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Bimetallic and trimetallic zinc amino-bis(phenolate) complexes for ring-opening polymerization of *rac*-lactide†

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The synthesis and structural characterization of bimetallic and trimetallic zinc complexes of amino-bis(phenolate) ligands are described. Bimetallic complexes $(ZnEt)_2$**[L1]** (**1a**), its THF adduct $(ZnEt)_2$**[L1]**·THF (**1a·THF**), and $(ZnEt)_2$**[L2]** (**1b**) (where **[L1]** = *n*-propylamine-*N*,*N*-bis(2-methylene-4,6-di-*t*-butylphenolate) and **[L2]** = *n*-propylamine-*N*,*N*-bis(2-methylene-6-*t*-butyl-4-methylphenolate) were prepared *via* reaction of the proligands H_2**[L1]** and H_2**[L2]** with $ZnEt_2$. The addition of isopropanol to complex **1a** to replace the ethyl groups with more nucleophilic alkoxyl groups afforded trimetallic zinc complex $Zn_3(i\text{-}PrO)_2$**[L1]**$_2$ (**3**). Their structures were confirmed by X-ray crystallography. Their catalytic activity towards ring-opening polymerization (ROP) of *rac*-lactide with or without exogenous alcohol as a co-initiator was studied. These complexes exhibit moderate to good activity for ROP of *rac*-lactide both in the melt phase and solution. The influence of catalyst and co-initiator loadings were studied and thermodynamic activation parameters were determined. Characterization of the polymers by Gel Permeation Chromatography (GPC) and Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) mass spectrometry showed controlled and living polymerizations for *rac*-lactide in the presence of alcohol.

Introduction

The development of sustainable plastics has become a rapidly growing and demanding research field with the depletion of petroleum feedstocks and growing environmental concerns. A perfect alternative to traditional polymers would be those that can be synthesized from renewable sources and easily disposed of or recycled while maintaining good physical strength. Polylactide (PLA) has gained significant interest both in industry and academia due to its biocompatibility, flexible waste management (recycling and composting),[1] and monomer renewability (obtained from biomass, *e.g.* corn and corn waste).[2] With these features, PLA based materials have already shown promising practical use in the medical field as sutures and prosthetics,[3,4] and have been considered as potent alternatives to traditional petrochemical-based polymers in the agricultural and food industries, especially for packaging.[5,6]

Metal catalyzed ring-opening polymerization (ROP) of lactide (LA) has been widely studied.[7–16] In particular, zinc complexes have attracted ongoing attention because they are cheap, abundant, non-toxic, colorless and can be monitored by NMR spectroscopy due to their diamagnetic properties.[10] Zinc complexes bearing various ligand scaffolds have been investigated for ROP of lactide, including β-diiminate (BDI),[17–28] tris(pyrazolyl)borate (TPB),[29] bis(pyrazolyl)amide (BPA),[30] phenolate,[31–50] N-heterocyclic carbenes,[51,52] and recently phosphinimine ligands.[53–56]

Amino-bis(phenolate) ligands exhibit tunable electronic effects and flexible steric properties, and their metal complexes as catalysts in different systems have been well studied.[42,57–68] Zinc amino-bis(phenolate) complexes have been studied for ROP of cyclic esters. For example, early work by Tolman, Hillmyer and co-workers reported monometallic zinc amino-bis(phenolate) complexes that perform controlled ROP of ε-caprolactone in the presence of benzyl alcohol (BnOH). They suggested good controllability was achieved *via* an activated monomer route.[68] Schaper and co-workers synthesized a bimetallic zinc complex with a chiral *N*-substituted amine-bis(phenolate) ligand for enantioselective ROP.[42] However, it showed only moderate activity (91% conversion after 20 h at 50 °C with 1 mol% initiator loading) and poor enantioselectivity (P_r = 0.59) for ROP of *rac*-lactide (*rac*-LA). The limited activity was attributed to the steric hindrance of the

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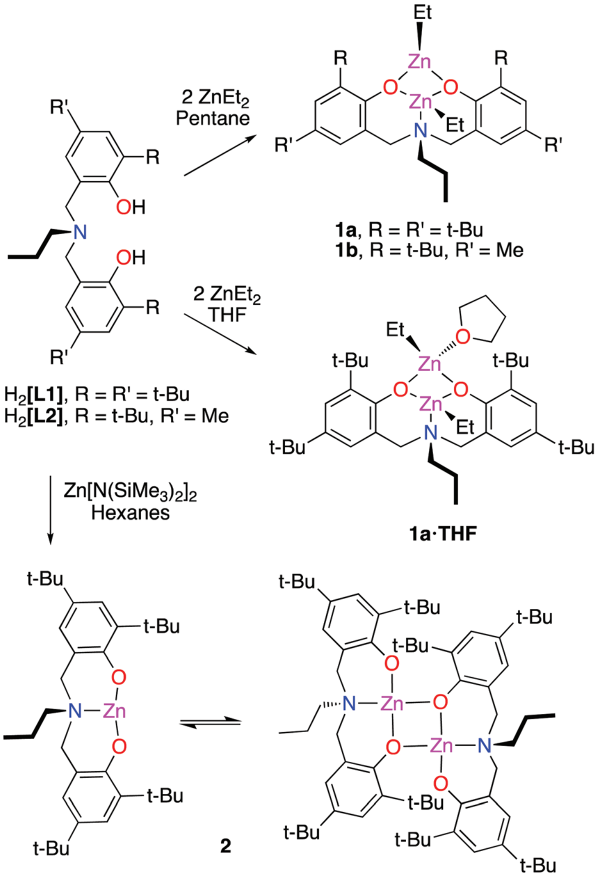
complex. Consequently, we synthesized less bulky zinc amino-bis(phenolate) complexes and tested their activity for the ROP of *rac*-lactide with and without exogenous alcohol, both in solution and in the melt (solvent-free). It has been reported that zinc alkoxide complexes in which the alkoxide group usually acts as initiating group have better catalytic activities than zinc ethyl complexes towards ROP of lactide.[25,28,47] For example, Hayes and co-workers have prepared a zinc methyl lactate complex, and the complex initiates polymerization of lactide at ambient conditions *via* a coordination–insertion mechanism.[54] Inspired by these works, we replaced the ethyl groups of the initial organozinc compound to generate a zinc alkoxide complex. Herein we report the preparation and characterization of zinc amino-bis(phenolate) complexes bearing bimetallic and trimetallic centers, their catalytic activities, and mechanistic insight into the ROP of *rac*-lactide using these complexes.



Scheme 1 Synthesis of zinc ethyl complexes.

Results and discussion

Synthesis and characterization of zinc amino-bis(phenolate) complexes

H_2[**L1**] and H_2[**L2**] can be easily prepared using a modified Mannich condensation reaction in water as previously reported.[69] Reaction of H_2[**L**] with a stoichiometric amount of $ZnEt_2$, yielded an intractable mixture of products. When the $ZnEt_2$ to ligand ratio was increased to 2 : 1 in pentane, single products were obtained in high yields (99%) by simply evaporating the volatile components. Zinc complexes **1a** and **1b** were obtained using H_2[**L1**] and H_2[**L2**] (Scheme 1), respectively. The ^1H NMR spectra of complexes **1a** and **1b** in $CDCl_3$ show two zinc ethyl environments (two triplets arising from two different $ZnC\mathit{H}_2CH_3$ methylene groups and two quartets arising from two $ZnCH_2\mathit{CH}_3$ methyl environments), which is supported by the ^{13}C NMR spectra. The NCH_2Ar protons of the ligand appear as a pair of doublets indicating they are diastereotopic, which confirms the coordination of the ligand to the zinc center. Together with the NMR data, the near quantitative yield and the absence of non-volatile byproducts, we proposed a bimetallic structure. A similar structure synthesized in 50% yield has been reported by Schaper and co-workers who used equimolar mixtures of a $ZnEt_2$ and a chiral tridentate amino-bis(phenolate) ligand.[42] However, the moderate yield may be explained by the bulkier methylbenzyl group on the central amine of the ligand and the lower $ZnEt_2$ to ligand ratio.

Single crystals of **1a** and **1b** could not be obtained from non-coordinating solvents but changing the reaction solvent from pentane to coordinating THF yielded the corresponding complex with one THF molecule coordinating to one of the zinc centers, $(ZnEt)_2$[**L1**]·(THF), **1a·THF** (Scheme 1). The ^1H NMR spectrum of complex **1a·THF** is almost identical to that of **1a**, except for the appearance of two additional multiplets at 3.92 and 1.93 ppm assigned to the coordinated THF. Also, the Zn-bound methylene groups of the ethyl ligands shift upfield upon THF coordination. The bimetallic structure of **1a·THF** was confirmed by X-ray crystallography (Fig. 1, with selected bond lengths and angles; crystallographic data are given in Table S1 in the ESI†). Complex **1a·THF** can be crystalized in pentane at room temperature. Each zinc atom is coordinated by an ethyl group and two bridging phenolate oxygens, which results in a nearly planar Zn_2O_2 core possessing a sum of angles of 359.8° and an O(1)–Zn(1)–O(2) angle of 84.87(4)°. Both of the zinc centers adopt distorted tetrahedral geometries, where the remaining site of one zinc center is filled by the dative amine donor of the ligand, and the empty site of the other zinc is filled by a THF molecule. The bonds between the two bridging oxygen atoms and the zinc atoms are similar, with Zn(1)–O(1) = 2.0570(11), Zn(1)–O(2) = 2.0435(10), Zn(2)–O(1) = 2.0031(10) and Zn(2)–O(2) = 2.0444(11) Å. As anticipated, the bond between the neutral THF oxygen and zinc is longer than the others, with Zn(2)–O(3) = 2.1581(11) Å.

The difficulty in removing the second alkyl group in diethylzinc *via* protonolysis is a known property of this reagent.[50,70] A monometallic zinc complex, **2**, can be obtained using $Zn[N(SiMe_3)_2]_2$ as the precursor in the manner of Hillmyer, Tolman and co-workers for a related amino-bis(phenolate) ligand bearing a methyl group on the central amino donor.[68] The solution behavior of **2** (Scheme 1) as determined by ^1H NMR in $CDCl_3$ showed the presence of monomeric and dimeric complexes (formulated as Zn[**L**] and {Zn[**L**]}$_2$). Due to the simi-

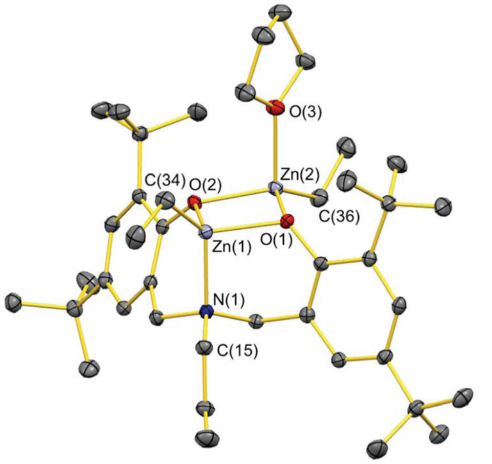
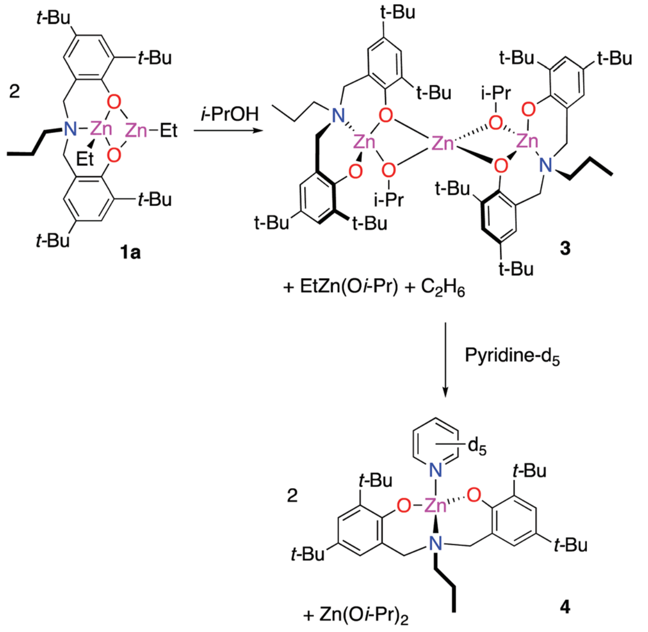


Fig. 1 Partially labeled molecular structure (ORTEP) of $(ZnEt)_2$**[L1]**·(THF), **1a·THF**. Thermal ellipsoids are drawn at 50% probability and H atoms are excluded for clarity. Selected bond lengths (Å) and angles (°): Zn(1)–O(1), 2.0570(11); Zn(1)–O(2), 2.0435(10); Zn(1)–N(1), 2.0860(12); Zn(1)–C(34), 1.9708(16); Zn(2)–O(1), 2.0031(10); Zn(2)–O(2), 2.0444(11); Zn(2)–O(3), 2.1581(11); Zn(2)–C(36), 1.9707(16); O(1)–Zn(1)–N(1), 92.80(4); O(2)–Zn(1)–O(1), 84.87(4); O(2)–Zn(1)–N(1), 91.54(5); C(34)–Zn(1)–O(1), 125.78(6); C(34)–Zn(1)–O(2), 120.18(6); C(34)–Zn(1)–N(1), 129.34(6); O(1)–Zn(2)–O(2), 86.24(4); O(1)–Zn(2)–O(3), 91.72(4); O(2)–Zn(2)–O(3), 96.09(4); C(36)–Zn(2)–O(1), 128.40(6); C(36)–Zn(2)–O(2), 129.02(6); C(36)–Zn(2)–O(3), 115.62(6).

larity to the previous work, further investigation of complex **2** was not pursued.

Reaction of zinc ethyl complex **1a** with i-PrOH in pentane resulted in the precipitation of the zinc alkoxide complex, Zn_3(i-PrO)$_2$**[L1]**$_2$, **3** (Scheme 2). Complex **3** was characterized by single crystal X-ray diffraction, which shows a trimetallic structure possessing two amino-bis(phenolate) ligands and two isopropoxyl groups (Fig. 2). Each zinc atom possesses a distorted tetrahedral geometry and the central Zn(2) atom is coordinated by two bridging phenolate oxygens and two bridging isopropoxyl groups. The ^{1}H NMR spectrum of complex **3** in $CDCl_3$ indicates four different aromatic protons, four different *t*-Bu group environments and one isopropyl group, which is consistent with a C_2 point group symmetry as shown by the crystal structure. When performed on an NMR scale, resonances attributable to EtZn(O-i-Pr) were observed, but slightly obscured by those of complex **3**, and shifted from those reported by Schaper and co-workers, who obtained its spectrum in benzene-d$_6$.[25]



Scheme 2 Synthesis of zinc alkoxide complex, **3** and pyridine adduct **4**.

Reactions of complexes **1a** and **1a·THF** with i-PrOH were also carried out in THF and yielded the same product, with no evidence for coordination of THF. Interestingly, after dissolving the trimetallic complex **3** in pyridine-d$_5$ a white precipitate was rapidly generated and NMR analysis of the solution shows a much simpler spectrum with only two different aromatic signals, two *t*-Bu environments, one diastereotopic NCH_2 methylene environment, and no isopropyl signals. This suggests the formation of a monometallic amino-bis(phenolate) complex with a coordinated pyridine-d$_5$ ligand, Zn(py-d$_5$)**[L1]** (**4**), where the deuterium signals of the pyridine are NMR silent. With the coordination of a planar pyridine, the resulting complex possesses C_s symmetry consistent with the NMR data. A related amine-bis(phenolato) zinc solvento adduct was reported by Tolman, Hillmyer and co-workers.[68]

Ring-opening polymerization of *rac*-lactide

We probed the catalytic activity of complex **1a** towards polymerization of *rac*-lactide in toluene and CH_2Cl_2 without added co-initiator. Initially, low activity was observed in both solvents at room temperature and at 80 °C in toluene (19 h, 50% conversion, Fig. S1†). To our delight, good activity was achieved in neat lactide under melt conditions (Fig. S2†). The catalyst loading can be lowered to 0.5 mol% while maintaining nearly quantitative conversion of lactide in 100 min. Further decrease of the catalyst loading to 0.2% resulted in diminished conversion, 65% (Table S2†). A study of lactide conversion over time was conducted using 0.5% catalyst loading at 130 °C (Table 1). Each entry was an independent run with polymerization being terminated by rapidly cooling each vessel to solidify the material at the appropriate time. After 15 min, 96% lactide conversion was observed (entry 5). The melt phase polymerization follows an approximate first order dependence on monomer concentration (Fig. S3†).

Interestingly, there appears to be no significant loss of control of the polymerization when conducted in the absence of alcohol co-initiator. Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) mass spectrometry shows cyclic polylactide, which is consistent with phenolate-initiated ROP and termination through backbiting. There are two dominant series of peaks corresponding to *cyclo*-$(C_3H_4O_2)_n$·Na^+ (A) and *cyclo*-$(C_3H_4O_2)_n$·K^+ (B) (Fig. S4†). The absence of a co-initiator and the slow polymerization rate

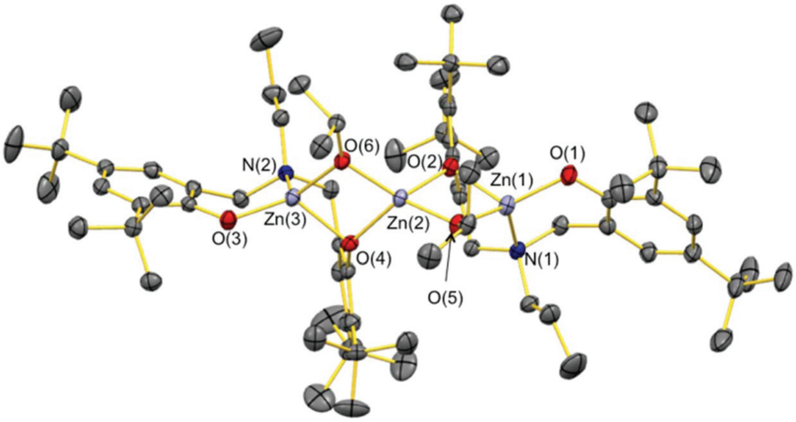
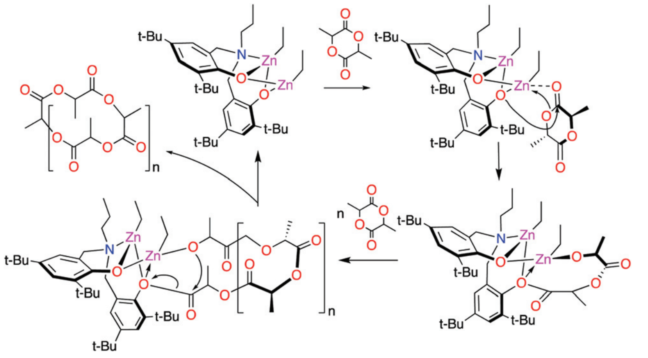


Fig. 2 Partially labeled molecular structure (ORTEP) of $Zn_3(i\text{-}PrO)_2$**[L1]**$_2$, **3**. Thermal ellipsoids are drawn at 50% probability and H atoms are excluded for clarity. Selected bond lengths (Å) and angles (°): Zn(1)–O(1), 1.8664(16); Zn(1)–O(2), 1.9966(15); Zn(1)–O(5), 1.9405(16); Zn(1)–N(1), 2.0726(19); Zn(2)–O(2), 1.9940(15); Zn(2)–O(4), 1.9944(15); Zn(2)–O(5), 1.9360(15); Zn(2)–O(6), 1.9358(14); Zn(3)–O(3), 1.8746(16); Zn(3)–O(4), 2.0083(15); Zn(3)–O(6), 1.9444(15); Zn(3)–N(2), 2.0744(19); O(1)–Zn(1)–O(2), 119.18(7); O(1)–Zn(1)–O(5), 131.97(7); O(1)–Zn(1)–N(1), 101.73(7); O(2)–Zn(1)–N(1), 95.43(6); O(5)–Zn(1)–O(2), 83.50(6); O(5)–Zn(1)–N(1), 118.67(7); O(2)–Zn(2)–O(4), 118.66(6); O(5)–Zn(2)–O(2), 83.68(6); O(5)–Zn(2)–O(4), 120.54(7); O(6)–Zn(2)–O(2), 119.96(7); O(6)–Zn(2)–O(4), 83.38(6); O(6)–Zn(2)–O(5), 134.91(6); O(3)–Zn(3)–O(4), 122.54(7); O(3)–Zn(3)–O(6), 134.48(7); O(3)–Zn(3)–N(2), 101.66(7); O(4)–Zn(3)–N(2), 96.11(6); O(6)–Zn(3)–O(4), 82.80(6); O(6)–Zn(3)–N(2), 113.27(7).

Table 1 Solvent-free ROP of *rac*-LA using complex **1a** ([LA] : [**1a**] = 200 : 1, 130 °C)

Entry	Time (min)	Conv.[a] (%)	T_g (°C)	M_n (Theo.)[b] (kg mol^{-1})	M_n (GPC)[c] (kg mol^{-1})	$Đ$ (M_w/M_n)[c]
1	3	2.9	—	—	—	—
2	5	27	—	—	—	—
3	7	70	—	—	—	—
4	10	87	46.4	25.0	36.4	1.52
5	15	96	45.6	27.6	37.3	1.40
6	20	96	44.2	27.6	27.6	1.17
7	30	97	47.5	28.0	28.6	1.24
8	40	97	47.5	28.0	26.1	1.29
9	60	98	—	—	—	—
10	80	98	—	—	—	—

[a] Calculated *via* integration of the methine resonances of *rac*-LA and PLA. [b] M_n (Theo.) = $[LA]_0/[\mathbf{1a}]_0$ × conv. × M(LA). [c] Determined by GPC in THF by triple detection using d*n*/d*c* = 0.049 mL g^{-1}.



Scheme 3 Proposed mechanism for ROP of LA by **1a** without added co-initiator *via* a phenolate initiation and backbiting termination.

allow for backbiting to occur, which has previously been observed for related Mg, Na and Li–phenolate catalysts where the phenolate anionic oxygens were proposed to initiate ROP.[58,59,71–73] A plausible mechanism is shown in Scheme 3. Characterization of the polymers obtained in the melt by gel permeation chromatography (GPC) showed that the molecular weights are in good agreement with the expected values and the molecular weight distributions are narrow ($Đ = M_w/M_n$ = 1.17 to 1.52). The polymers obtained from longer reaction times show molecular weights that are close to the theoretical values. However, for those obtained from shorter reaction times (Table 1, entries 4 and 5), the agreement between the experimental and theoretical molecular weights is diminished, with slightly higher than expected molecular weights. This may be the result of slow initiation *versus* propagation rates.[74] The stability of the complex at the high temperatures used for LA ROP was evaluated by heating a solution of **1a** in toluene-d_8 to 150 °C for 10 min in a microwave reactor. The ^{1}H NMR spectrum of this solution was identical before and after heating and showed no evidence of complex decomposition.

We also investigated the polymerization of *rac*-lactide with crystallographically authenticated **1a·THF** in the presence of benzyl alcohol (BnOH). Complex **1a·THF** with 1 : 1 ratio of BnOH shows better activity and controllability than complex **1a** alone or with added BnOH (Fig. S5†). Kinetic data were obtained by monitoring the reaction *via* ^{1}H NMR spectroscopy. The plots of $\ln[LA]_0/[LA]_t$ *vs.* time for different catalyst loadings ranging from 0.2 to 1.0 mol% of **1a·THF**/BnOH were obtained (Fig. 3). The plot of $\ln k_{obs}$ *vs.* ln[**1a·THF**] (Fig. 4) indicates a first order dependence on monomer concentration.

The ROP of *rac*-LA initiated by **1a·THF** was investigated under immortal conditions using benzyl alcohol or isopropanol as chain-transfer agents. The polymerization rate increases with an increase of BnOH concentration (Fig. 5), and

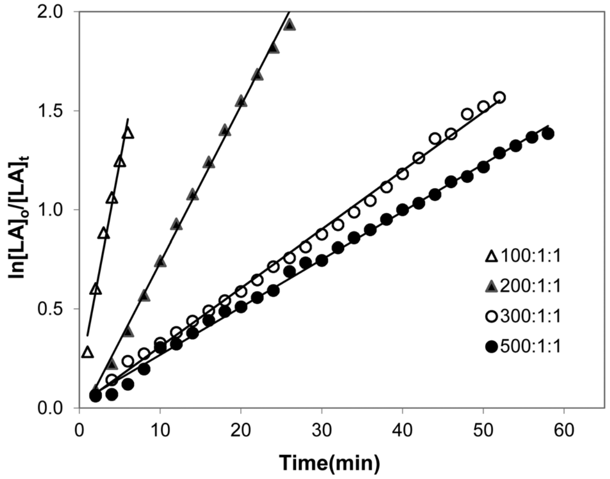


Fig. 3 First order plots of $\ln[LA]_0/[LA]_t$ *vs.* time for ROP of *rac*-LA catalyzed by complex **1a·THF**/BnOH ([LA] : [**1a·THF**] : [BnOH] = 100 : 1 : 1 ($y = 0.1093x + 0.1467$, $R^2 = 0.9765$), 200 : 1 : 1 ($y = 0.0772x + 0.0384$, $R^2 = 0.99973$), 300 : 1 : 1 ($y = 0.0296x + 0.0124$, $R^2 = 0.9969$) and 500 : 1 : 1 ($y = 0.0241x + 0.0269$, $R^2 = 0.9968$); [LA] = 0.66 M in toluene-d_8, 80 °C).

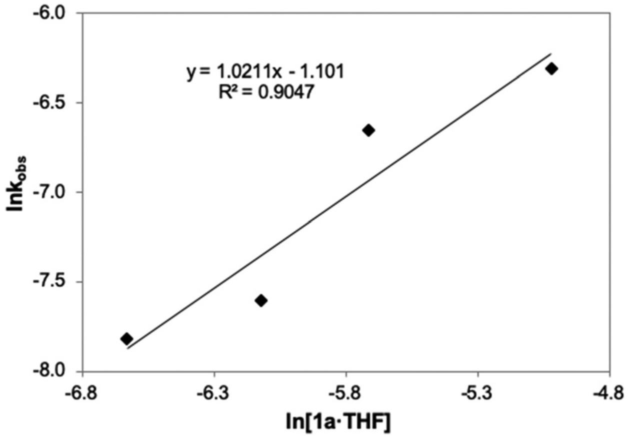


Fig. 4 Plot of $\ln k_{obs}$ *vs.* ln[**1a·THF**]. Polymerization conditions: [LA] : [**1a·THF**] : [BnOH] = 100 : 1 : 1, 200 : 1 : 1, 300 : 1 : 1 and 500 : 1 : 1; [LA] = 0.66 M in toluene-d_8, 80 (°C).

a linear dependence of the reaction rate on [polymer chain] : [**1a·THF**] (*i.e.* [BnOH] : [**1a·THF**]) was observed (Fig. S6†). While the rate increases, the polymer molecular weight decreases with the increasing number of co-initiators per catalyst (a linear fit is shown in Fig. S8†). The molecular weight distributions of the polymers are narrow, *Đ* = 1.04–1.16. The molecular weight of the polymer can be increased by using a higher lactide to catalyst ratio, where co-initiator to catalyst ratio was maintained as 1 : 1 (shown in Table 2 (entries 1, 2 and 5), and a linear fit is shown in Fig. S7†). A high molecular weight of 38.9 kg mol^{-1} can be obtained with only slightly diminished control, of molecular weight dispersity *Đ* = 1.25 (Table 2, entry 5). The broader dispersity is likely due to transesterification by impurities in the *rac*-LA or adventitious water and the longer reaction time. The relationship of the conversion to molecular weight was also found to be linear as shown in Fig. 6. Overall, these studies have demonstrated a living polymerization system. The polymers obtained are atactic, giving $P_r = 0.53$ by homonuclear decoupled ^{1}H NMR analysis, and we have not yet pursued enantioselective polymerization.

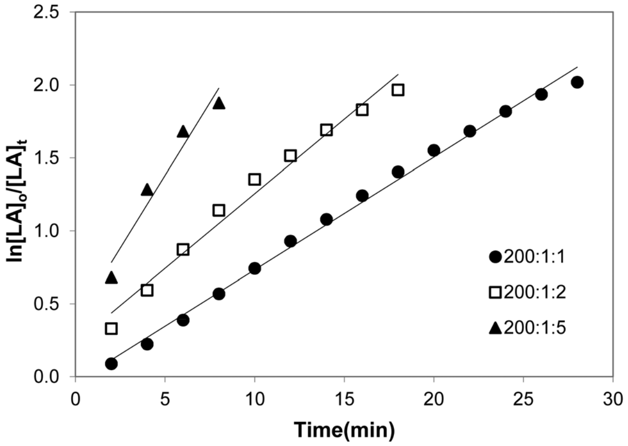


Fig. 5 First order plots of $\ln[LA]_0/[LA]_t$ *vs.* time for the ROP of *rac*-LA catalyzed by **1a·THF**/BnOH (where [LA] : [**1a·THF**] : [BnOH] = 200 : 1 : 1 ($y = 0.0772x + 0.0384$, $R^2 = 0.9951$), 200 : 1 : 2 ($y = 0.1022x + 0.2329$, $R^2 = 0.9808$) and 200 : 1 : 5 ($y = 0.1992x + 0.3848$, $R^2 = 0.9500$); [LA] = 0.66 M in toluene-d_8 at 80 °C). The solid lines are the best linear fits to the equations shown.

Further study of the repeating units and end groups of the polymers was carried out using MALDI-TOF mass spectrometry. Polymers produced using different ratios of [LA] : [**1a·THF**] : [BnOH] (100 : 1 : 1, 200 : 1 : 1, 200 : 1 : 2 or 200 : 1 : 5) show the same repeating units of *m*/*z* 72, indicating transesterification during the polymerization. Three dominant series of peaks corresponding to *cyclo*-$(C_3H_4O_2)_n·Na^+$ (A), *cyclo*-$(C_3H_4O_2)_n·K^+$ (B) and $BnO(C_3H_4O_2)_nH·Na^+$ (C) were observed in the polymer obtained using [LA] : [**1a·THF**] : [BnOH] ratio of 100 : 1 : 1 (Fig. S9†). A closer examination of the lower mass range showed additional peaks corresponding to $HO(C_3H_4O_2)_nH·Na^+$ (Fig. S10†), which could result from adventitious water. The observation of both cyclic polymers and polymers with OBn end groups suggests two mechanisms may be occurring in these systems, *i.e.* both the Zn–phenolate and the Zn–OBn group can act as the initiator for ROP of LA. The mass spectrum of the polymer obtained using lower catalyst loading, [LA] : [**1a·THF**] : [BnOH] = 500 : 1 : 1, shows exclusively the cyclic polymer (Fig. S11 and S12†). This indicates that the interaction of BnOH with the catalyst may be hindered by the high concentration of LA, and as a consequence, the reaction proceeds preferentially through Zn–phenolate initiation and backbiting termination mechanism.

To our surprise, polymerization of *rac*-lactide using complex **3** containing more nucleophilic alkoxyl groups exhibits sluggish activity. Complex **3** has a k_{obs} of 0.665 × 10^{-3} s^{-1}, whereas **1a·THF** exhibits a k_{obs} of 1.833 × 10^{-3} s^{-1} under identical conditions ([LA] : [complex] : [BnOH] = 100 : 1 : 1 in

Table 2 ROP of *rac*-LA using **1a·THF** ([LA] = 0.66 M in toluene, 80 °C)

Entry	[LA] : [**1a·THF**] : [BnOH]	Time (min)	Conv.[a] (%)	M_n (Theo.)[b] (kg mol^{-1})	M_n (GPC)[c] (kg mol^{-1})	M_w/M_n	P_r[d]
1	100 : 1 : 1	40	99	14.3	9.1	1.16	0.53
2	200 : 1 : 1	60	98	28.2	20.1	1.11	0.53
3	200 : 1 : 2	40	99	14.3	15.5	1.16	—
4	200 : 1 : 5	40	99	5.73	6.72	1.04	—
5	500 : 1 : 1	140	83	59.8	38.9	1.25	—

[a] Calculated *via* integration of the methine resonances of *rac*-LA and PLA. [b] M_n (Theo.) = $[LA]_0/[\mathbf{1a{\cdot}THF}]_0$ × conv. × M(LA). [c] Determined by GPC in THF by triple detection using dn/dc = 0.049 mL g^{-1}. [d] Determined from homonuclear decoupled ^{1}H NMR by $P_r = 2I_1/(I_1 + I_2)$, with $I_1 = \delta$ 5.19–5.24 (rmr, mmr/rmm), $I_2 = \delta$ 5.13–5.19 (mmr/rmm, mmm, mrm).

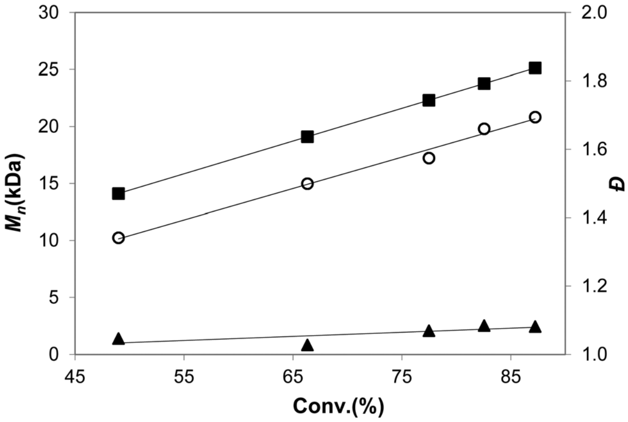


Fig. 6 Plots of calculated and experimental (GPC) molecular weights and dispersity *vs*. lactide conversion for the ROP of *rac*-LA catalyzed by **1a·THF**/BnOH (where [LA] : [**1a·THF**] : [BnOH] = 200 : 1 : 1 and [LA] = 0.66 M in toluene at 80 °C). Black squares: $M_{n(\text{calculated})}$; circles: $M_{n(\text{GPC})}$; black triangles: Đ (M_w/M_n).

toluene-d_8 at 80 °C). The diminished reactivity of complex **3** may be due to its rigid structure, which makes dissociation to generate the active catalyst more difficult. As mentioned above, a strongly coordinating solvent is required to break apart the trimetallic structure. ROP of *rac*-lactide using i-PrOH or BnOH as the co-initiator with **3** was studied and kinetic data were obtained for polymerization performed at various temperatures in toluene-d_8. Whereas the increase of BnOH concentration increases the rate significantly for **1a·THF** (Fig. 5 and S6†), the polymerization rate appears to be independent of the amount of i-PrOH used with complex **3** (Fig. S13†). Elevating the reaction temperature from 70 to 90 °C gave increased reaction rate (the temperature range is limited by the solubility of LA in toluene and the probe temperature of the NMR spectrometer using for monitoring the reaction). An Arrhenius analysis gave an activation energy (E_a) of 83.19 ± 15.29 kJ mol^{-1} for *rac*-lactide polymerization in the presence of one equivalent of BnOH (Fig. S14†). An Eyring analysis of the data (Fig. S15†) gave thermodynamic activation parameters of $\Delta H^\ddagger$ = 80.25 ± 15.31 kJ mol^{-1} and $\Delta S^\ddagger$ = −78.71 ± 43.35 J K^{-1} mol^{-1}. The negative $\Delta S^\ddagger$ value indicates an ordered transition state and is consistent with a coordination insertion mechanism;[75–77] however the possibility of an activated monomer mechanism cannot be ruled out.

The influence of co-initiator concentration was studied. Increasing the [i-PrOH] : [**3**] ratio from 1 : 1 to 5 : 1 shows minimum effect on the polymerization rate, but a further increase of the ratio to 10 : 1 gave a more significant increase in the reaction rate (Fig. S16†). Zinc complex **3** contains two i-PrO– groups that can act as initiating units and three zinc centers, and it is likely that dissociation of this complex occurs with large excess of i-PrOH, yielding potentially multiple initiators, such as Zn[**L1**], Zn(O-i-Pr)$_2$ or other species.

MALDI-TOF mass spectra were obtained for the polymers produced by complex **3** in the presence of i-PrOH. The major peak series corresponds to polymers with i-PrO– end groups, i-PrO$(C_3H_4O_2)_n$H·Na$^+$ (Fig. S17†). The MALDI-TOF mass spectrum of the polymer obtained using BnOH as the co-initiator is more informative. As shown in Fig. 7 (using reflectron mode), polymers with BnO– or i-PrO– end groups were observed (the linear mode spectrum is shown in Fig. S18†), demonstrating both the i-PrO– from the complex and the added BnOH can act as initiators.

Mechanistic studies

In order to gain some mechanistic insight, experiments were conducted in a J-Young NMR tube at 353 K using toluene-d_8 under similar conditions to the catalytic reaction. After heating the reaction mixture, ^{1}H NMR spectra were collected upon cooling, as the resonances at higher temperature were broad and not readily assignable. The ^{1}H NMR spectrum of BnOH in toluene-d_8 was first obtained. The hydroxyl proton appeared as a triplet at 4.70 ppm and the methylene protons coupling with the hydroxyl proton appeared as a doublet at 4.37 ppm. A 1 : 1 ratio of [LA] : [BnOH] was heated for 30 min and the ^{1}H NMR spectrum was collected after cooling to 298 K (Fig. S19†). The peaks corresponding to *rac*-lactide showed little change; however, the methylene protons of the BnOH appeared as a singlet at 4.29 ppm and the hydroxyl proton was absent. A new peak appeared at 1.03 ppm, which may be the hydroxyl proton resulting from reaction of BnOH with lactide or possibly due to hydrogen bonding between BnOH and LA. Regardless, a reaction is clearly observed between BnOH and lactide upon heating to 353 K.

Reactions of 1 : 1 or 1 : 2 mixtures of **1a·THF** and BnOH were conducted under the same NMR monitoring conditions. ^{1}H NMR spectra were collected at 298 K after heating the

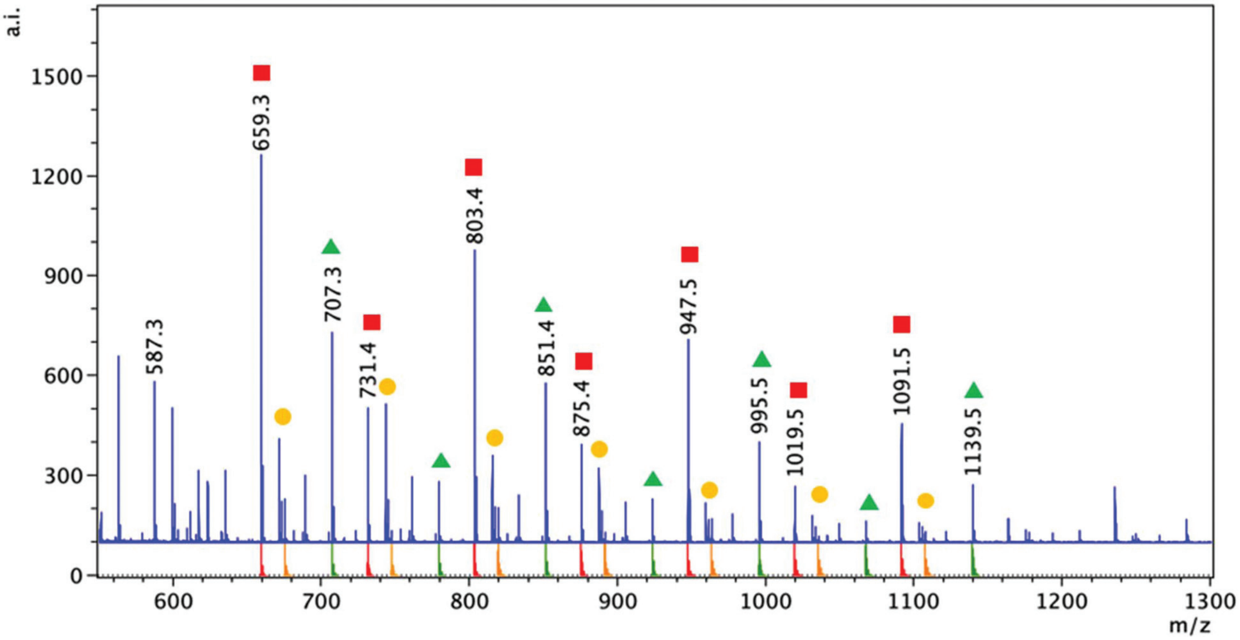


Fig. 7 MALDI mass spectrum of PLA (reflectron mode) obtained using complex **3**/BnOH ([LA] : [**3**] : [BnOH] = 100 : 1 : 1, [LA] = 0.66 M in toluene-d_8 at 80 °C). Red squares: (i-PrO)($C_3H_4O_2$)$_n$H·Na^+; orange circles: (i-PrO)($C_3H_4O_2$)$_n$H·K^+; green triangles (BnO)($C_3H_4O_2$)$_n$H·Na^+. Calculated masses for *n* = 8–14 are shown in the lower portion of spectrum.

mixture for 30 min (Fig. S20†). It was found that the THF peaks had shifted upfield, from 3.91 to 3.54 ppm, indicating its dissociation from the zinc center. A new peak is observed at 0.81 ppm corresponding to the ethane formed from protonolysis of an ethyl group. The presence of one set of sharp ethyl resonances is observed as well as a singlet at 4.52 ppm, which are attributed to a newly formed species with one zinc-bound benzyloxide. Reaction of **1a·THF** with two equivalents of BnOH showed a more intense ethane resonance and broadening of the remaining resonances including those of the aromatic groups. The diagnostic methylene doublets of **1a·THF** were no longer clearly visible, implying the complete conversion of **1a·THF** to another species, likely one containing two benzyloxide groups. Therefore, it is likely that reaction of **1a·THF** with BnOH gives a product related to **3**, however, it is more fluxional than **3** at these conditions. Disproportionation of zinc-benzyloxides supported by β-diketiminate ligands to give trimetallic alkoxide-bridged zinc complexes similar to **3** has been previously reported.[27]

A stochiometric amount of *rac*-lactide, **1a·THF** and BnOH was analyzed by ^{1}H NMR (Fig. S21†). It was found that after heating the mixture for 1 h, there was only a slight upfield shift of the THF peaks from complex **1a·THF**. This suggests the THF remains coordinated, or if displacement of THF by LA or BnOH does occur at 353 K, the zinc site is not sufficiently hindered to prevent re-coordination of the displaced THF upon cooling to 298 K. Upon heating, a downfield change of the methine peak from 3.80 ppm to become coincident with the THF peak near 3.90 ppm occurred, indicating the ring opening of the lactide. Interestingly, when lactide is present the ethyl groups of **1a·THF** do not appear to undergo protonation by the alcohol. This is consistent with the MALDI-TOF MS result described above where the cyclic polymer was obtained exclusively using a high LA to catalyst/co-initiator ratio.

An experiment with the use of an extra equivalent of BnOH was conducted under the same conditions as above. It showed that when lactide is present protonolysis of the ethyl groups does not fully proceed even with excess BnOH and displacement of both ethyl groups by BnOH is clearly unfavored (Fig. S22†). We then carried out the experiment with an extra equivalent of lactide. Ethyl group protonation by BnOH cannot be completely suppressed, as ethane was still observed. Since the presence of lactide was found to hinder the reaction of BnOH and **1a·THF**, the experiment was repeated, but now with lactide being added *after* the addition of BnOH to a solution of **1a·THF** in toluene-d_8 (Fig. S24†). It is apparent that a zinc–ethyl group is lost along with the appearance of PLA resonances between 4.5 and 5.5 ppm upon heating (Fig. S24,† spectra B and C).

A coordination–insertion mechanism requires formation of a ZnOBn complex *via* protonolysis of a Zn–Et bond and evidence for this has been observed by ^{1}H NMR. Unfortunately, crystalline product of this reaction suitable for X-ray diffraction could not be obtained. Complex **3**, which already possesses ZnOR sites, shows evidence of dissociation in solution under catalytic conditions. The low solubility of (i-PrO)$_2$Zn in toluene likely makes it unavailable to act as an initiator, but its presence in low concentrations cannot be ignored and it may play a role in the activity of that system. Benzyl alcohol concentration does, however, exhibit an influence on reaction rates, therefore the nature of the alcohol co-initiator may be an important factor in the mechanism.

Conclusions

Bimetallic and trimetallic zinc complexes of tridentate amino-bis(phenolate) ligands were synthesized and structurally characterized. Zinc complex **1a** showed good activity in melt phase *rac*-lactide polymerization, giving 92% conversion after only 15 min and producing polymers with narrow molecular weight distributions. ROP of *rac*-lactide using **1a·THF** in the presence of BnOH was studied by ^{1}H NMR spectroscopy in toluene-d$_8$. Kinetic data showed the reaction is first order in monomer concentration and the rate is proportional to the concentration of added benzyl alcohol. The reaction appears to be first order in metal complex concentration. A linear relationship of reaction rate to [polymer chain] : [complex] ratio was obtained reflecting immortal polymerization in the presence of BnOH. Complex **1a·THF** showed good control toward ROP of *rac*-lactide, providing polymers with narrow molecular weight distributions, linear relationships of M_n *vs.* lactide conversion, M_n *vs.* lactide to complex ratio, and M_n *vs.* lactide to ROH ratio. Activity of complex **3** for ROP of *rac*-lactide in the presence of BnOH or i-PrOH was studied and the thermodynamic activation parameters were determined and suggested a coordination–insertion mechanism. Similarly, investigations of **1a·THF** with stoichiometric amounts of BnOH suggested the formation of ZnOBn groups, which further supports a coordination–insertion mechanism.

Experimental

General methods

Unless otherwise stated, all manipulations were performed under an atmosphere of dry oxygen-free nitrogen by means of Schlenk techniques or using an MBraun LabmasterDP glove box. Anhydrous diethyl ether was purified using an MBraun Solvent Purification System. THF was stored over sieves and distilled from sodium benzophenone ketyl under nitrogen. Diethylzinc (1.0 M in hexanes) was purchased from Sigma-Aldrich. *rac*-Lactide was purchased from either Aldrich or Alfa Aesar and dried over sodium sulphate in THF, recrystallized and stored under an inert atmosphere prior to use. Benzyl alcohol was purchased from Alfa Aesar and dried over activated 4 Å molecular sieves, distilled under reduced pressure and stored under nitrogen in an ampule prior to use. Other reagents were purchased from Strem, Aldrich or Alfa Aesar and used without further purification. The proligands H$_2$[**L1**] and H$_2$[**L2**] were prepared according to the previously reported procedure.[69]

Instrumentation

MALDI-TOF MS was performed using an Applied Biosystems 4800 MALDI TOF/TOF Analyzer equipped with a reflectron, delayed ion extraction and high-performance nitrogen laser (200 Hz operating at 355 nm). Samples were prepared in the glove box and sealed under nitrogen in a Ziploc bag for transport to the instrument. Anthracene was used as the matrix for the zinc compounds and 2,5-dihydroxybenzoic acid (DHBA) was used as the matrix for the polymers. The matrix was dissolved in THF at a concentration of 10 mg mL^{-1}. Polymer was dissolved in THF at approximately 1 mg mL^{-1}. The matrix and polymer solutions were mixed together at 3 : 1 ratios; 1 μL of this was spotted on the MALDI plate and left to dry. Images of mass spectra were prepared using mMass software (http://www.mmass.org).

GPC analysis was performed on a Wyatt Triple Detection (triple angle light scattering, viscometry and refractive index) system with Agilent 1260 series sample and solvent handling and two Phenogel columns (10^3 Å 300 × 4.60 mm) covering mass ranges of 1–75 kDa. Samples were prepared at a concentration of 2 mg mL^{-1} in CHCl$_3$ and left to equilibrate for ∼2 h before being filtered through 0.2 μm nylon syringe filters and eluted with HPLC grade THF at flow rates of 0.25 mL min^{-1} with 100 μL injection volumes. The appropriate d*n*/d*c* values were employed for polylactide in THF (0.049 mL g^{-1}).

NMR spectra were recorded at 300 MHz for ^{1}H and 75.5 MHz for ^{13}C or at 500 MHz for ^{1}H NMR kinetic studies. The NMR spectra of the synthesized compounds are shown in Fig. S25–S38.† CDCl$_3$ and C$_6$D$_6$ were purchased from Cambridge Isotope Laboratories, toluene-d$_8$ and pyridine-d$_5$ from Aldrich. Deuterated solvents used in the analysis of the zinc complexes were dried over calcium hydride (CDCl$_3$ and pyridine-d$_5$) or sodium/potassium alloy (C$_6$D$_6$ and toluene-d$_8$), vacuum transferred and stored under nitrogen in ampules fitted with Teflon valves. Glass transition temperatures (T_g) were measured using a Mettler Toledo DSC 1 STAR^e System equipped with a Julabo FT 100 immersion cooling system. Samples (∼5 mg) were weighed into 40 μL aluminum pans and subjected to three heating cycles. The first heating cycle consisted of heating from 0 to 100 °C at a rate of 10 °C min^{-1}, held for 2 min at 100 °C and then cooled back to 0 °C at 10 °C min^{-1}. The sample was held at this temperature for 2 min and subjected to a two heating cycles from 0 to 190 °C at a rate of 10 °C min^{-1}. Elemental analyses were performed at Canadian Microanalytical Service Ltd, Delta, British Columbia, Canada.

(ZnEt)$_2$[L1], 1a

ZnEt$_2$ (1.00 g, 8.06 mmol) in hexane was added to a solution of H$_2$[**L1**] (2.00 g, 4.03 mmol) in pentane. The reaction mixture was stirred for 2 h at ambient temperature. The solvent was removed under vacuum to yield a pale yellow solid (yield: 2.78 g, 99%). Anal. calc'd for C$_{37}$H$_{61}$NO$_2$Zn$_2$: C 65.10, H 9.01, N 2.05%; found: C 65.25, H 8.93, N 2.10%. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.29 (d, J = 2.6 Hz, 2H, ArH), 6.91 (d, J = 2.5 Hz, 2H, ArH), 4.15 (d, J = 14.0 Hz, 2H, ArCH$_2$), 3.74 (d, J = 14.0 Hz, 2H, ArCH$_2$), 2.72–2.55 (m, J = 4.6 Hz, J = 3.7 Hz, 2H, NCH_2CH$_2$CH$_3$), 1.65–1.54 (m, 2H, NCH$_2$CH_2CH$_3$), 1.48 (s, 18H, C(CH$_3$)$_3$), 1.30 (s, 18H, C(CH$_3$)$_3$), 0.96 (t, J = 8.1 Hz, 3H, ZnCH$_2$CH_3), 0.82 (t, J = 7.3 Hz, 3H, NCH$_2$CH$_2$CH_3), 0.75 (t, J =

8.1 Hz, 3H, $\mathrm{ZnCH_2}\mathit{CH}_3$), 0.35 (q, J = 8.1 Hz, 2H, $\mathrm{Zn}\mathit{CH}_2\mathrm{CH_3}$), −0.12 (q, J = 8.1 Hz, 2H, $\mathrm{Zn}\mathit{CH}_2\mathrm{CH_3}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.75 (Ar), 140.64 (Ar), 139.25 (Ar), 125.13 (Ar), 125.10 (Ar), 124.74 (Ar), 64.07 ($\mathrm{Ar}\mathit{C}\mathrm{H_2}$), 60.14 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_3}$), 35.51 ($\mathit{C}\mathrm{(CH_3)_3}$), 34.30 ($\mathit{C}\mathrm{(CH_3)_3}$), 31.82 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 30.47 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 18.68 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2CH_3}$), 12.20 ($\mathrm{ZnCH_2}\mathit{C}\mathrm{H_3}$), 11.86 ($\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_3}$), 11.46 ($\mathrm{ZnCH_2}\mathit{C}\mathrm{H_3}$), 1.00 ($\mathrm{Zn}\mathit{C}\mathrm{H_2CH_3}$), −2.07 ($\mathrm{Zn}\mathit{C}\mathrm{H_2CH_3}$).

$(ZnEt)_2$[L2], 1b

$ZnEt_2$ (1.00 g, 8.06 mmol) in hexane was added to a solution of H_2**[L2]** (1.66 g, 4.03 mmol) in pentane. The reaction mixture was stirred for 2 h at ambient temperature. The solvent was removed under vacuum to yield a pale yellow solid (yield: 2.36 g, 98%). Anal. calc'd for $C_{31}H_{49}NO_2Zn_2$: C 62.21, H 8.25, N 2.34%; found: C 62.50, H 8.30, N 2.50%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, J = 2.1 Hz, 2H, ArH), 6.74 (d, J = 1.9 Hz, 2H, ArH), 4.15 (d, J = 14.1 Hz, 2H, $ArCH_2$), 3.69 (d, J = 14.1 Hz, 2H, $ArCH_2$), 2.74–2.58 (t, J = 7.3 Hz, 2H, $\mathrm{N}\mathit{CH}_2\mathrm{CH_2CH_3}$), 2.27 (s, 6H, $ArCH_3$), 1.69–1.57 (m, 2H, $\mathrm{NCH_2}\mathit{CH}_2\mathrm{CH_3}$), 1.47 (s, 18H, $\mathrm{C(}\mathit{CH}_3\mathrm{)_3}$), 1.03 (t, 3H, J = 8.0 Hz, $\mathrm{ZnCH_2}\mathit{CH}_3$), 0.84 (t, J = 7.3 Hz, 3H, $\mathrm{NCH_2CH_2}\mathit{CH}_3$), 0.75 (t, J = 8.0 Hz, 3H, $\mathrm{ZnCH_2}\mathit{CH}_3$), 0.41 (q, J = 8.1 Hz, 2H, $\mathrm{Zn}\mathit{CH}_2\mathrm{CH_3}$), −0.12 (q, J = 8.1 Hz, 2H, $\mathrm{Zn}\mathit{CH}_2\mathrm{CH_3}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.00 (Ar), 140.00 (Ar), 128.83 (Ar), 128.57 (Ar), 127.33 ($\mathrm{Ar}\mathit{C}\mathrm{H_2}$), 125.99 ($\mathrm{Ar}\mathit{C}\mathrm{H_2}$), 64.35 ($\mathrm{Ar}\mathit{C}\mathrm{H_2}$), 60.58 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_3}$), 35.53 ($\mathit{C}\mathrm{(CH_3)_3}$), 35.21 ($\mathit{C}\mathrm{(CH_3)_3}$), 31.58 ($\mathrm{Ar}\mathit{C}\mathrm{H_3}$), 30.40 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 20.98 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 19.26 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2CH_3}$), 12.21 ($\mathrm{ZnCH_2}\mathit{C}\mathrm{H_3}$), 12.01 ($\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_3}$), 11.52 ($\mathrm{ZnCH_2}\mathit{C}\mathrm{H_3}$), 0.88 ($\mathrm{Zn}\mathit{C}\mathrm{H_2CH_3}$), −2.08 ($\mathrm{Zn}\mathit{C}\mathrm{H_2CH_3}$).

$(ZnEt)_2$[L1](THF), 1a·THF

$ZnEt_2$ (1.00 g, 8.06 mmol) in hexane was added to a solution of H_2**[L1]** (2.00 g, 4.03 mmol) in THF. The reaction mixture was stirred for 2 h at ambient temperature. The solvent was removed under vacuum to yield a white solid. The solid was then washed with pentane (yield: 3.00 g, 99%). Anal. calc'd for $C_{41}H_{69}NO_3Zn_2$: C 65.25, H 9.22, N 1.86%; found: C 65.25, H 9.10, N 1.98%. ^{1}H NMR (300 MHz, toluene-d_8) δ 7.49 (d, J = 2.6 Hz, 2H, ArH), 6.93 (d, J = 2.6 Hz, 2H, ArH), 4.07 (d, J = 13.7 Hz, 2H, $ArCH_2$), 3.94–3.86 (m, 4H, THF CH_2), 3.51 (d, J = 13.7 Hz, 2H, $ArCH_2$), 2.42–2.31 (t, J = 7.3 Hz, 2H, $\mathrm{N}\mathit{CH}_2\mathrm{CH_2CH_3}$), 1.59 (s, 18H, $C(CH_3)_3$), 1.57–1.51 (m, 4H, THF CH_2), 1.38 (s, 18H, $C(CH_3)_3$), 0.92 (t, J = 8.1 Hz, 3H, $\mathrm{ZnCH_2}\mathit{CH}_3$), 0.50 (t, J = 7.3 Hz, 3H, $\mathrm{NCH_2CH_2}\mathit{CH}_3$), 0.44 (t, J = 8.1 Hz, 3H, $\mathrm{ZnCH_2}\mathit{CH}_3$), 0.15 (q, J = 8.1 Hz, 2H, $\mathrm{Zn}\mathit{CH}_2\mathrm{CH_3}$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, J = 2.6 Hz, 2H, ArH), 6.88 (d, J = 2.6 Hz, 2H, ArH), 4.14 (d, J = 13.8 Hz, 2H, $ArCH_2$), 3.95–3.87 (m, 4H, THF CH_2), 3.74 (d, J = 13.8 Hz, 2H, $ArCH_2$), 2.64–2.53 (m, 2H, $\mathrm{N}\mathit{CH}_2\mathrm{CH_2CH_3}$), 1.97–1.89 (m, 4H, THF CH_2), 1.64–1.52 (m, 2H, $\mathrm{NCH_2}\mathit{CH}_2\mathrm{CH_3}$), 1.47 (s, 18H, $C(CH_3)_3$), 1.29 (s, 18H, $C(CH_3)_3$), 0.85 (t, J = 8.0 Hz, 3H, $\mathrm{ZnCH_2}\mathit{CH}_3$), 0.81 (t, J = 8.0 Hz, 3H, $\mathrm{ZnCH_2}\mathit{CH}_3$), 0.80 (t, J = 7.3 Hz, 3H, $\mathrm{NCH_2CH_2}\mathit{CH}_3$), 0.11 (q, J = 8.0 Hz, 2H, $\mathrm{Zn}\mathit{CH}_2\mathrm{CH_3}$), −0.07 (q, J = 8.0 Hz, 2H, $\mathrm{Zn}\mathit{CH}_2\mathrm{CH_3}$). ^{13}C NMR (75 MHz, $CDCl_3$-d) δ 159.22 (Ar), 139.97 (Ar), 138.93 (Ar), 125.32 (Ar), 124.76 (Ar), 124.47 (Ar), 68.66 (CH_2), 62.44 ($ArCH_2$), 59.41 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2CH_3}$), 35.39 ($\mathit{C}\mathrm{(CH_3)_3}$), 34.21 ($\mathit{C}\mathrm{(CH_3)_3}$), 31.94 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 30.39 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 25.66 ($CH_2$), 12.29 ($\mathrm{ZnCH_2}\mathit{C}\mathrm{H_3}$), 12.11 ($\mathrm{ZnCH_2}\mathit{C}\mathrm{H_3}$), 11.68 ($\mathrm{Zn}\mathit{C}\mathrm{H_2CH_3}$), −2.03 ($\mathrm{Zn}\mathit{C}\mathrm{H_2CH_3}$).

Zn[L1], 2

$Zn[N(SiMe_3)_2]_2$ (0.50 g, 1.29 mmol) was added to a solution of H_2**[L1]** (0.64 g, 1.29 mmol) in hexanes. The mixture was stirred for 10 h at 25 °C resulting in a white precipitate that was collected by filtration and washed twice with pentane to produce a colorless powder (yield 0.56 g, 80%). Anal. calc'd for $C_{33}H_{51}NO_2Zn$: C 70.89, H 9.19, N 2.51%; found: C 70.66, H 9.05, N 2.29%. ^{1}H NMR (300 MHz, $CDCl_3$) Major product: δ 7.28 (d, J = 2.5 Hz, 2H, ArH), 7.15 (d, J = 2.5 Hz, 2H, ArH), 6.90 (d, J = 2.5 Hz, 2H, ArH), 6.58 (d, J = 2.5 Hz, 2H, ArH), 4.72 (d, J = 13 Hz, 2H, CH_2), 4.02 (d, J = 13 Hz, 2H, CH_2), 3.76 (t, J = 12 Hz, 2H, $\mathrm{N}\mathit{CH}_2\mathrm{CH_2}$) 3.25 (d, J = 13 Hz, 2H, CH_2), 2.78–2.95 (m, 4H, $\mathrm{N}\mathit{CH}_2\mathrm{CH_2CH_3}$) 2.81 (d, J = 13 Hz, 2H, CH_2), 2.30 (m, 4H, $\mathrm{NCH_2}\mathit{CH}_2\mathrm{CH_3}$), 1.45 (s, 18H, $C(CH_3)_3$), 1.39 (s, 18H, $C(CH_3)_3$), 1.26 (s, 18H, $C(CH_3)_3$), 1.21 (s, 18H, $C(CH_3)_3$), 0.44 (t, J = 9 Hz, 6H, $\mathrm{NCH_2CH_2}\mathit{CH}_3$). Minor product (some peaks obscured by major product): 7.13 (d, J = 2.5 Hz, 2H, ArH), 6.72 (d, J = 2.5 Hz, 2H, ArH), 4.95 (d, J = 13 Hz, 2H, CH_2), 2.78–2.95 (m, 4H, $\mathrm{N}\mathit{CH}_2\mathrm{CH_2CH_3}$), 1.29 (s, 18H, $C(CH_3)_3$), 1.22 (s, 18H, $C(CH_3)_3$), 0.87 (t, J = 9 Hz, 3H, $\mathrm{NCH_2CH_2}\mathit{CH}_3$).

$Zn_3(Oi\text{-}Pr)_2[L1]_2$, 3

A solution of i-PrOH (0.18 g, 2.92 mmol) in pentane was added to a pentane solution of complex **1a** (1.00 g, 1.45 mmol). A white precipitate was obtained after adding i-PrOH. The reaction mixture was stirred for 4 h at ambient temperature. The upper solution was removed using a pipet. The remaining solvent was removed under vacuum to yield a white powder. The white powder was then washed twice with pentane to yield a pure product (yield: 0.92 g, 97%). Anal. cal. for $C_{72}H_{116}N_2O_6Zn_3$: C 62.21, H 8.25, N 2.34%; found: C 62.50, H 8.30, N 2.50%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, J = 2.5 Hz, 2H, ArH), 7.15 (d, J = 2.6 Hz, 2H, ArH), 6.60 (d, J = 2.6 Hz, 2H, ArH), 6.54 (d, J = 2.5 Hz, 2H, ArH), 4.32 (sep, J = 6.0 Hz, 2H, $\mathit{CH}\mathrm{(CH_3)_2}$), 4.13 (sep, J = 6.0 Hz, 2H, $\mathit{CH}\mathrm{(CH_3)_2}$), 3.51 (d, J = 13.4 Hz, 2H, $ArCH_2$), 3.12 (d, J = 13.4 Hz, 2H, $ArCH_2$), 2.70 (d, J = 13.2 Hz, 2H, $ArCH_2$), 2.55 (d, J = 13.2 Hz, 2H, $ArCH_2$), 2.59 (m, 4H, $\mathrm{N}\mathit{CH}_2\mathrm{CH_2CH_3}$), 1.50 (s, 18H, $C(CH_3)_3$), 1.42 (d, J = 6.0 Hz, 6H, $\mathrm{CH(}\mathit{CH}_3\mathrm{)_2}$), 1.39 (s, 18H, $C(CH_3)_3$), 1.30 (s, 18H, $C(CH_3)_3$), 1.29–1.26 (m, 4H, $\mathrm{NCH_2}\mathit{CH}_2\mathrm{CH_3}$), 1.23 (d, J = 6.0 Hz, 6H, $\mathrm{CH(}\mathit{CH}_3\mathrm{)_2}$), 1.19 (s, 18H, $C(CH_3)_3$), 0.73 (t, J = 7.3 Hz, 6H, $\mathrm{NCH_2CH_2}\mathit{CH}_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.34 (Ar), 157.31 (Ar), 141.42 (Ar), 139.52 (Ar), 137.93 (Ar), 135.72 (Ar), 126.40 (Ar), 125.73 (Ar), 125.66 (Ar), 124.30 (Ar), 123.94 (Ar), 120.08 (Ar), 68.00 (CH), 58.15 ($\mathrm{Ar}\mathit{C}\mathrm{H_2}$), 56.28 ($\mathrm{Ar}\mathit{C}\mathrm{H_2}$), 54.86 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_3}$), 35.39 ($\mathit{C}\mathrm{(CH_3)_3}$), 35.37 ($\mathit{C}\mathrm{(CH_3)_3}$), 34.28 ($\mathit{C}\mathrm{(CH_3)_3}$), 33.92 ($\mathit{C}\mathrm{(CH_3)_3}$), 31.91 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 31.12 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 29.84 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 28.63 ($\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$), 28.04 ($\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$), 14.75, 11.50 ($\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_3}$).

Zn(py-d_5)[L1], 4

Not isolated, therefore no elemental analysis was obtained. ^{1}H NMR (300 MHz, pyridine-d_5) δ 7.60 (d, J = 2.7 Hz, 4H, ArH), 7.14 (d, J = 2.6 Hz, 3H, ArH), 4.06 (d, J = 12.4 Hz, 2H, ArCH$_2$), 3.74 (d, J = 12.4 Hz, 2H, ArCH$_2$), 2.70–2.60 (m, 2H, NCH_2CH$_2$CH$_3$), 1.68 (s, 18H, C(CH$_3$)$_3$), 1.43–1.45 (m, 2H, NCH$_2$CH_2CH$_3$), 1.44 (s, 18H, C(CH$_3$)$_3$), 0.47 (t, J = 7.3 Hz, 3H, NCH$_2$CH$_2$CH_3).

General procedure of melt phase *rac*-lactide polymerization

In the glove box, *rac*-lactide (0.5 g, 3.47 mmol) and the appropriate amount of zinc complex **1a** (according to the desired lactide to complex ratio) were added to a vial equipped with a magnetic stir bar. The vial was removed from the glove box and placed on a preheated hot plate where it was heated and stirred for the specified time. The vial was removed from the hot plate and cooled in an ice bath to terminate polymerization. A sample of the solidified material was analyzed by NMR. The polymer was dissolved in $CHCl_3/CH_2Cl_2$, precipitated with MeOH and the upper solution decanted off the polymer, which was subsequently dried under vacuum.

General procedure of *rac*-lactide polymerization in toluene

In the glove box, *rac*-lactide (0.5 g, 3.47 mmol) was added to an ampule equipped with a magnetic stir bar, followed by 6 mL of toluene. Individual stock solutions for BnOH and complex **1a·THF** were prepared in toluene and the appropriate amounts of each were added to the ampule in sequence. The ampule was removed from the glove box and placed on a preheated oil bath where it was heated and stirred for the specified time. The ampule was removed from the oil bath and a sample of the reaction mixture was analyzed by NMR. The reaction mixture was transferred in to a vial followed by adding 20 mL hexane to precipitate the polymer. The upper solution was decanted off and the polymer was dried under vacuum.

General procedure of *rac*-lactide polymerization in NMR scale

In the glove box, 75 mg (0.521 mmol) lactide was added to a J-Young NMR tube, followed by adding 700 μL toluene-d_8. Individual stock solutions for BnOH or i-PrOH and complex **1a·THF** or **3** were prepared in toluene-d_8 and the appropriate amounts of each were added to the NMR tube in sequence. The appropriate amount of toluene-d_8 was added to the NMR tube to make the total volume 790 μL ([LA] = 0.66 M). The NMR tube was sealed, removed from the glove box and loaded into the spectrometer. Before preparing the NMR sample, the spectrometer was preheated to desired temperature and the lock, tune and shimming were conducted and saved using a blank sample, which contained the same concentration of *rac*-lactide in toluene-d_8. The measurements were started upon the stabilization of spin with a time interval of 120 s and a sufficient relaxation delay time for completing the polymerization.

Conflicts of interest

There are no conflicts to declare.

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