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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Introduction

Over the past 15 years, polyesters such as poly(e-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 calcium8e,9 and zinc derivatives8f,k,10 have been reported to be effective catalysts/initiators for 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.10c 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.22,3f,k,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 ε-lactide in the presence of BnOH as an initiator. The sodium complexes had much higher catalytic activities than the lithium complexes, and BnOH gives an unusual rate expression $R_p = -d[C]/dt = k_p[BnOH]_0[3]_0^{0.5}$ for which a tentative kinetic model is proposed.

Reaction of the OOO-coordinating tridentate bis(phenolate) protio-ligand 2,2'-{oxybis(methylene)}bis-[4,6-di(1-methyl-1-phenylethyl)phenol] (L(O3-H2), with 1 equiv. of KN(SiMe3)2 in toluene or THF yielded [K(L(O3-H)) (1) or [K(L(O3-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-H) also reacts with 1 equiv. of ZnEt2 or Mg2Bu2 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 $R_p = -d[C]/dt = k_p[BnOH]_0[3]_0^{0.5}$ for which a tentative kinetic model is proposed.

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Results and discussion

Syntheses and X-ray crystal structures

As shown in Scheme 1, the mononuclear potassium complex [K(LO\textsubscript{3}-H)] \((1)\), containing a mono-deprotonated L\textsuperscript{O3}-H ligand, can be prepared by the reaction of L\textsubscript{O3}-H\textsubscript{2} with a stoichiometric amount of KN(SiMe\textsubscript{3})\textsubscript{2} in toluene in 82% yield. When complex \(1\) is dissolved in hot THF the Lewis base adduct [K(LO\textsubscript{3}-H)-(THF)] \((2)\) is formed. Compound 2 can also be prepared directly by the reaction of L\textsubscript{O3}-H\textsubscript{2} with a stoichiometric amount of KN(SiMe\textsubscript{3})\textsubscript{2} in THF. Compound 2 dissolves in hot toluene to lose THF, reforming complex 1 in high yield. In addition, reaction of L\textsubscript{O3}-H\textsubscript{2} with a stoichiometric amount of ZnEt\textsubscript{2} in toluene in the asymmetric unit reveals a mononuclear complex in which the potassium centre is π\textsuperscript{2}O\textsubscript{3}O\textsubscript{3}-coordinated to the three oxygen atoms of a mono-deprotonated L\textsubscript{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\textsuperscript{2} and/or C\textsubscript{ipso}\textsuperscript{2} interactions with the metal centre (e.g., K···C(1), K···C(14), K···C(19), K···C(20), and K···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\textsubscript{O3}-H)] molecule forms half of a dimeric unit connected through O···H···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.

Diffraction-quality crystals of [K(L\textsubscript{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 π\textsuperscript{2}O\textsubscript{3}O\textsubscript{3}-coordinated to the three oxygen atoms of a mono-deprotonated L\textsubscript{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\textsuperscript{2} and/or C\textsubscript{ipso}\textsuperscript{2} interactions with the metal centre (e.g., K···C(1), K···C(14), K···C(19), K···C(20), and K···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\textsubscript{O3}-H)] molecule forms half of a dimeric unit connected through O···H···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.

Diffraction-quality crystals of [K(L\textsubscript{O3}-H)][THF] \((2)\) were obtained on slow cooling of a concentrated toluene 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 π\textsuperscript{2}O\textsubscript{3}O\textsubscript{3}O\textsubscript{3}-bound L\textsubscript{O3}-H ligand and an additional THF ligand. The phenyl rings of L\textsubscript{O3}-H again contribute to π\textsuperscript{2} and/or C\textsubscript{ipso}\textsuperscript{2} 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\textsubscript{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.

Fig. 1 Displacement ellipsoid plot (20% probability) of [K(L\textsubscript{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).

Fig. 2 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).

Scheme 1 Preparation of potassium, zinc, and magnesium complexes 1–4 (ring π-interactions for \(1\) and \(2\) omitted – see Fig. 1 and 2).
Diffraction-quality crystals of the closely related dinuclear complexes \([\text{Zn}_2(\text{L}^{\text{O}_3})_2]\) (3) and \([\text{Mg}_2(\text{L}^{\text{O}_3})_2]\) (4) were grown by slow cooling of toluene solutions. The molecular structures are shown in Fig. 4 and 5, respectively. Each structure possesses a dinuclear motif having crystallographically-imposed inversion symmetry, with each four-coordinate metal \(\kappa^3\text{O}_3\text{O}_2\text{O}\)-bound to three oxygens of one doubly-deprotonated \(\text{L}^{\text{O}_3}\) ligand (O(1), O(2), O(3)) and also to a bridging phenolate oxygen (O(3A)) of another. In 3 the resultant \(\text{Zn}_2(\mu-\text{O})_2\) moiety is more or less symmetric with \(\text{Zn}--\text{O}(3)\) and \(\text{ZnA}--\text{O}(3)\) bond distances of 1.9792(13) and 1.9622(14) Å. The \(\text{Zn}--\text{ZnA}\) separation of 2.9245(5) Å is in good agreement with previously described dizinc complexes containing \(\mu-\text{O}(\text{phenolate})\) bridges.\(^{10d,12d,13}\) In 4 the central \(\text{Mg}_2(\mu-\text{O})_2\) moiety is less symmetric with \(\text{Mg}(1)--\text{O}(1)\) and \(\text{Mg}(1)--\text{O}(3A)\) distances of 1.8901(18) and 1.9428(19) Å, respectively. Again the \(\text{Mg}(1)--\text{Mg}(1A)\) separation of 2.936(2) Å is in good agreement with previously described dimagnesium complexes containing \(\mu-\text{O}(\text{phenolate})\) bridges.\(^{12d,12a}\)

The \(^1\text{H}\) NMR spectra of the two complexes \([\text{Mg}_2(\text{L}^{\text{O}_3})_2]\) (3 and 4) in \(\text{C}_6\text{D}_6\) at room temperature support the dinuclear structures determined by X-ray diffraction. Thus, each exhibits four signals for the diastereotropic methylene hydrogens for the \(\text{OCH}_2\text{Ar}\) linkages, and four inequivalent \(\text{CMe}_2\text{Ph}\) groups for the inequivalent \(1,2-\text{C}_\text{Me}_2\text{H}_2(\text{CMe}_2\text{Ph})_2\) aryl rings of each \(\text{L}^{\text{O}_3}\) ligand.

The ROP of \(\text{L-LA}\) and \(\text{rac-LA}\) employing complexes 1 and 2 as catalysts in the presence of \(\text{BnOH}\) 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 \(\text{L-LA}\), producing PLA with expected molecular weights and low polydispersity indices (PDIs, \(M_w/M_n\)). The decreasing order of activity of \([\text{K}(\text{L}^{\text{O}_3})\text{H})(\text{THF})]\] ≈ \([\text{K}(\text{L}^{\text{O}_3})\text{H}]) > \left[\text{Na}(\text{L}^{\text{O}_3})\text{H}\right] \gg \left[\text{Li}(\text{L}^{\text{O}_3})\text{H}\right] is consistent with the order of the charge : size ratio of the alkali metal ion (entries 1–5).\(^{1k}\) All of the PLA was isotactic as expected, showing no evidence of epimerisation of the \(\text{C}(\text{H})\text{Me}\) centre.

We have also assessed the ROP capability of complexes 1 and 2 for \(\text{rac-Lactide}\) (Table 1, entries 8–17). In the absence of added \(\text{BnOH}\) (entry 8) the polymerisation was much slower and gave PLA with a broad polydispersity index (PDI). In the presence of 1 equiv. \(\text{BnOH}\) as the initiator (entry 9) the polymerisation reached completion in a shorter time (35 vs. 5).
180 min), and the resultant PLA had a much narrower PDI (1.13 vs. 2.12). Use of 2 equiv. 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 \(^2\) (confirmed by entries 11–17). Complex 1 is more active in CH$_2$Cl$_2$ 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.

The $^1$H 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.

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<th>Time (min)</th>
<th>Conv (%)</th>
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<th>$M_n$ (GPC)$^d$</th>
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$^a$[Catalyst]$_0$ = 2.5 mM. $^b$Obtained from $^1$H NMR analysis. $^c$Calculated from $M_n$(LA) × [LA]$_0$ : [BnOH]$_0$ × conversion plus $M_n$(BnOH). $^d$Obtained from GPC analysis relative to polystyrene standards with the appropriate corrections for $M_n$ ($M_n$(GPC) = 0.58 × $M_n$(GPC without corrections)).$^{14}$

$^e$Ref. 3k.

Fig. 5 Displacement ellipsoid plot (20% probability) of [Mg$_2$(LO$_3$)$_2$] (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), O(1)–Mg(1)–O(3) 135.51(8), O(1)–Mg(1)–O(3A) 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).

Fig. 6 Plot of $M_n$ (■) and PDI (Δ) vs. [rac-LA]$_0$: [BnOH]$_0$ for the ROP of rac-lactide initiated by [K(LO$_3$-H)] (1) in CH$_2$Cl$_2$ at with BnOH initiator at 20 °C.
judged by $^1$H 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 \( \text{LO}_3\cdot\text{H}_2 \) 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 ref. 3o and 3p.

The ROP of \( \varepsilon \)-caprolactone (CL) in toluene using [Zn\(_2\)(L\(_{O3}\))\(_2\)] (3, [3] \(_0\) = 5.0 mM) as a 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, \(^1\)H 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 \(^1\)H 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.\(^{8d,10c,12}\) 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 equiv CL were successively polymerised (entry 6) gave PCL with comparable \( M_n \) and PDI to that formed when [CL] \(_0\) : [BnOH] \(_0\) = 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] \(_0\) : [BnOH] \(_0\) = 200 : 1 : 2 entry 2) and [CL] \(_0\) : [BnOH] \(_0\) = 1600 : 1 : 16 (entry 8) had comparable \( M_n \) and PDI, confirming that the catalyst has ‘immortal’ character.

The ROP of CL \( \varepsilon \)-caprolactone and \( l \)-lactide in toluene catalysed by [Zn\(_2\)(L\(_{O3}\))\(_2\)] (3, [3] \(_0\) = 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 \(^1\)H NMR spectroscopy and GPC. For example, \(^1\)H NMR spectrum of the copolymer MPEG-\( l \)-PCL (entry 3) displayed characteristic resonances at 4.06, 3.65, 3.40, 2.30, 1.62

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**Table 2** Ring-opening polymerisation of \( \varepsilon \)-caprolactone catalysed by complex [Zn\(_2\)(L\(_{O3}\))\(_2\)] (3)

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<th>Entry</th>
<th>[CL] (_0) : [3] (_0) : [BnOH] (_0)</th>
<th>Time (min)</th>
<th>Conv(^b) (%)</th>
<th>( M_n ) (calcd)(^c)</th>
<th>( M_n ) (GPC)(^d)</th>
<th>( M_n ) (NMR)(^e)</th>
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<td>99</td>
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<td>97</td>
<td>10 000</td>
<td>8700</td>
<td>10 700</td>
<td>1.09</td>
<td>84</td>
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</table>

\(^a\)Toluene 10 mL, 50 °C, [3] \(_0\) = 5.0 mM. \(^b\)Obtained from \(^1\)H NMR analysis. \(^c\)Calculated from \( M_n (\text{CL}) \times [\text{CL}]_0 \times [\text{BnOH}]_0 \times \text{conversion} + M_n (\text{BnOH}) \). \(^d\)Obtained from GPC analysis relative to polystyrene standards with the appropriate corrections for \( M_n \) (GPC) = 0.56 × \( M_n \) (GPC without corrections)).\(^e\)Isolated yield.\(^f\)30 °C. \(^g\)Toluene 15 mL.
and 1.36 ppm, which can be ascribed to C(O)OCH$_2$ of PCL, \( \text{OCH}_2\text{CH}_2\text{O}, \text{CH}_2\text{O} \) of MPEG, \( \text{COCH}_3 \) of PCL, \( \text{OCH}_2\text{CH}_2\text{O} \) and C(O)OCH$_2$ of PCL and \( \text{OCH}_2\text{CH}_2\text{O} \) of PCL, respectively (Fig. 9(c)). By comparing the peak integration of the methylene protons of the PCL block (C(O)OCH$_2$, \( \delta = 4.06 \text{ ppm} \)) to that of the PEG block (OCH$_2$CH$_2$O, \( \delta = 3.65 \text{ ppm} \)), it was confirmed that the NMR-calculated \( M_n \) was very similar to that detected by GPC (7500 vs. 7400).

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 \( \varepsilon \)-lactide using BnOH, ethylene glycol, \( \varepsilon \)-caprolactone and \( \varepsilon \)-lactide catalysed by \( [\text{Zn}_2(\text{LO}_3)_2] \) \( (3) \) and \( [\text{Mg}_2(\text{LO}_3)_2] \) \( (4) \) using different initiators, \( "I" \)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator (I)</th>
<th>[Catalyst]</th>
<th>[M]</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Conv (%)</th>
<th>( M_n ) (GPC)</th>
<th>( M_n ) (NMR)</th>
<th>PDI</th>
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<td>1</td>
<td>HOCH$_2$CH$_2$OH</td>
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<td>CL</td>
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<tr>
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*Obtained from GPC analysis without corrections.*

![Fig. 9](image-url) \(^{(1)}\)\(^{(1)}\) 1H NMR spectra (CDCl$_3$, 298 K) of the PCL prepared using [CL]:[I]$_0$ = 50 and 3 as catalyst for various functional initiators, \( "I" \): (a) ethylene glycol; (b) 1,4-benzenedimethanol; (c) MPEG-2000.

![Fig. 10](image-url) \(^{(1)}\)\(^{(1)}\) 1H NMR spectra (CDCl$_3$, 298 K) of the PLA prepared using [LA]:[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 \( \varepsilon \)-caprolactone using \( [\text{Zn}_2(\text{LO}_3)_2] \) \( (3) \). 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 eqn (1) typically applies,

\[
R_p = \frac{-d[CL]}{dt} = k_p[CL]^a[BnOH]^b[3]^c
\]

where \( \text{CL} \) is the rate of monomer consumption and \( k_p \) is the overall propagation rate constant.

The polymerisation of CL using 3 in toluene at 50 °C was monitored by \( ^1\text{H} \) 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 min. Interestingly, plots of [CL]$_0$ vs. time with [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 >90% conversion (e.g. Fig. 11, top) after this induction period, whereas first order semi-
logarithmic plots (or second order plots for $1/\text{[CL]}_t$ vs. time) were non-linear (Fig. 11, bottom). For $[3]_0 = 2.5$ mM, $[\text{BnOH}]_0 = 10$ mM and $[\text{CL}]_0 = 1.0, 1.5$ or 2.0 M the $k_{\text{obs}}$ values lay in the range 0.015(1)–0.017(1) s$^{-1}$ consistent with the implication that the propagation proceeds with an apparent zero-order dependence on $[\text{CL}]$ (i.e., $a = 0$ in eqn (1)). This unexpected observation is discussed further below.

Further experiments were carried out to determine the order of reaction with respect to $[\text{BnOH}]_0$ and $[3]$ (i.e., $b$ and $c$ in eqn (1)). Fixing $[\text{CL}]_0 = 2.0$ M and $[3]_0 = 2.5$ mM, $[\text{BnOH}]_0$ varied as $[\text{BnOH}]_0 = 30, 20, 15, 10$ mM and the observed rate constant ($k_{\text{obs}}$) determined from the linear $[\text{CL}]_t$ vs. time plots. The corresponding plot of ln($k_{\text{obs}}$) vs. ln($[\text{BnOH}]_0$) (Fig. 12) allows the determination of the order in $[\text{BnOH}]$ 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 $[\text{BnOH}]_0$. In a final set of experiments, fixed initial concentrations of $[\text{CL}]_0 = 1.0$ M and $[\text{BnOH}]_0 = 10$ mM were used while $[3]_0$ was varied as $[3]_0 = 4.0, 3.0, 2.5, 2.0$ M. The $[\text{CL}]_t$ vs. time plots were again linear giving the corresponding $k_{\text{obs}}$ values. The experimental gradient of the least-squares fitted line for ln($k_{\text{obs}}$) 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 13, the propagation rate constant $k_p$ was determined as $35 \pm 7$ M$^{-0.5}$ min$^{-1}$. Overall the values of $a$, $b$ and $c$ in eqn (1) are 0, 1, and 0.5 giving a rate expression: $R_p = -d[\text{CL}]/dt = k_p[\text{BnOH}]_0[3]_0^{0.5}$.  

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 $R_p$ ($-d[\text{LA}]/dt$) on $[3]_0$ suggests$^6$ (partial) dissociation of 3 into a monomeric species $3_{\text{ROH}}$ in which the otherwise 3-coordinate Zn being stabilised by adduct formation with ROH ($R = \text{Bn}$ initially or $-[\text{CL}]_n$–OBn as ROP proceeds; Scheme 2(a)). The steady state equilibrium concentration of the catalytically active species $3_{\text{ROH}}$ is given by eqn (2). The proposed intermediate $3_{\text{ROH}}$ is related to the crystallographically characterised potassium complex $[\text{K(L}$-H$(\text{THF})]$ (2).

$$[3_{\text{ROH}}] = K^{-0.5}_{\text{eq}}[\text{BnOH}]_0[3]_0^{0.5}$$
intermediate \([\text{Zn}(\text{LO}_3)(\text{ROH})(\text{CL})]\) \((3_{\text{ROH-CL}})\). This intermediate can either release CL (rate constant \(k_{-1}\)) to reform \(3_{\text{ROH}}\), or proceed to the irreversible ring-opening of the CL to form \([\text{Zn}(\text{LO}_3)(\text{H-}[\text{CL}]-\text{OBn})]\) \((3_{\text{RO}[\text{CL]-H}})\) with a composite rate constant represented by \(k_2\).

In this model the rate of polymerisation via the active catalyst \(3_{\text{ROH}}\) can be represented by the Michaelis–Menten equation (eqn (3)) with the Michaelis constant \(K_M\) defined as eqn (4). Using an analogous approach, Tolman and Hillmyer\(^{10}\) have shown how eqn (3) can lead to saturation kinetics in terms of monomer concentration if \(K_M \ll [\text{CL}]\). In this case eqn (3) can approximate to eqn (5), and substituting eqn (2) into this gives eqn (6), consistent with the experimental rate expression determined in the previous section.

\[
\begin{align*}
\frac{-d[\text{CL}]}{dt} &= \frac{k_2[3_{\text{ROH}}][\text{CL}]}{K_M + [\text{CL}]} \quad (3) \\
K_M &= k_{-1} + \frac{k_2}{k_1} \quad (4) \\
\frac{-d[\text{CL}]}{dt} &= k_2[3_{\text{ROH}}] \quad (\text{if } K_M \ll [\text{CL}]) \quad (5) \\
\frac{-d[\text{CL}]}{dt} &= k_p[\text{BnOH}]_0^{0.5} \quad (k_p = k_2K_{eq}^{0.5}) \quad (6)
\end{align*}
\]

While Scheme 2 and eqn (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 \(K_M\) (and its composite terms) and [CL], from those reported previously for related dimeric zinc phenolates 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 \(3_{\text{ROH}}\) (Scheme 2(a), eqn (2)) that is rate limiting, and that subsequent (Scheme 2(b)) binding of CL to this monomeric species (once formed) is favourable (favourable \(k_3\)). 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.

**Conclusions**

The bulky OOO-tridentate phenolate ligands \(\text{L}^{\text{O3}}\)-H and \(\text{L}^{\text{O3}}\) provide a suitable coordination environment for the synthesis of the monomeric complexes \([\text{K}([\text{L}^{\text{O3}}\text{-H}])](1)\) and \([\text{K}([\text{L}^{\text{O3}}\text{-H}])\text{-(THF)}](2)\), and the dimeric complexes \([\text{Zn}_2([\text{L}^{\text{O3}}]\text{]}_2\) (3) and \([\text{Mg}^\text{2+}([\text{L}^{\text{O3}}]\text{]}_2\) (4). Complexes 1 and 2 have shown high activities toward the ring-opening polymerisation of \(\ell\)-lactide and rac-lactide in the presence of BnOH. Complexes 3 and 4 have lower but still effective activities toward the ROP of \(\epsilon\)-caprolactone and \(\ell\)-lactide in the presence of BnOH and (for 3) other different initiators. Kinetic studies for the ROP of \(\epsilon\)-caprolactone using 3 and BnOH gives an unusual rate expression \(R_p = -d[\text{CL}] / dt = \frac{k_p[\text{BnOH}]_0^{[3]}_0.5}{[3]}\) which for a tentative model in proposed.

**Experimental**

**General**

All manipulations, unless otherwise mentioned, were carried out under an inert atmosphere of dry argon. KN(SiMe\(\text{3}_{12}\) (s), ZnEt\(\text{2}\) (1.0 M solution in heptanes), and Mg\(\text{2+}\)Bu\(\text{3}\) (1.0 M in hexane) were purchased from Aldrich and used as received. Solvents, BnOH, \(\epsilon\)-caprolactone, \(\ell\)-lactide, rac-Lactide, and deuterated solvents were purified before use according to previously described procedures.\(^{3,4,5,9,11}\) \(\text{H}\) and \(\text{C}^{13}\) NMR spectra were recorded on a Varian Mercury-400 (400 MHz for \(\text{H}\) and 100 MHz for \(\text{C}^{13}\) ) spectrometer with chemical shifts given in ppm and referenced either to TMS or residual proto-solvent peaks. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. TheGPC 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\(^{\text{O}3}\)-H] (1)**

To an ice cold solution of L\(^{\text{O}3}\)-H\(_2\) (0.703 g, 1.0 mmol) in toluene (40 mL) was slowly added a solution of KN(SiMe\(_3\))\(_2\) (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 overnight. Yield: 218 mg (30%).

**[Mg\(_2\)(L\(^{\text{O}3}\))-THF] (2)**

A typical polymerisation procedure can be illustrated by the synthesis of PLA-100 (the number 100 indicates the designed molecular weight). To a rapidly stirred solution of L\(^{\text{O}3}\)-H\(_2\) (0.703 g, 1.0 mmol) in THF (20 mL) was slowly added a solution of K(LO3-H) (1) as catalyst at 20 °C. \(^1\)H NMR spectroscopic studies. To a rapidly stirred solution of L\(^{\text{O}3}\)-H\(_2\) (0.703 g, 1.0 mmol) in THF (20 mL) was slowly added a solution of K(LO3-H) (1) as catalyst at 20 °C. \(^1\)H NMR spectroscopic studies. To a rapidly stirred solution of L\(^{\text{O}3}\)-H\(_2\) (0.703 g, 1.0 mmol) in THF (20 mL) was slowly added a solution of K(LO3-H) (1) as catalyst at 20 °C. \(^1\)H NMR spectroscopic studies.
Kinetic studies of the polymerisation of ε-caprolactone by [Zn₂(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 [Zn₂(L⁢O₃)₂] \( ^{3} \) (with 2.0, 2.5, 3.0, and 4.0 mM) and BnOH (10 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 \(^{1}H \)NMR. (b) In the glovebox, CL (40 mmol) was added to a solution of [Zn₂(L⁢O₃)₂] \( ^{3} \) (77 mg, 2.5 mM) 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 \(^{1}H \)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 \( \omega \) (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 ESI (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).

Acknowledgements

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References


For examples: 

(i) L. Wang and H. Ma, *Dalton Trans.*, 2010, 7897;  

10 For examples: 
(i) L. Wang and H. Ma, *Dalton Trans.*, 2010, 7897;  


14 The $M_n$(GPC) is multiplied by a factor of 0.58, giving the $M_n$ of polylactide:  