman and M. D. Jones, *Dalton Trans.*, 2016, **45**, 5374.
- 107 H.-Y. Chen, H.-Y. Tang and C.-C. Lin, *Polymer*, 2007, **48**, 2257.
- 108 A. Kowalski, A. Duda and S. Penczek, *Macromolecules*, 1998, **31**, 2114.
- 109 Commercial PLA (Ingeo) was sourced from NatureWorks. 2500HP grade is suitable for extrusion and thermoforming; 4043D grade is suitable for films; 6202D grade is suitable for fibres. For more information see <https://www.natureworksllc.com/Products>.
- 110 A. J. Nijenhuis, D. W. Grijpma and A. J. Pennings, *Polym. Bull.*, 1991, **26**, 71.
- 111 A. J. Nijenhuis, D. W. Grijpma and A. J. Pennings, *Macromolecules*, 1992, **25**, 6419.

