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Potassium, zinc, and magnesium complexes of a bulky OOO-tridentate bis(phenolate) ligand: synthesis, structures, and studies of cyclic ester polymerisation

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Abstract

Reaction **OOO-coordinating** tridentate bis(phenolate) protio-ligand of the 2,2'-{oxybis(methylene)}bis{4,6-di(1-methyl-1-phenylethyl)phenol} (L^{O_3} -H₂), with 1 equiv. of $KN(SiMe_3)_2$ in toluene or THF yielded $[K(L^{O_3}-H)]$ (1) or $[K(L^{O_3}-H)(THF)]$ (2), respectively. Single-crystal X-ray diffraction studies of 1 and 2 revealed mononuclear structures with the phenyl rings of the bulky ligand displaying stabilising π -interactions to the potassium centre. L^{O3} -H₂ also reacts with 1 equiv. of ZnEt₂ or MgⁿBu₂ to give [M₂(L^{O3})₂] (M = Zn (3) or Mg (4)) in good yield. The molecular structures of complex 3 and 4 reveal dinuclear species in which the metal centres are tetra-coordinated to the three oxygen atoms of one L^{O3} ligand, and to the bridging oxygen atom of one phenolate group of another. Complexes 1 - 4 are catalysts for ring-opening polymerisation of ε -caprolactone and L- and *rac*-lactide in the presence of benzyl alcohol (BnOH) and also other initiators to give the corresponding polyesters. Kinetic studies for the ROP of ε -caprolactone using 3 and BnOH gives an unusual rate expression $R_p = -d[CL]/dt =$ $k_{\rm p}[{\rm BnOH}]_0[\mathbf{3}]_0^{0.5}$ for which a tentative kinetic model is proposed.

Introduction

Over the past 15 years, polyesters such as $poly(\varepsilon$ -caprolactone) (PCL), polylactide (PLA) and their copolymers have attracted a great deal of attention because of their reduced environmental impact compared to polyolefins, and increasing applications in the biomedical and pharmaceutical fields.¹ A number of strategies have been developed for the preparation of these polyesters. The method of choice (from both an academic and industrial point of view) is the ring-opening polymerisation (ROP) of the corresponding cyclic esters.² Many types of metal complexes based predominantly (but not exclusively) on, alkali metal,^{2h,3} aluminum,⁴ tin,⁵ trivalent lanthanides,⁶ iron,⁷ magnesium,⁸ calcium^{3p,8o,9} and zinc derivatives^{8c,8k,10} have been reported to be effective catalysts/initiators that catalyse the ROP of lactones and lactides giving polymers with both high and controlled molecular weights.

There are two principal mechanisms that apply to the synthesis of polyesters by the ROP of cyclic esters using metal complex as catalysts/initiators.^{10e} The "coordination-insertion" pathway, ideally involving a pre-prepared metal alkoxide catalyst (L)M–OR, is the conventional pathway to provide rapid and stereoselective conversion. A number of mechanistic studies have provided detailed insight pertaining to this. However, another important approach is *via* the "activated-monomer" mechanism which has some unique advantages, such as the ability to introduce a range of different functionalities as the polymer end groups (e.g., by using vitamins, steroidal alcohols, and sugars as the co-initiators) without catalyst modification.¹¹ We have recently been interested in developing the catalytic ROP applications of metal complexes supported by diphenolate-based and related ligands. These ligands are generally inexpensive and easily prepared, and have little or no toxicity. Studies of these complexes for the ROP of cyclic esters suggest that they operate *via* the activated-monomer mechanism.^{2i,3k,8d,12}

In our previous work, a series of lithium and sodium complexes based on an OOO-donor tridentate bulky ligand were synthesised.^{3k} Most of these were shown to be active toward the ROP of L-lactide in the presence of BnOH as an initiator. The sodium complexes had much higher catalytic activities than their lithium analogous, presumably because of the smaller charge:size ratio for Na⁺ compared to Li⁺. In this contribution we describe the preparation of bis(phenolate)ether derivatives of potassium, zinc, and magnesium coordinated using the sterically demanding OOO-donor tridentate singly- and doubly-deprotonated phenolate ligands, L^{O3}-H and

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 L^{O_3} (Scheme 1). The catalytic ROP activities of these complexes for ε -caprolactone (CL), L-lactide (L-LA) and *rac*-lactide (*rac*-LA) with different alcohol initiators are presented. Kinetic studies of the ROP of CL using **3** in the presence of BnOH as an initiator are also reported.



Scheme 1. Preparation of potassium, zinc, and magnesium complexes 1 - 4 (ring π -interactions for 1 and 2 omitted – see Figs. 1 and 2).

Results and discussion

Syntheses and X-ray crystal structures

As shown in Scheme 1, the mononuclear potassium complex $[K(L^{O3}-H)]$ (1), containing a mono-deprotonated L^{O3} -H ligand, can be prepared by the reaction of L^{O3} -H₂ with a stoichiometric amount of KN(SiMe₃)₂ in toluene in 82% yield. When complex 1 is dissolved in hot THF the Lewis base adduct $[K(L^{O3}-H)(THF)]$ (2) is formed. Compound 2 can also be prepared directly by the reaction of L^{O3} -H₂ with a stoichiometric amount of KN(SiMe₃)₂ in THF. Compound 2 dissolves in hot toluene to lose THF, reforming complex 1 in high yield. In addition, reaction of L^{O3} -H₂ with a stoichiometric amount of ZnEt₂ in toluene at ambient temperature gave the dinuclear complex $[Zn_2(L^{O3})_2]$ (3) in high yield. Likewise, the dinuclear magnesium analogue $[Mg_2(L^{O3})_2]$ (4) can be prepared directly by the reaction of L^{O3} -H₂ with a stoichiometric amount of Mg^n Bu₂ in hexane at -78 °C. All of these metal complexes have been characterised on the basis of

¹H and ¹³C NMR spectroscopic studies, elemental analysis, as well as by X-ray crystallography (see the ESI for further details (CIF files)).

Diffraction-quality crystals of $[K(L^{O3}-H)]$ (1) were obtained on slow cooling of a concentrated toluene solution. Complex 1 crystallises with one molecule of 1 and one molecule of toluene in the asymmetric unit. The molecular structure of 1 reveals a mononuclear complex in which the potassium centre is $\kappa^3 O, O, O$ -coordinated to the three oxygen atoms of a mono-deprotonated L^{O3} -H ligand as shown in Fig. 1. To compensate for the otherwise low coordination number at potassium, all four aryl rings of the ligand contribute to π - and/or C_{ipso} -interactions with the metal centre (e.g., $K \cdots C(1), K \cdots C(14), K \cdots C(19), K \cdots C(20)$, and $K \cdots C(50)$ distances of 3.230(2) 3.294(2) 3.333(2) 3.322(2) and 3.437(2) Å, respectively). In addition, each $[K(L^{O3}-H)]$ molecule forms half of a dimeric unit connected through O-H \cdots O intermolecular hydrogen bonds between a phenol hydroxy group and a deprotonated phenolate oxygen. These dimeric units are further connected by intermolecular aryl ring-potassium π -type interactions, forming a one-dimensional chain structure as shown in Fig. 2.

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Fig. 1 Displacement ellipsoid plot (20% probability) of [K(L^{O3}-H)] (1). C-bound hydrogen atoms and toluene of crystallisation omitted for clarity. Selected bond distances (Å) and angles (°): K-O1 2.6662(15), K-O2 2.7954(14), K-O3 2.6293(16), K…C1 3.230(2), K…C14 3.294(2), K…C19 3.333(2), K…C20 3.322(2), K…C50 3.437(2), O1-K-O2 70.06(4), O3-K-O2 71.98(4), O1-K-O3 108.50(4).

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Fig. 2 One-dimensional chain generated by pairwise intermolecular O-H···O hydrogen bonds (blue dashed lines) and intermolecular aryl ring-potassium π -interactions (yellow dashed lines). Selected bond distances and angles: O3-H2a···O1′ 2.444 Å, 173.89 °, K···C30′ 3.450(3) Å, K···C31′ 3.491(2) Å.



Fig. 3 Displacement ellipsoid plot (20% probability) of [K(L^{O3}-H)(THF)] (**2**). C-bound hydrogen atoms and THF of crystallisation omitted for clarity. Selected bond distances (Å) and angles (°): K-O(1) 2.681(2), K-O(2) 2.8780(14), K-O(3) 2.6501(15), K-O(4) 2.6830(17), K…C(1) 3.280(2), K…C(14) 3.319(2), K…C(19) 3.438(2), K…C(20) 3.493(2), O(1)-K-O(2) 68.50(4), O(3)-K-O(2) 70.05(4), O(1)-K-O(4) 113.17(5), O(3)-K-O(4) 113.28(5), O(4)-K-O(2) 78.70(5).

Diffraction-quality crystals of $[K(L^{O3}-H)(THF)]$ (2) were obtained on slow cooling of a mixed hexane:THF solution. The solid-state structure (Fig. 3) of 2 reveals, like that for 1, a mononuclear complex. In 2 the potassium is principally four-coordinate with a $\kappa^3 O, O, O$ -bound L^{O3} -H ligand and an additional THF ligand. The phenyl rings of L^{O3} -H again contribute to π -and/or C_{ipso}-interactions with the metal centre (e.g., K···C(1), K···C(14), K···C(19), and K···C(20) separations of 3.280(2), 3.319(2), 3.438(2), and 3.493(2) Å, respectively) which help stabilise the metal centre. Each [K(L^{O3} -H)(THF)] moiety forms half of a dimeric unit connected through pairs of O-H···O intermolecular hydrogen bonds, but does not form a one-dimensional chain structure

analogous to 1 due to the coordination of THF which blocks any additional aryl ring-potassium π -type interactions.

Diffraction-quality crystals of the closely related dinuclear complexes $[Zn_2(L^{O3})_2]$ (**3**) and $[Mg_2(L^{O3})_2]$ (**4**) were grown by slow cooling of toluene solutions. The molecular structures are shown in Figs. 4 and 5, respectively. Each structure possesses a dinuclear motif having crystallographically-imposed inversion symmetry, with each four-coordinate metal $\kappa^3 O, O, O$ -bound to three oxygens of one doubly-deprotonated L^{O3} ligand (O(1), O(2), O(3)) and also to a bridging phenolate oxygen (O(3A)) of another. In **3** the resultant $Zn_2(\mu$ -O)₂ moiety is more or less symmetric with Zn-O(3) and ZnA-O(3) bond distances of 1.9792(13) and 1.9622(14) Å. The Zn…ZnA separation of 2.9245(5) Å is in good agreement with previously described dizinc complexes containing μ -O(phenolate) bridges.^{10e,12b,13} In **4** the central Mg₂(μ -O)₂ moiety is less symmetric with Mg(1)-O(1) and Mg(1)-O(3A) distances of 1.8901(18) and 1.9428(19) Å, respectively. Again the Mg(1)…Mg(1A) separation of 2.936(2) Å is in good agreement with previously described dimagnesium complexes containing μ -O(phenolate) bridges.^{8d,12a}

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Fig. 4 Displacement ellipsoid plot (20% probability) of $[Zn_2(L^{O_3})_2]$ (**3**). Hydrogen atoms, toluene of crystallisation, and two phenyl groups omitted for clarity. Selected bond distances(Å) and angles (°): Zn-O(1) 1.8509(16), Zn-O(3A) 1.9628(14), Zn-O(3) 1.9799(14), Zn-O(2) 2.0780(15), Zn···ZnA 2.9246(5), O(1)-Zn-O(3A) 133.62(7), O(1)-Zn-O(3) 135.57(7), O(3A)-Zn-O(3) 84.24(6), O(1)-Zn-O(2) 97.76(6), O(3A)-Zn-O(2) 104.57(6), O(3)-Zn-O(2) 91.77(6), Zn-O(3)-ZnA 95.76(6).

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Fig. 5 Displacement ellipsoid plot (20% probability) of $[Mg_2(L^{O_3})_2]$ (4). Hydrogen atoms and two phenyl groups omitted for clarity. Selected bond distances (Å) and angles (°): Mg(1)-O(1) 1.8901(18), Mg(1)-O(3A) 1.9428(19), Mg(1)-O(3) 2.0037(17), Mg(1)-O(2) 2.0396(17), Mg(1)-···Mg(1A) 2.936(2), O(1)-Mg(1)-O(3A) 135.51(8), O(1)-Mg(1)-O(3) 134.02(8), O(3A)-Mg(1)-O(3) 83.88(8), O(1)-Mg(1)-O(2) 94.87(8), O(3A)-Mg(1)-O(2) 109.09(7), O(3)-Mg(1)-O(2) 90.71(7), Mg(1)-O(3)-Mg(1A) 96.12(8).

The ¹H NMR spectra of the two complexes $[M_2(L^{O_3})_2]$ (3 and 4) in C₆D₆ at room temperature support the dinuclear structures determined by X-ray diffraction. Thus, each exhibits four signals for the diastereotopic methylene hydrogens for the OC<u>H</u>₂Ar linkages, and four inequivalent CMe₂Ph groups for the inequivalent 1,2-C₆H₂(CMe₂Ph)₂ aryl rings of each L^{O3} ligand.

Ring-opening polymerisation of *ɛ*-caprolactone and lactide

The ROP of L-LA and *rac*-LA employing complexes **1** and **2** as catalysts in the presence of BnOH was systematically studied as shown in Table 1, entries 1-7. The initial results showed that complexes **1** and **2** are active for the ROP of L-LA, producing PLA with expected molecular weights and low polydispersity indices (PDIs, M_w/M_n). The decreasing order of activity of $[K(L^{O_3}-H)(THF)] \approx [K(L^{O_3}-H)] > [Na(L^{O_3}-H)] >> [Li(L^{O_3}-H)]$ is consistent with the order of the charge:size ratio of the alkali metal ion (entries 1-5).^{3k} All of the PLA was isotactic as expected, showing no evidence of epimerisation of the <u>C</u>(H)Me centre.

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[LA]: Time Temp Conv $M_{\rm n}$ $M_{\rm n}$ PDI^d Entry Catalyst Monomer [Catalyst] Solv. $(GPC)^d$ $(\%)^{b}$ $(^{\circ}C)$ (min) (calcd)^c :[BnOH] 1 CH_2Cl_2 1.06 1 L-LA 0 200:1:2 24 92 13400 16300 2 2 L-LA 0 200:1:2 CH₂Cl₂ 24 90 13100 13800 1.07 [Na(L^{O3}-H)] 3^e 13900 0 14500 L-LA 200:1:2 CH₂Cl₂ 35 96 1.08 $[Li(L^{O_3}-H)]$ 4^e L-LA 200:1:2 CH₂Cl₂ 15200 1.09 20 120 91 13200 5 1 L-LA 0 200:1:4 CH_2Cl_2 8 98 7300 7450 1.08 6^{*e*} [Na(L^{O3}-H)] CH₂Cl₂ 7300 L-LA 0 200:1:4 10 95 6900 1.07 7 2 CH_2Cl_2 8 93 6900 L-LA 0 200:1:4 6800 1.09 8 1 rac-LA 20 100:1:0 CH₂Cl₂ 12960 8354 2.12 180 90 9 1 rac-LA 100:1:1 CH_2Cl_2 13900 11800 20 35 96 1.13 7500 1.09 10 1 rac-LA 20 100:1:2 CH_2Cl_2 12 98 7300 THF 6300 11 1 rac-LA 20 100:1:2 105 93 6800 1.46 12 1 rac-LA 20 100:1:4 CH_2Cl_2 5 99 3700 3758 1.16 1 13 rac-LA 20 100:1:4 THF 25 95 3528 3600 1.14 14 1 50:1:2 CH_2Cl_2 9 3500 3550 1.19 rac-LA 20 94 15 1 rac-LA 20 150:1:2 CH_2Cl_2 15 96 10500 11200 1.12 16 1 rac-LA 20 200:1:2 CH_2Cl_2 18 96 13900 14800 1.12 17 2 rac-LA 100:1:4 THF 25 92 3400 20 3300 1.15

Table 1. Ring-opening polymerisation of lactides catalysed by $[K(L^{O_3}-H)]$ (1) and $[K(L^{O_3}-H)(THF)]$ (2) and related complexes.^{*a*}

^{*a*} [Catalyst]₀ = 2.5 mM. ^{*b*} Obtained from ¹H NMR analysis. ^{*c*} Calculated from $M_w(LA) \times [LA]_0$:[BnOH]₀ × conversion plus $M_w(BnOH)$. ^{*d*} Obtained from GPC analysis relative to polystyrene standards with the appropriate corrections for $M_n(M_n(GPC) = 0.58 \times M_n(GPC)$ without corrections)).^{14 e} Ref. 3k.

We have also assessed the ROP capability of complexes **1** and **2** for *rac*-lactide (Table 1, entries 8-17). In the absence of added BnOH (entry 8) the polymerisation was much slower and gave PLA with a broad polydispersity index (PDI). In the presence of 1 equiv. BnOH as the initiator (entry 9) the polymerisation reached completion in a shorter time (35 *vs.* 180 min), and the resultant PLA had a much narrower PDI (1.13 *vs.* 2.12). Use of 2 equivs. of BnOH (entry 10) again reduced the polymerisation time and the M_n of the resulting PLA was half of those found in the reactions when 1 equiv. of BnOH was used, indicating that the catalyst system has "immortal" character^{2*i*} (confirmed by entries 11-17). Complex **1** is more active in CH₂Cl₂ than in THF (entry 10 *vs.* 11, for example) due to competition between THF and lactide for available coordination sites at the metal centre. Increasing the [*rac*-LA] loading with a constant [**1**]₀:[BnOH]₀ ratio (entries 14-16) gave a predictable increase in M_n of the PLAs.

8

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The ¹H NMR spectra of the PLAs prepared as above confirm that the polymer is of the type HO-[PLA]-OBn, capped with a benzyl ester group on one end and a hydroxyl group on the other, consistent with BnOH acting as an initiator. The linear increase in M_n with conversion and the low PDI of the polymers (Fig. 6) confirms that the level of ROP control is high. Compound **2** has a similar catalytic efficiency when using BnOH as an initiator and the ROP of *rac*-lactide is well-controlled with a narrow PDI (Table 1, entry 17). In all cases the PLA obtained from **1** and **2** with *rac*-lactide were atactic as judged by ¹H NMR spectroscopy. Overall, these data are consistent with **1** and **2** operating *via* the "activated monomer" mechanism. Consistent with this, addition of BnOH to NMR tube samples of **1** (or **3**, see below) gave no release of L^{O3}-H₂ and formation of complexes with K-OBn or Zn-OBn moieties. For a recent discussion of the ROP of LA using an alkali metal monophenolate ligand and BnOH initiator see references 3*o* and 3*p*.



Fig. 6 Plot of M_n (**•**) and PDI (Δ) *vs.* [*rac*-LA]₀:[BnOH]₀ for the ROP of *rac*-lactide initiated by [K(L^{O3}-H)] (1) in CH₂Cl₂ at with BnOH initiator at 20 °C.

The ROP of ε -caprolactone (CL) in toluene using $[Zn_2(L^{O_3})_2]$ (**3**, $[\mathbf{3}]_0 = 5.0$ mM) as catalyst in the presence of BnOH was systematically studied as shown in Table 2. Compound **3** is a slow but well-behaved catalyst for the ROP of CL under mild conditions. The polymerisation reached completion within 90 min at 50 °C in with $[CL]_0:[BnOH]_0$ in the range 50:1 – 200:1. The resulting PCLs have well-controlled and predictable molecular weights (measured using both GPC and NMR spectroscopy) with narrow PDIs ranging from 1.07 to 1.21 (Fig. 7), consistent with a very well controlled polymerisation process. To better understand this system, ¹H NMR studies of the PCL prepared using a $[CL]_0:[BnOH]_0$ loading of 50:1 were carried out as shown in Fig. 8. The ¹H NMR spectrum confirmed the presence of BnO-terminated PCL (HO-[PCL]-OBn) which is likely to be formed by an activated-monomer process as described for related metal complexes.^{8d,10e,12} Lowing the polymerisation temperature from 50 °C to 30 °C (Table 2, entry 5) resulted in a longer polymerisation time. A polymerisation resumption experiment when two batches of 100 equivs. CL were successively polymerised (entry 6) gave PCL with comparable M_n and PDI to that formed when $[CL]_0:[3]_0:[BnOH]_2 = 200:1:2$ was used (entry 2). While the M_n and PDI of the resulting PCL was experimentally identical to that found in the corresponding reaction at 50 °C (Table 2, entry 2). In addition, the PLAs formed using $[CL]_0:[3]_0:[BnOH]_2 = 200:1:2$ entry 2) and $[CL]_0:[3]_0:[BnOH]_2 = 1600:1:4$ (entry 8) had comparable M_n and PDI, confirming that the catalyst has 'immortal' character.

Entry	[CL] ₀ :[3] ₀	Time	Conv	M _n	$M_{\rm n}$	M _n	DDI	Yield
	:[BnOH]0	(min)	$(\%)^{b}$	(calcd) ^c	$(\text{GPC})^d$	$(NMR)^b$	PDI	(%) ^e
1	100:1:2	90	>99	5800	5200	6100	1.21	90
2	200:1:2	90	99	11400	10300	11800	1.11	91
3	300:1:2	90	95	16400	15000	17000	1.09	85
4	400:1:2	90	90	20600	18400	20700	1.07	87
5^{f}	200:1:2	210	98	11300	10100	11600	1.09	95

100(100):1:2

200:1:0

1600:1:16

6

7

 8^g

90(90)

90

90

>99

19

87

Table 2. Ring-opening polymerisation of ε -caprolactone catalysed by complex $[Zn_2(L^{O_3})_2]$ (3).^a

^{*a*} Toluene 10 mL, 50 °C, $[\mathbf{3}]_0 = 5.0$ mM. ^{*b*} Obtained from ¹H NMR analysis. ^{*c*} Calculated from $M_w(CL) \times [CL]_0:[BnOH]_0 \times \text{conversion plus } M_w(BnOH)$. ^{*d*} Obtained from GPC analysis relative to polystyrene standards with the appropriate corrections for $M_n (M_n(GPC) = 0.56 \times M_n(GPC \text{ without corrections}))$. ^{14 *e*} Isolated yield. ^{*f*} 30 °C. ^{*g*} Toluene 15 mL.

11400

_

10000

9600

20000

8700

13000

-

10700

92

9

84

1.14

1.12

1.09

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Fig. 7 Plot of M_n (\Box) and PDI(\bullet) *vs.* [CL]₀:[BnOH]₀ for the ROP of ε -caprolactone initiated by $[Zn_2(L^{O3})_2]$ (**3**) in toluene with BnOH initiator at 50 °C.



Fig. 8 ¹H NMR spectrum (CDCl₃, 298 K) of the PCL prepared using $[CL]_0:[BnOH]_0 = 50$ and **3** as catalyst.

The ROP of CL ε -caprolactone and L-lactide in toluene catalysed by $[Zn_2(L^{O_3})_2]$ (3) and $[Mg_2(L^{O_3})_2]$ (4) ([3 or 4]₀ = 5.0 mM) in the presence of different alcohols was also studied as shown in Table 3. The resulting polyesters were again obtained with the expected molecular weights with low PDIs. As shown in Table 3, entries 1-3, various PCLs were prepared by using ethylene glycol, 1,4-benzenedimethanol and MPEG-2000 (poly(ethylene glycol)methyl ether, M_n ca 2000) as functional initiators The M_n values of the purified polymers were determined by ¹H

NMR spectroscopy and GPC. For example, ¹H NMR spectrum of the copolymer MPEG-*b*-PCL (entry 3) displayed characteristic resonances at 4.06, 3.65, 3.40, 2.30, 1.62 and 1.36 ppm, which can be ascribed to C(O)OC<u>H₂</u> of PCL, OC<u>H₂CH₂O, CH₃O of MPEG, COC<u>H₂</u> of PCL, OCH₂C<u>H₂</u> and C(O)OCH₂C<u>H₂</u> of PCL and OCH₂CH₂C<u>H₂</u> of PCL, respectively (Fig. 9(c)). By comparing the peak integration of the methylene protons of the PCL block (C(O)OC<u>H₂, δ 4.06 ppm) to that of the PEG block (OC<u>H₂CH₂O, δ 3.65 ppm), it was confirmed that the NMR-calculated *M*_n was very similar to that detected by GPC (7500 *vs*. 7400).</u></u></u>

Table 3. Ring-opening polymerisation of ε -caprolactone and L-lactide catalysed by $[Zn_2(L^{O_3})_2]$ (3) and $[Mg_2(L^{O_3})_2]$ (4) using different initiators, "I".^{*a*}

Entry	Initiator (I)	[Catalyst]	[M]	Temp	Time	Conv	$M_{\rm n}$	$M_{\rm n}$	$M_{\rm n}$	ורום	
				(°C)	(h)	$(\%)^b$	$(calcd)^{d}$	$(GPC)^{c}$	$(NMR)^b$	PDI	
1	HOCH ₂ CH ₂ OH	3	CL	50	2	95	5500	5500	6500	1.02	
2	1,4-HOCH ₂ C ₆ H ₄ CH ₂ OH	3	CL	50	2	98	5700	6000	6200	1.08	
3	MPEG-2000	3	CL	50	2	96	7500	7400	7900	1.16	
4	BnOH	3	L-LA	110	4	95	6900	6800	7100	1.21	
5	HOCH ₂ CH ₂ OH	3	L-LA	110	4	93	6800	8400	8400	1.24	
6	1,4-HOCH ₂ C ₆ H ₄ CH ₂ OH	3	L-LA	110	4	97	7100	7100	7000	1.21	
7	MPEG-2000	3	L-LA	110	4	95	8800	6400	8200	1.27	
8	BnOH	4	CL	50	0.4	90	5200	5600	5800	1.12	
9	BnOH	4	L-LA	110	0.5	93	6800	7200	7300	1.18	

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^{*a*} Toluene 10 mL, [**3** or **4**]₀ = 5.0 mM, [CL or L-LA]₀:[**3** or **4**]₀:[**1**]₀ = 200:1:4. ^{*b*} Obtained from ¹H NMR analysis. ^{*c*} Obtained from GPC analysis and calibrated by a polystyrene standard. Obtained from GPC analysis relative to polystyrene standards with the appropriate corrections for M_n (M_n (GPC) = 0.56 (PCL) or 0.58 (PLA) x M_n (GPC without corrections)).^{14 d} Calculated from M_w (CL or LA) × [CL or LA]₀:[BnOH]₀ × conversion plus M_w (I).

The corresponding isotactic PLAs (entries 4-6, Table 3) and the block copolymer with MPEG-2000 (entry 7) were likewise prepared by the ROP of L-lactide using BnOH, ethylene glycol, 1,4-benzenedimethanol and MPEG-2000, respectively, as functional initiators at 110° C. The polymers were characterised by ¹H NMR spectroscopy (Fig. 10). In addition to the signals for the PLA block (C(O)C<u>H</u>CH₃, δ 5.17 ppm; C(O)CHC<u>H₃</u>, δ 1.60 ppm) the characteristic signals for the initiators groups segments can be observed clearly. The M_n of the purified polymers as determined by ¹H NMR were once again in good agreement with those determined by GPC.

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Fig. 9 ¹H NMR spectra (CDCl₃, 298 K) of the PCL prepared using $[CL]_0:[I]_0 = 50$ and **3** as catalyst for various functional initiators, "I": (a) ethylene glycol; (b) 1,4-benzenedimethanol; (c) MPEG-2000.

Finally, Table 3 (entries 8 and 9) also summarises the ROP results for PCL and PLA using $[Mg_2(L^{O3})_2]$ (4) as a catalyst for [CL or L-LA]₀:[4]₀:[BnOH]₀ = 200:1:4. A conversion of *ca*. 90% was achieved within 24 min at 50 °C for the ROP of CL and within 30 min at 110 °C for ROP of L-LA. The PDIs of polyesters obtained were quite low (1.12 to 1.18) and the M_n values were in good agreement with those predicted assuming an "immortal" ROP type mechanism. Based on the data in Table 3 we conclude that the magnesium catalyst 4 is more active than its zinc counterpart 3, consistent with previous reports.^{8a,8c,10c,15}

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Fig. 10 ¹H NMR spectra (CDCl₃, 298 K) of the PLA prepared using $[LA]_0$: $[I]_0 = 50$ and **3** as catalyst for various functional initiators, "I": (a) BnOH; (b) ethylene glycol; (c) 1,4-benzenedimethanol; (d) MPEG-2000.

Kinetic Studies of the ROP of ε *-caprolactone using* $[Zn_2(L^{O_3})_2]$ (3). The BnOH-initiated ROP of CL with **3** occurs at a suitable rate at 50 °C in toluene for kinetic studies. For an activated-monomer propagation mechanism a rate law of the type shown in Eq. 1 typically applies^{3i,9h} where -d[CL]/dt is the rate of monomer consumption and k_p is the overall propagation rate constant.

$$R_{\rm p} = \frac{-\mathrm{d}[\mathrm{CL}]}{\mathrm{dt}} = k_{\rm p}[\mathrm{CL}]^a [\mathrm{BnOH}]_0{}^b [\mathbf{3}]_0{}^c \qquad (1)$$

The polymerisation of CL using **3** in toluene at 50 °C was monitored by ¹H NMR aliquot sampling with various initial concentrations of CL, BnOH, and **3** until monomer consumption was effectively completed. In all cases there was an induction period of *ca*. 30 – 40 mins. Interestingly, plots of [CL]_t *vs*. time with $[\mathbf{3}]_0 = 2.5$ mM, [BnOH]₀ = 10 or 20 mM and [CL]₀ = 1.0, 1.5 or 2.0 M were linear to \geq 90% conversion (e.g. Fig. 11, top) after this induction period, whereas first order semi-logarithmic plots (or second order plots for 1/[CL]_t *vs*. time) were non-linear (Fig. 11, bottom). For $[\mathbf{3}]_0 = 2.5$ mM, [BnOH]₀ = 10 mM and [CL]₀ = 1.0, 1.5 or 2.0 M the *k*_{obs} values lay in the range 0.015(1) – 0.017(1) s⁻¹ consistent with the implication that the propagation proceeds

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with an apparent *zero-order* dependence on [CL] (i.e., a = 0 in Eq. 1). This unexpected observation is discussed further below.



Fig. 11. Top: Plot of [Cl] *vs.* time for $[CL]_0 = 2.0$ M, $[Zn_2(L^{O_3})_2]_0 = 2.5$ mM, and $[BnOH]_0 20$ mM; the linear fit shown after the induction period (*ca.* 30 min) has $R^2 = 0.998$ and $k_{obs} = 0.031(1)$ s⁻¹. Bottom: corresponding non-linear semi-logarithmic plot of $ln([CL]_0/[CL]_t)$ *vs.* time.

Further experiments were carried out to determine the order of reaction with respect to $[BnOH]_0$ and [3] (i.e., *b* and *c* in Eq. 1). Fixing $[CL]_0 = 2.0$ M and $[3]_0 = 2.5$ mM, $[BnOH]_0$ was varied as $[BnOH]_0 = 30$, 20, 15, 10 mM and the observed rate constant (k_{obs}) determined from the linear $[CL]_t$ vs. time plots. The corresponding plot of $ln(k_{obs})$ vs. ln[BnOH] (Fig.12) allows the determination of the order in BnOH concentration. The experimental gradient of the least-squares fitted line was 0.99(1) ($R^2 = 0.992$) consistent with a first-order dependence on $[BnOH]_0$. In a final set of experiments, fixed initial concentrations of $[CL]_0 = 1.0$ M and $[BnOH]_0 = 10$ mM were used while $[3]_0$ was varied as $[3]_0 = 4.0$, 3.0, 2.5, 2.0 mM. The $[CL]_t$ vs. time plots were again linear giving the corresponding k_{obs} values. The experimental gradient of the least-squares fitted line for

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ln(k_{obs}) vs. ln[**3**]₀ (Fig.13) was 0.53(1) ($R^2 = 0.999$), consistent with a half order dependence of R_p on [**3**]₀. From the vertical intercepts of the regression lines in Fig.12 and Fig.13, the propagation rate constant k_p was determined as $35 \pm 7 \text{ M}^{-0.5} \text{ min}^{-1}$. Overall the values of a, b and c in Eq. 1 are 0, 1, and 0.5 giving a rate expression: $R_p = -d[\text{CL}]/dt = k_p[\text{BnOH}]_0[\textbf{3}]_0^{-0.5}$.



Fig. 12. Plot of $\ln k_{obs} vs. \ln[BnOH]_0$ for $[CL]_0 = 2.0$ M, $[Zn_2(L^{O3})_2]_0 = 2.5$ mM, and $[BnOH]_0 = 30$ mM, 20 mM, 15 mM, 10 mM.



Fig. 13. Plot of $\ln k_{obs} vs. \ln[Zn_2(L^{O3})_2]_0$ for $[CL]_0 = 1.0$ M, $[BnOH]_0 = 10$ mM, and $[Zn_2(L^{O3})_2]_0 = 4.0$ mM, 3.0 mM, 2.5 mM, 2.0 mM.

Proposed mechanism for the ROP of CL using 3 and BnOH. The kinetic and other experimental data for the ROP of CL in the presence of 3 and BnOH is consistent with the activated-monomer mechanism shown in Scheme 2. The half-order dependence of R_p (-d[LA]/dt) on [3]₀ suggests^{6q} (partial) dissociation of 3 into a monomeric species 3_ROH in which the otherwise 3-coordinate Zn being stabilised by adduct formation with ROH (R = Bn initially or -[CL]_n-OBn as ROP proceeds; Scheme 2(a)). The steady state equilibrium concentration of the catalytically active

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species 3 ROH is given by Eq. 2. The proposed intermediate 3 ROH is related to the crystallographically characterised potassium complex $[K(L^{O_3}-H)(THF)]$ (2).

$$[3_ROH] = K_{eq}^{0.5}[BnOH]_0[3]_0^{0.5}$$
(2)

(a) Dimer-monomer adduct pre-equilibrium



(b) Ring-opening via monomeric complex 3 ROH



Scheme 2. Proposed mechanism for the ROP of CL catalysed by $[Zn_2(L^{O3})_2]$ (3).

Scheme 2(b) shows the CL ring-opening step by a conventional activated monomer mechanism, consistent with previous studies.^{2i,3o,3p} Coordination of CL to monomeric catalyst **3_ROH** (rate constant k_1) forms the five-coordinate intermediate [Zn(L^{O3})(ROH)(CL)] (3_ROH_CL). This intermediate can either release CL (rate constant k_{-1}) to reform 3_ROH, or proceed to the irreversible ring-opening of the CL to form [Zn(L^{O3})(H-[CL]-OBn)] (3 RO-[CL]-H) with a composite rate constant represented by k_2 .

In this model the rate of polymerisation *via* the active catalyst **3_ROH** can be represented by the Michaelis–Menten equation (Eq. 3) with the Michaelis constant (K_M) defined as Eq. 4. Using an analogous approach, Tolman and Hillmyer⁴⁰ have shown how Eq. 3 can lead to saturation kinetics in terms of monomer concentration if $K_M \ll$ [CL]. In this case Eq. 3 can approximate to Eq. 5, and substituting Eq. 2 into this gives Eq. 6, consistent with the experimental rate expression determined in the previous section.

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$$\frac{-d[CL]}{dt} = \frac{k_2[3_ROH][CL]}{K_M + [CL]}$$
(3)

$$K_{\rm M} = \frac{k_{-1} + k_2}{k_1} \tag{4}$$

$$\frac{-\mathrm{d}[\mathrm{CL}]}{\mathrm{dt}} = k_2[\mathbf{3}_{\mathrm{ROH}}] \quad (\mathrm{if} \ K_{\mathrm{M}} \ll [\mathrm{CL}]) \tag{5}$$

$$\frac{-d[CL]}{dt} = k_{p}[BnOH]_{0}[\mathbf{3}]_{0}^{0.5} \qquad (k_{p} = k_{2}K_{eq}^{0.5})$$
(6)

While Scheme 2 and Eqs. 2 – 6 appear to provide an adequate model to explain the kinetic behaviour of **3**, it remains less clear why this system behaves differently in terms of the relationship between $K_{\rm M}$ (and its composite terms) and [CL], from those reported previously for related dimeric zinc phenolate complexes. For these an experimental dependence of rate on [CL] has typically been inferred from monomer conversion *vs*. time plots (although in many instances a rate law has not been explicitly determined).¹⁰ Nonetheless, for the system under study here, it seems that it is the formation of the active catalyst **3_ROH** (Scheme 2(a), Eq. 2) that is rate limiting, and that subsequent (Scheme 2(b)) binding of CL to this monomeric species (once formed) is favourable (favourable k_1). Further studies are underway in our laboratories to determine the scope and wider occurrence of this phenomenon for analogues and homologues of **3** and other cyclic esters.

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Conclusions

The bulky OOO-tridentate phenolate ligands L^{O3} -H and L^{O3} provide a suitable coordination environment for the synthesis of the monomeric complexes $[K(L^{O3}-H)]$ (1) and $[K(L^{O3}-H)(THF)]$ (2), and the dimeric complexes $[Zn_2(L^{O3})_2]$ (3) and $[Mg_2(L^{O3})_2]$ (4). Complexes 1 and 2 have shown high activities toward the ring-opening polymerisation of L-lactide and *rac*-lactide in the presence of BnOH. Complexes 3 and 4 have lower but still effective activities toward the ROP of ε -caprolactone and L-lactide in the presence of BnOH and (for 3) other different initiators. Kinetic studies for the ROP of ε -caprolactone using 3 and BnOH gives an unusual rate expression $R_p =$ $-d[CL]/dt = k_p[BnOH]_0[3]_0^{0.5}$ for which a tentative model in proposed.

Experimental

General. All manipulations, unless otherwise mentioned, were carried out under an inert atmosphere of dry argon. KN(SiMe₃)₂ (s), ZnEt₂ (1.0 M solution in heptanes), and MgⁿBu₂ (1.0 M in hexane) were purchased from Aldrich and used as received. Solvents, BnOH, *e*-caprolactone, L-lactide, *rac*-Lactide, and deuterated solvents were purified before use according to previously described procedures.^{3j,4j,9g} ¹H and ¹³C NMR spectra were recorded on a Varian Mercury-400 (400 MHz for ¹H and 100 MHz for ¹³C) spectrometer with chemical shifts given in ppm and referenced either to TMS or residual protio-solvent peaks. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. The GPC measurements were performed on a Hitachi L-7100 system equipped with a differential Bischoff 8120 RI detector. All polymer samples were eluted at 35° C with THF (HPLC grade) using a flow rate of 1.0 mL min⁻¹. Molecular weight and polydispersity indices (PDIs = M_w/M_n) of the polymers were measured using polystyrene as a standard reference and appropriate corrections (see Tables 1 - 3).

K(L^{03} -**H**) (1). To an ice cold solution of L^{03} -H₂ (0.703 g, 1.0 mmol) in toluene (40 mL) was slowly added a solution of KN(SiMe₃)₂ (0.219 g, 1.0 mmol) in toluene (20 mL). The mixture was stirred for 6 h and then concentrated under reduced pressure. The residue was extracted with toluene (20 mL), and the extract was then concentrated to *ca*. 10 mL. Colourless crystals were obtained at RT after several days. Yield: 608 mg (82%). ¹H NMR (C₆D₆, ppm): δ 7.20 (d, 2H, Ph), 7.12 (d, 4H, Ph), 6.95-6.86 (m, 6H, Ph), 6.80-6.74 (m, 6H, Ph), 6.50 (m, 6H, Ph), 3.94 (s & b, 4H, CH₂), 1.46 (s, 12H, CH₃), 1.15 (s, 12H, CH₃). ¹³C NMR (CDCl₃, ppm): δ 161.78, 154.12, 151.80,

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150.32, 138.22, 132.39, 128.55, 128.24, 127.94, 127.30, 126.87, 125.55, 125.20, 124.98 (Ph); 72.82(OCH₂); 42.65, 42.05 (Ph*C*(CH₃)₂); 31.19 (PhC(*C*H₃)₂). Anal. Calcd for C₅₀H₅₃KO₃: C, 81.04; H, 7.21%. Found: C, 80.72; H, 6.88%.

K(L⁰³-**H**)(**THF**) (2). To an ice cold solution of L⁰³-H₂ (0.703 g, 1.0 mmol) in THF (20 mL) was slowly added a solution of KN(SiMe₃)₂ (0.219 g, 1.0 mmol) in THF (20 mL). The mixture was stirred for 6 h and then concentrated under reduced pressure. Recrystallisation with a solvent mixture of hexane and THF afforded colourless block crystals. Yield: 585 mg (72%). ¹H NMR (C₆D₆, ppm): δ 7.40 (d, 2H, Ph), 7.32 (d, 4H, Ph), 7.15-7.06 (m, 6H, Ph), 7.00-6.94 (m, 6H, Ph), 6.69 (m, 6H, Ph), 4.16 (b, 4H, CH₂), 3.47 (m, 4H, OCH₂CH₂), 1.67 (s, 12H, CH₃), 1.42-1.29 (s, 16H, CH₃ & OCH₂CH₂). ¹³C NMR (CDCl₃, ppm): δ 162.28, 153.72, 151.96, 150.63, 137.67, 131.57, 128.53, 128.22, 127.84, 126.91, 126.86, 125.61, 125.37, 124.98 (Ph); 72.75 (OCH₂); 67.41 (OCH₂CH₂) 42.41, 41.87 (PhC(CH₃)₂); 31.17 (PhC(CH₃)₂); 25.42 (OCH₂CH₂). Anal. Calcd for C₅₄H₆₁KO₄: C, 79.76; H, 7.56%. Found: C, 79.38; H, 7.23%.

[Zn₂(L^{O3})₂] (3). To an ice cold solution of L^{O3}-H₂ (1.41 g, 2.0 mmol) in toluene (40 mL) was slowly added a ZnEt₂ (2.2 mL, 1.0 M in heptanes, 2.2 mmol) solution. The mixture was stirred for 6 h and then concentrated under reduced pressure. The residue was extracted into warm toluene (25 mL), and the extract was then concentrated to *ca*. 10 mL. Colourless crystals were obtained at RT overnight. Yield: 1.23 g (80%). Diffraction-quality crystals were obtained from a saturated toluene solution at RT. Mp: 180-182 °C. ¹H NMR (C₆D₆, ppm): δ 7.45 (d, 4H, Ph), 7.41 (t, 4H, Ph), 7.31-6.97 (m, 30H, Ph), 6.79-6.73 (m, 8H, Ph), 6.65-6.61 (m, 2H, Ph), 4.50 (d, 2H, *CH*₂), 3.74 (d, 2H, *CH*₂), 3.41 (d, 2H, *CH*₂), 3.32 (d, 2H, *CH*₂), 1.74 (d, 12H, *CH*₃), 1.68 (s, 12H, *CH*₃), 1.64 (s, 6H, *CH*₃), 1.52 (s, 6H, *CH*₃), 1.42 (s, 6H, *CH*₃), 1.12 (s, 6H, *CH*₃). ¹³C NMR (CDCl₃, ppm): δ 161.16, 155.87, 152.00, 151.34, 150.82, 150.21, 142.20, 138.66, 137.45, 136.79, 128.53, 128.04, 127.74, 127.59, 127.39, 126.87, 126.81, 126.78, 126.69, 125.64, 125.56, 125.27, 125.21, 124.96, 124.56, 124.30, 122.49 (Ph); 73.91, 73.10(OCH₂); 42.56, 42.30, 42.20, 42.15(PhC(CH₃)₂); 33.56, 31.05, 29.37, 29.12, 27.82 (PhC(*C*H₃)₂). Anal. Calcd for C₁₀₀H₁₀₄O₆Zn₂: C, 78.36; H, 6.84%. Found: C, 78.32; H, 6.70%.

 $[Mg_2(L^{O_3})_2]$ (4). To a cold solution (-78°C) of Mg^nBu_2 (1.0 mL, 1.0 M in hexane) in hexane (30 mL) was slowly added a solution of L^{O_3} -H₂ (0.703 g, 1.0 mmol) in hexane (30 mL). The mixture was stirred overnight and then concentrated in vacuo. The residue was extracted with toluene (20

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mL), and the extract was then concentrated under reduced pressure to *ca*. 10 mL. Colourless crystals were obtained at RT overnight. Yield: 218 mg (30%). Diffraction-quality crystals were obtained from a saturated toluene solution at -20°C. ¹H NMR (C₆D₆, ppm): δ 7.22 (d, 4H, Ph), 7.14 (t, 4H, Ph), 7.02-6.61 (m, 30H, Ph), 6.33 (t, 8H, Ph), 6.65-6.61 (m, 2H, Ph), 4.12 (d, 2H, CH₂), 3.55 (d, 2H, CH₂), 3.03 (d, 2H, CH₂), 2.97 (d, 2H, CH₂), 1.49 (d, 12H, CH₃), 1.45 (s, 6H, CH₃).1.39 (s, 6H, CH₃), 1.35 (s, 6H, CH₃), 1.29 (s, 6H, CH₃), 1.13 (s, 6H, CH₃), 0.81 (s, 6H, CH₃).¹³C NMR (C₆D₆, ppm): δ 167.09, 163.43, 162.26, 157.39, 151.61, 150.81, 150.19, 143.98, 141.37, 138.76, 137.40, 135.02, 132.75, 129.38, 128.09, 127.86, 126.93, 126.90, 126.71, 126.27, 125.84, 125.79, 125.37, 125.06, 124.20, 124.12, 122.55 (Ph); 74.75, 73.38(OCH₂); 42.42, 42.30, 42.22, 42.13(PhC(CH₃)₂); 32.55, 31.18, 30.91, 29.91, 29.77, 28.77 (PhC(CH₃)₂). Anal. Calcd for C₁₀₀H₁₀₄O₆Mg₂: C, 82.80; H, 7.23%. Found: C, 82.35; H, 7.04%.

Polymerisation of lactide using [K(L⁰³-H)] (1) and [K(L⁰³-H)(THF)] (2). A typical polymerisation procedure can be illustrated by the synthesis of PLA-100 (the number 100 indicates the designed [LA]₀:[BnOH]₀, Table 1, entry 1). To a rapidly stirred solution of **1** (0.0185 g, 0.025 mmol) and BnOH (0.038 g, 0.050 mmol) in CH₂Cl₂ (10 mL) was added L-lactide (0.72 mL, 5.0 mmol) at 0°C. The reaction mixture was stirred for 24 min and then quenched with 2 drops of H₂O, and the polymer was precipitated on pouring the mixture into *n*-hexane (50 mL) to give white crystalline solids. Yield: 0.61 g (85%).

General procedure for ε -caprolactone polymerisation catalysed by $[M_2(L^{O3})_2]$ (M = Zn (3) or Mg (4)). A typical polymerisation procedure was exemplified by the synthesis of PCL-50 (the number 50 indicates the designed $[CL]_0$:[BnOH]_0, Table 1, entry 1,) using $[Zn_2(L^{O3})_2]$ as catalyst at 50 °C. The conversion yield (99%) of PCL-50 was analysed by ¹H NMR spectroscopic studies. To a rapidly stirred solution of $[Zn_2(L^{O3})_2]$ (0.077 g, 0.05mmol) in toluene (10 mL) was added a mixture of ε -caprolactone (0.53 mL, 5 mmol) and BnOH (0.1 mmol). The reaction mixture was stirred for 1.5 h and then quenched with 2 drops of H₂O, and the polymer was precipitated on pouring the mixture into *n*-hexane (40 mL) to give white crystalline solids. The *n*-hexane/H₂O was decanted, and the polymer was dried in vacuo. The dry polymer was then dissolved in CH₂Cl₂, reprecipitated with *n*-hexane, and dried to a constant weight prior to analyses by GPC.

CL were examine to a solution of [. mL). The mixtur aliquots were rem constant weight u added to a solution toluene (20 mL). mL aliquots were constant weight *in* X-ray crystallog determination we mounted on a Bru were collected in correction was bas space group deter and confirmed us: SHELXTL packa

Kinetic studies of the polymerisation of ε -caprolactone by $[Zn_2(L^{O3})_2]$ (3). Kinetic studies of CL were examined by following two step methods. (a) In the glovebox, CL (20 mmol) was added to a solution of $[Zn_2(L^{O3})_2]$ (with 2.0, 2.5, 3.0, and 4.0 mM) and BnOH (10mM) in toluene (20 mL). The mixture was then stirred at 50°C under N₂. At appropriate time intervals, 0.5 mL aliquots were removed and quenched with methanol (1 drop). The aliquots were then dried to constant weight under vacuum and analysed by ¹H NMR. (b) In the glovebox, CL (40 mmol) was added to a solution of $[Zn_2(L^{O3})_2]$ (77 mg, 2.5mM) and BnOH (with 10, 15, 20, and 30 mM) in toluene (20 mL). The mixture was then stirred at 50°C under N₂. At appropriate time intervals, 0.5 mL aliquots were removed and quenched with methanol (1 drop). The aliquots were then dried to constant weight under vacuum and analysed by ¹H NMR. (b) In the glovebox, CL (40 mmol) was added to a solution of $[Zn_2(L^{O3})_2]$ (77 mg, 2.5mM) and BnOH (with 10, 15, 20, and 30 mM) in toluene (20 mL). The mixture was then stirred at 50°C under N₂. At appropriate time intervals, 0.5 mL aliquots were removed and quenched with methanol (1 drop). The aliquots were then dried to constant weight *in vacuo* and analysed by ¹H NMR.

X-ray crystallographic studies. Suitable crystal of complexes **1-4** for X-ray structural determination were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer for collection at 293(2) K. Intensity data were collected in 1350 frames with increasing *ö* (width of 0.3° per frame). An absorption correction was based on the symmetry equivalent reflections using the SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences and confirmed using the structure solutions. The structures were solved by direct methods using a SHELXTL package. All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Other details of the structure solution and refinements are given in the Electronic Supplementary Information (CIF data). A full listing of atomic coordinates, bond lengths and angles and displacement parameters for all the structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC 917258 - 917261).

Electronic supplementary information. Details of the crystallography in CIF format (CCDC 917258 - 917261). See DOI: 10.1039/b000000x/xx.

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Table of Contents Entry

The new potassium, zinc and magnesium complexes illustrated have been prepared and structurally characterised. In the presence of alcohol initiators all are catalysts for the controlled ring-opening polymerisation of L-lactide, *rac*-lactide and ε -caprolactone.

