Synthesis of aluminum complexes supported by 2-(1,10-phenanthrolin-2-yl)phenolate ligands and their catalysis in the ring-opening polymerization of cyclic esters†

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A series of aluminum complexes supported by 2-(1,10-phenanthrolin-2-yl)phenolate ligands were synthesized and characterized. The reaction of o-bromophenol with n-butyllithium followed by nucleophilic addition to the phenanthroline and oxidation process gave the ligand precursors 2-(1,10-phenanthrolin-2-yl)phenol derivatives 1a–1d. Treatment of 1a–1d with an equiv. of AlR3 (R = Et, Bu) afforded the corresponding aluminum aryloxides 2a–2e. Treatment of 2b with 2 equiv. of benzyl alcohol formed complex 2f. All new compounds were characterized by 1H and 13C NMR spectroscopy and elemental analyses. The structure of complex 2c was further characterized by single crystal X-ray diffraction techniques. Complexes 2a–2e/BnOH and 2f were active to catalyze the ring-opening polymerization of ε-caprolactone, leading to polycaprolactone with good molecular weight control and relatively narrow molecular weight distribution. Complexes 2a–2e/BnOH and 2f catalyzed the polymerization of rac-lactide and 2b, 2c, 2e and 2f were demonstrated to lead to isotactic enriched polylactides. The above catalysts also catalyzed the ROP of rac-(β-butyl)lactone and led to atactic polylactide.

Introduction

Aliphatic polyesters such as poly(lactic acid) (PLA) and poly(ε-caprolactone) (PCL), as well as their copolymers have attracted considerable attention due to their biocompatible, biodegradable, and permeable properties which are important in biomedical and pharmaceutical applications. PLA, whose starting materials can be derived from renewable resources such as corn and sugar beet, is a promising material for long-term drug delivery due to its slow degradation in comparison to other polymers. Poly(β-hydroxybutyrate) (PHB) as an environmentally friendly polymer material offers many advantages over traditional petrochemically derived plastics. For example, it possesses better physical properties than polypropylene for food packaging applications and is nontoxic and biodegradable. PLA and PCL are generally synthesized by the ring-opening polymerization (ROP) of corresponding cyclic esters initiated by metal complexes. PHB is mainly produced using bacterial fermentation techniques from renewable resources. It can also be synthesized via catalytic ROP of β-butylactone (β-BL). The metal complexes for the ROP of the cyclic esters include alkali metals, alkaline-earth metals, group IIIA metals, group IVA metals, rare earth metals, and transition metals complexes, etc. However, different catalysts can lead to the polymers with different molecular weights, polydispersity indices, and stereo-microstructures. Hence search for new catalysts for synthesis of the polymers is still an important topic. In the previous studies on metal catalysts for the ROP of cyclic esters, aluminum complexes have attracted considerable attention due to oxophilicity and Lewis acidity of the metal center. Numerous Al complexes bearing a range of multidentate ligands including NO, ONO, NNO, NNN, NNNN frameworks have been evaluated. We reported several aluminum complexes bearing pyridine- or quinoline-based NNO-chelate ligands and demonstrated them to be able to...
catalyze the ROP of ε-caprolactone (ε-CL) in the presence of benzyl alcohol.\textsuperscript{4d,11} However, the complexes were inactive towards the ROP of rac-lactide (rac-LA) in the presence or absence of BnOH. Based on previous work and the results reported in literatures,\textsuperscript{7d,7e,12} we designed and synthesized aluminum complexes supported by 2-(1,10-phenanthroline-2-yl)phenol ligands and found these complexes to be active catalysts in the ROP of rac-LA, ε-CL and rac-β-BL. Here we report the results.

### Results and Discussion

#### Synthesis and characterization of complexes 2a–2f

Synthetic routes of the ligand precursors and the complexes are summarized in Scheme 1. 2-(1,10-Phenanthroline-2-yl)phenol derivatives 1a–1d were synthesized according to improved literature procedures and characterized by \(^1\)H and \(^{13}\)C NMR spectroscopy and elemental analysis.\textsuperscript{13} Reaction of 1a–1d with AlEt\(_3\) in toluene at room temperature afforded complexes 2a–2d, respectively. 2e was similarly prepared by treatment of 1b with triisobutylaluminum in toluene. 2f was obtained via reaction of 1b with 1.1 equiv. of AlEt\(_3\) followed by \textit{in situ} alcoholysis of the resultant complex with 2 equiv. of BnOH at room temperature. Complexes 2a–2d are soluble in toluene and can be crystallized from the toluene solutions. Complex 2f was crystallized from a diethyl ether solution. Complexes 2a–2f were characterized by \(^1\)H and \(^{13}\)C NMR spectroscopy and elemental analyses. The analytical results are accordant with their respective formula. The \(^1\)H NMR spectrum of each of 2a–2e exhibits two sets of Al–R signals, which correspond two Al–R groups in different chemical environments. This might result from the fact that the phenanthroline ring and the phenolic ring are noncoplanar. The \(^1\)H NMR spectrum of complex 2f exhibits two sets of Al–OCH\(_2\)Ph signals due to similar reason. But we cannot rule out the possibility of a dimeric structure. Attempts to grow its single crystals for X-ray di fractionation were unsuccessful. Complex 2e was further characterized by single crystal X-ray diffraction. The ORTEP drawing is presented in Fig. 1, along with selected bond lengths and angles. In the molecule, the aluminum atom is five-coordinate and the coordination geometry of the aluminum atom can be best described as a distorted trigonal bipyramid. The N1A1C37C39 atoms are approximately coplanar, sum of the angles at aluminum center being 357.68°. The axial positions are occupied by N2 and O1 atoms, the angle of O(1)–Al(1)–N(2) being 161.86°(13). This angle is smaller than corresponding ones in enolato aluminum complexes \([\text{Al}2\text{Me2}(\text{OC}(\text{Bu}’))\text{C}(\text{Ph})\text{H}(\text{Ph})=\text{N}(8\text{-C}6\text{H}4\text{N})])\) \([168.01(14)°]\) and \([\text{Al}2\text{Me2}(\text{OC}(\text{Me})\text{C}(\text{Me})=\text{CH}(\text{Me})=\text{N}(8\text{-C}6\text{H}4\text{N})])\) \([164.67(8)°]\).\textsuperscript{7d} Larger than that in bipyridine–phenolate based aluminum complex \([\text{Al}2\text{Me2}(\text{BpyPh}2,4\text{-Bu})]\) \([155.87(10)°]\).\textsuperscript{7d} The Al1–N1 distance of 2.065(2) Å is shorter than that of Al1–N3 [2.183(3) Å], and both are within normal range for a five-coordinate aluminum complex.\textsuperscript{7k,7e} The Al1–O1 distance of 1.813(2) Å is comparable to that in \([\text{Al}2\text{Me2}(\text{BpyPh}2,4\text{-Bu})]\) \([1.819(2)Å]\).\textsuperscript{7k}

#### The ring-opening polymerization of ε-caprolactone

The ROP of ε-CL in toluene using 2a–2f as the catalysts has been conducted as shown in Table 1. Each of complexes 2a–2e is active for the ROP of ε-CL in the presence of BnOH, and complex 2f is active without requirement of BnOH. In the presence of BnOH, complex 2b exhibits highest activity. It led to 99% monomer conversion of 100 equiv. of ε-CL in 1 h at 50 °C. Complexes 2c and 2e exhibited close catalytic activity to each other, but both are a little lower than complex 2b under the same conditions. Complexes 2a and 2d showed the lowest activity in this series. Complex 2f is more active than 2b. For example, 2f catalyzed 100 equiv. of ε-CL to reach 99% monomer conversion in 1.5 h at 25 °C; whereas 2b drove 100 equiv. of ε-CL to only 89.3% monomer conversion in 1.5 h at 25 °C. An approximate catalytic activity order is 2f > 2b > 2e ≈ 2c > 2d, 2a.

![Scheme 1 Synthesis of ligand precursors 1a–1d and complexes 2a–2f](image-url)
Complex 2f also exhibits higher activity than aluminum bipyridine phenolate complex \([\text{AlMe}_2(\text{Bpy}2,4-	ext{Bu})]\) reported in literature.\(^7\) From above activity order of 2a–2f it can be seen that bulky ortho-position substituents on the aromatic rings of phenoxy groups benefit increase of the catalytic activity of the complexes. 2-Position substituent on the phenanthroline ring makes against catalysis of the complex (Table 1, entry 6). The GPC molecular weights of the polymers match the calculated values very well when complexes 2a–2c were employed as the catalysts (Table 1, entries 1–5). However, the GPC molecular weights of the polymers are lower than the calculated values when complexes 2d and 2e were employed as the catalysts (Table 1, entries 6–8). In most cases, the polydispersities are narrow. However, the polydispersities were broadened with increase of polymerization temperatures (Table 1, entries 2–4, 7 and 8).

Kinetic study of \(\varepsilon\)-CL polymerization catalyzed by complex 2f was performed. Plots of \(\ln([\text{CL}]_0/[\text{CL}])\) versus time revealed a linear relationship (Fig. 2), which indicates that the polymerization proceeds with first-order dependence on monomer concentration. This implies that the polymerization catalyzed by 2f is well controlled. The linear relationship of molecular weights of the polymers versus \(\varepsilon\)-CL conversion along with narrow PDI is another characteristic of living polymerization (Fig. 3). The corresponding SEC traces (Fig. 4) of the obtained polymers showed monomodal peaks with narrow PDI (1.07–1.08). The end group analysis of the PCL proved that the polymer was capped with a benzyloxy group ([H]) and a hydroxymethyl group ([H]) (Fig. 5). All these facts imply that the polymerization initiated through insertion of \(\varepsilon\)-CL into an Al-OCH\(_2\)Ph bond via acyl-oxygen cleavage.

### Table 1: The ROP of \(\varepsilon\)-CL catalyzed by complexes 2a–2f

| Entry | Cat. | \([\text{Cat.}]_0 : [\text{BnOH}]_0 : [\text{CL}]_0\) | \(T\) (°C) | Time (h) | Conv.\(^b\) (%) | \(M_n,\text{calc}\)^\(c\) (kg mol\(^{-1}\)) | \(M_n,\text{GPC}\)^\(d\) (kg mol\(^{-1}\)) | \(D\)^\(e\) |
|-------|------|--------------------------|--------|--------|-------------|----------------|----------------|------|
| 1     | 2a   | 1 : 1 : 100              | 50     | 5      | 48.1        | 5.6            | 5.2             | 1.14 |
| 2     | 2b   | 1 : 1 : 100              | 70     | 0.5    | 99          | 11.4           | 11.0            | 1.31 |
| 3     | 2b   | 1 : 1 : 100              | 50     | 1      | 99          | 11.4           | 11.0            | 1.21 |
| 4     | 2b   | 1 : 1 : 100              | 25     | 1.5    | 89.3        | 10.3           | 8.6             | 1.08 |
| 5     | 2c   | 1 : 1 : 100              | 50     | 2      | 99          | 11.4           | 9.6             | 1.19 |
| 6     | 2d   | 1 : 1 : 100              | 50     | 8      | 93.2        | 10.7           | 6.1             | 1.03 |
| 7     | 2e   | 1 : 1 : 100              | 25     | 3      | 36.3        | 4.2            | 3.2             | 1.07 |
| 8     | 2e   | 1 : 1 : 100              | 50     | 1.5    | 96.3        | 11.1           | 7.9             | 1.10 |
| 9\(^f\) | 2f | 1 : 0 : 100              | 25     | 1.5    | 99          | 11.4           | 8.6             | 1.12 |

\(^a\) Unless otherwise specified, the polymerization reactions were carried out in toluene, \([\text{Cat.}]_0 = 0.01\) M. \(^b\) Measured by \(^1\)H NMR spectra. \(^c\) Calculated from the molecular weight of \(\varepsilon\)-CL times the conversion of monomer and the ratio of \([\text{CL}]_0/[\text{BnOH}]_0\) plus the molecular weight of BnOH. \(^d\) \(M_n\) was obtained from GPC which was timed 0.56.\(^e\) \(D\) was obtained from GPC analyses. \(^f\) \(M_n,\text{calc}\) was calculated from the molecular weight of \(\varepsilon\)-CL times the conversion of monomer and the ratio of \([\text{CL}]_0/[\text{Cat}]_0\) plus the molecular weight of BnOH.

### The ring-opening polymerization of rac-lactide

Catalysis of complexes 2a–2f toward the ROP of rac-LA was evaluated, and the results showed that each of these complexes can catalyze the polymerization of rac-LA at elevated temperature (Table 2). Both 2a and 2b exhibited close activity in catalyzing polymerization of 100 equiv. of rac-LA in toluene at 70 °C in the presence of BnOH, leading to higher than 97% monomer conversion in 24 h (Table 2, entries 1 and 2). Complexes 2c and 2d revealed much lower catalytic activity than 2a and 2b under the same conditions. 89.9% conversion of 100 equiv. of rac-LA was achieved in 72 h when 2c/BnOH was employed as catalyst.

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**Fig. 2** Plot of \(\ln([\text{CL}]_0/[\text{CL}])\) versus time for the polymerization of \(\varepsilon\)-CL catalyzed by 2f. Conditions: \([\text{Cat}]_0 : [\text{BnOH}]_0 : [\text{CL}]_0 = 1 : 0 : 200; [\text{Cat}]_0 = 0.01\) M; solvent: toluene; temperature: 25 °C.

**Fig. 3** Plots of PCL \(M_n\) (○, obtained from GPC analysis) and dispersity (■, \(M_w/M_n\)) as a function of \(\varepsilon\)-CL conversion using complex 2f as the catalyst. Conditions: \([\text{CL}]_0 : [\text{BnOH}]_0 : [\text{CL}]_0 = 1 : 0 : 200; [\text{CL}]_0 = 0.01\) M; solvent: toluene; temperature: 25 °C.
and 60.9% of 100 equiv. of the monomer was converted in 72 h when 2d/BnOH was employed as catalyst (Table 2, entries 3 and 4). Complex 2e showed a little lower activity than 2a and 2b (Table 2, entry 5). The approximate activity order is 2a ≈ 2b > 2c > 2d. This activity order is different from that in catalyzing ε-CL polymerization. A bulky ortho-position substituent on the aromatic ring of phenoxys group is no longer necessary to increase the catalytic activity, and even unfavorable. However, the 2-position substituent on the phenanthroline ring is still unfavorable as that shown in catalyzing ε-CL polymerization. Catalysis of 2f did not require presence of extra BnOH. Its catalytic activity was close to that of 2b under comparable conditions. It also drove polymerization of 200 equiv. of rac-LA in good activity, 88.5% monomer conversion being achieved in 25 h (Table 2, entries 7 and 8). At lower temperature than 70°C, the catalytic activity of the complexes was markedly reduced. For example, 2e/BnOH led to only 13.5% conversion of 100 equiv. of rac-LA at 50°C in 96 h (Table 2, entry 6); 2f drove 97.1% conversion of 100 equiv. of rac-LA at 50°C in 72 h (Table 2, entry 9). Compared with aluminum bipyridine phenolate complexes, complexes 2a, 2b and 2f exhibit slightly higher activity than [AlMe2(BpyPh3,4-Me)]+ but have lower activity than [AlMe2(BpyPh3-Bu)]+ and [AlMe2(BpyPh3,4-Me)]. The GPC analysis revealed that molecular weight of the polymer catalyzed by 2a/BnOH matched the calculated value very well, but the PDI value is relatively wide (Table 2, entry 1). The GPC molecular weights of the polymers catalyzed by 2b–e/BnOH and 2f were lower than the calculated values (Table 2, entries 2–9). A plausible reason could be the presence of side reactions such as trans-esterification and chain transfer in the process of polymerization. Catalysis of 2b was further evaluated with different BnOH or monomer loadings. The polymerization rate is almost same in the presence of 2 equiv. of BnOH using 2b as catalyst (Table 2, entry 10). In the absence of benzyl alcohol, the reaction catalyzed by 2b resulted in very viscous species at 70°C in 14 h. The 1H NMR analysis indicated 84.2% monomer conversion and the GPC determination showed higher molecular weight of the final polymer than the expected value (Table 2, entry 11). This is

![Fig. 4](image1) The GPC curves of PCL depending different conversion catalyzed by 2f. Conditions: [Cat.]: [BnOH]: [CL]0 = 1: 0: 200; [Cat.] = 0.01 M; solvent: toluene; temperature: 25°C.

![Fig. 5](image2) 1H NMR spectrum of PCL initiated by 2b/BnOH (Table 1, entry 3).

| Entry | Cat. | [Cat.]: [BnOH]: [LA]0 | Time (h) | Conv. (%) | M_n,calc a (kg mol−1) | M_n,GPC b (kg mol−1) | D' c | Pd f |
|-------|------|------------------------|----------|-----------|----------------------|----------------------|------|------|
| 1     | 2a   | 1: 1: 100              | 24       | 97.4      | 14.1                 | 13.6                 | 1.46 | 0.48 |
| 2     | 2b   | 1: 1: 100              | 24       | 97.1      | 14.1                 | 7.6                  | 1.19 | 0.74 |
| 3     | 2c   | 1: 1: 100              | 72       | 89.9      | 13.1                 | 5.1                  | 1.11 | 0.62 |
| 4     | 2d   | 1: 1: 100              | 72       | 60.9      | 8.9                  | 6.2                  | 1.06 | 0.47 |
| 5     | 2e   | 1: 1: 100              | 90       |           | 13.1                 | 6.9                  | 1.10 | 0.76 |
| 6a    | 2e   | 1: 1: 100              | 96       | 13.5      |                      |                      |      |      |
| 7     | 2f   | 1: 0: 100              | 24       | 94.5      | 13.7                 | 6.6                  | 1.13 | 0.75 |
| 8     | 2f   | 1: 0: 200              | 25       | 88.5      | 25.6                 | 17.9                 | 1.11 | 0.76 |
| 9a    | 2f   | 1: 0: 100              | 72       | 97.1      | 14.1                 | 7.2                  | 1.11 | 0.78 |
| 10    | 2b   | 1: 2: 100              | 24       | 96.2      |                      |                      |      |      |
| 11    | 2b   | 1: 2: 100              | 14       | 84.2      |                      |                      |      |      |
| 12    | 2b   | 1: 1: 50               | 23       | 93.8      | 6.9                  | 4.4                  | 1.15 | 0.72 |
| 13    | 2b   | 1: 1: 150              | 24       | 94.9      | 20.6                 | 12.9                 | 1.24 | 0.76 |
| 14    | 2b   | 1: 1: 200              | 24       | 98.7      | 28.6                 | 16.0                 | 1.21 | 0.77 |

a Unless otherwise specified, the polymerization reactions were carried out at 70°C in toluene, [Cat.] = 0.01 M. b Measured by 1H NMR spectra. c Calculated from the molecular weight of rac-LA times the conversion of monomer and the ratio of [LA]/[BnOH]. d M_n was obtained from GPC which was timed 0.58. e D was obtained from GPC analyses. f Pd is the probability of meso linkages between monomer units determined from the methine region of the homonuclear decoupled 1H NMR spectroscopy at 25°C in CDCl3 (Fig. S2, ESI). g The polymerization reactions were carried out at 50°C. h M_n,calc was calculated from the molecular weight of rac-LA times the conversion of monomer and the ratio of [LA]/[Cat.].
probably caused by trace amount of water or other impurities in the reaction system. Higher or lower than 100 equiv. of rac-LA loadings gave high monomer conversion at 70 °C in 24 h when catalyzed by 2b/BnOH (Table 2, entries 12–14). A linear relationship between the number average molecular weights and [LA]0/[LA]/[BnOH]2 is observed (Fig. 6). This fact, combined with the narrow PDI values, imply the “living” character of the polymerization process and the possibility of the presence of multiple active species at high temperature, such as LAI/EtOBn and LAI(OBn)2. Meanwhile, side reactions such as trans-esterification and chain transfer are also present from the MALDI-TOF MS of PLA (Fig. S1, ESI†).

Homonuclear decoupled 1H NMR spectra in the methine regions of the PLA showed that isotactic enriched PLA were obtained when complexes 2b, 2c, 2e and 2f were employed as the catalysts. The Pm value range from 0.62 to 0.78. Complex 2c led to lower iso-selectivity and complexes 2b and 2f showed higher iso-selectivity. The iso-selectivity could be further enhanced by lowering the reaction temperature (Table 2, entry 9). Complexes 2a and 2d exhibited poor selectivity. They showed slightly heterotactic bias. These results proved that a bulky ortho-position substituent on the aromatic ring of phenoxycarbonyl group is important to increase the selectivity, but too bulky substituted like cumyl group is disadvantageous to enhance the selectivity of the polymerization. That is to say, the steric hindrance of the substituent is too large or too small to be disadvantageous for the selectivity of the polymerization. This is inconsistent with previous studies that the enhancement of stereoselectivity requires bulky substituent.15 The presence of 2-position substituent on the phenanthroline ring is also disadvantageous to improve the selectivity. In addition, the catalytic selectivity of complexes 2b and 2f is also higher than that of aluminum bipyridine phenolate complex [AlMe2(BpyPh2,4-Bu)]2, which led to polymer with a Pm value of 0.70 at 70 °C.

In order to better understand the polymerization process, the kinetics of rac-LA polymerization with complex 2f as the catalyst was studied. The plots of ln([LA]0/[LA]t) versus reaction time at different catalyst concentrations are shown in Fig. 7. The plots revealed linear relationship in each case, indicating the first order dependence of the polymerization on monomer concentration. The linear increase of Kapp with complex 2f concentration (Fig. 8) also indicates the order to be first-order. Therefore, the overall rate law in the form of −d[L]/dt = 1;([LA]/[Al])0 = 20, Kapp = 0.26936 ± 0.0041 h−1; (●) [LA]0/[Al]0 = 30, Kapp = 0.15847 ± 0.00445 h−1; (▲) [LA]0/[Al]0 = 40, Kapp = 0.11997 ± 0.00376 h−1; (▼) [LA]0/[Al]0 = 60, Kapp = 0.10436 ± 0.0034 h−1.

The ring-opening polymerization of rac-β-butyrolactone

Complexes 2a–2d and 2f were also assessed in the ring opening polymerization of rac-β-BL. Polymerizations were carried out in toluene solution at 70 °C (Table 3). Both 2b/BnOH and 2f showed good catalytic activity towards the ROP of rac-β-BL. They drove polymerization of 100 equiv. of monomer in higher than 90% conversions in 12 h. Complex 2d exhibited the lowest activity in catalyzing the ROP. 2.9% conversion be achieved in 24 at the same monomer loading and reaction temperature as above. The molecular weights determined by GPC are markedly lower than the calculated values. This is ascribed to the presence of transesterification and chain transfer side reactions, which is further confirmed by MALDI-TOF MS analysis of PHB.

Fig. 6 Plots of Mw (●, obtained from GPC analysis) and dispersity (▲, Mw/Mn) as a function of [LA]0/[LA]/[BnOH] for the polymerization of rac-LA catalyzed by 2b/BnOH at 70 °C. Conditions: [Cat.]0 = 0.01 M; solvent: toluene.

Fig. 7 Plot of ln([LA]0/[LA]t) versus time for the polymerization of rac-LA catalyzed by 2f in toluene at 70 °C, [LA]0 = 0.5 M. (■) [LA]0/[Al]0 = 20, Kapp = 0.26936 ± 0.0041 h−1; (●) [LA]0/[Al]0 = 30, Kapp = 0.15847 ± 0.00445 h−1; (▲) [LA]0/[Al]0 = 40, Kapp = 0.11997 ± 0.00376 h−1; (▼) [LA]0/[Al]0 = 60, Kapp = 0.10436 ± 0.0034 h−1.

Fig. 8 Kapp versus the concentration of 2f for the rac-LA polymerization at 70 °C in toluene ([LA]0 = 0.5 M, k0 = 10.3 dm3 mol−1 h−1).
Table 3: The ROP of β-butyrolactone catalyzed by complexes 2a–2d and 2f

| Entry | Cat. | \([\text{Cat.}]_0 : [\text{BnOH}]_0 : [\beta-\text{BL}]_0\) | Time (h) | Conv. (%) | \(M_{n,\text{calc}}^c\) (kg mol\(^{-1}\)) | \(M_{n,\text{GPC}}^d\) (kg mol\(^{-1}\)) | \(\delta^f\) |
|-------|------|-------------------------------------------------|----------|-----------|---------------------------------|---------------------------------|----------|
| 1     | 2a   | 1 : 1 : 100                                      | 12       | 37.9      | 3.4                             | 2.2                             | 1.10     |
| 2     | 2b   | 1 : 1 : 100                                      | 5        | 41.9      | 3.7                             | 1.2                             | 1.23     |
| 3     | 2b   | 1 : 1 : 100                                      | 12       | 94.4      | 8.3                             | 3.5                             | 1.14     |
| 4     | 2c   | 1 : 1 : 100                                      | 24       | 72.1      | 6.3                             | 2.0                             | 1.14     |
| 5     | 2d   | 1 : 1 : 100                                      | 24       | 2.9       |                                  |                                 |          |
| 6     | 2f   | 1 : 0 : 100                                      | 12       | 93.5      | 8.1\(^f\)                       | 2.3                             | 1.11     |

\(^a\) Unless otherwise specified, the polymerization reactions were carried out at 70 °C in toluene, [Cat.] = 0.01 M. \(^b\) Measured by \(^1\)H NMR spectra. \(^c\) Calculated from the molecular weight of \(\text{rac-BL}\) times the conversion of monomer and the ratio of \([\text{BL}]_0/[\text{BnOH}]_0\) plus the molecular weight of BnOH. \(^d\) \(M_n\) was obtained from GPC which was timed 0.54. \(^f\) \(D\) was obtained from GPC analysis. \(^f\) \(M_{n,\text{calc}}\) was calculated from the molecular weight of \(\text{rac-BL}\) times the conversion of monomer and the ratio of \([\text{BL}]_0/[\text{Cat}]_0\) plus the molecular weight of BnOH.

(Fig. S3, ESI†). It seems that the controllability showed by these complexes is lower than those found in the ROP of \(\epsilon-\text{CL}\) and \(\text{rac-LA}\). The polymer was atactic, as determined by the \(^{13}\)C NMR analysis in the carbonyl and methylene regions (Fig. S4, ESI†).

**Block copolymerization**

The synthesis of block copolymers was attempted by using catalyst 2f in toluene at different temperature (Table 4). For instance, the polymerization of 100 equiv. of \(\epsilon\text{-CL}\) in toluene catalyzed by 2f at 25 °C went to completion in 1.5 hour. Then 100 equiv. of \(\text{rac-LA}\) were added to the reaction system and the reaction was run for further 24 hours at 70 °C. \(^1\)H NMR spectrum of the resulting mixture showed \(\epsilon\text{-CL}\) and \(\text{rac-LA}\) were almost completely converted (Table 4, entry 2). The sequential addition of the two monomers led to the achievement of a PCL-b-PLA copolymer, which represents an experimental evidence of the living behavior of the polymerization promoted by this class of initiators. Other block copolymers can be synthesized in a similar manner (Fig. S5 and S6, ESI†). In order to obtain the PHB-b-PLA copolymer, \(\text{rac-LA}\) had to be added to living PHB chains. The opposite sequence of monomers addition led mainly to PLA and a low amount of the block copolymer (Table 4, entry 3). The importance of the order of the monomer addition in the block copolymerization was previously underlined in literature.\(^{16}\)

In order to confirm formation of the copolymers, we monitored the polymerization process of \(\epsilon\text{-CL}\) and \(\text{rac-LA}\) catalyzed by 2f and characterized the polymers. When 100 equiv. of \(\epsilon\text{-CL}\) monomer conversion approached to 99%, a 1/8 volume of sample was taken from the polymerization system for testing and showed its GPC \(M_n = 11\ 174\). Then 100 equiv. of \(\text{rac-LA}\) was added into the reaction system to generate the block copolymer PCL-b-PLA with GPC \(M_n = 17\ 187\) at 84.7% \(\text{rac-LA}\) conversion (Fig. S7, ESI†). \(^1\)H NMR and \(^{13}\)C NMR spectra of the PCL-b-PLA displayed all the characteristic signals, including the main bodies of the two blocks, BnO end and the monomer ends (Fig. 9 and 10). The \(^{13}\)C NMR spectra show the connecting portions of diblock copolymers of PCL-b-PLA, which proved the formation of block copolymers.\(^{17}\) The 2D DOSY NMR spectrum of the copolymer provided further evidence for the copolymerization (Fig. S8, ESI†). The spectrum showed that the multiplets of the poly(\(\epsilon\text{-caprolactone}\)) block (centered at 4.05, 2.30 and 1.65 ppm) and the multiplets of the poly(\(\text{rac-lactide}\)) block (centered at 5.15 and 1.57 ppm) lied at the same diffusion coefficient, and therefore belonged to the same polymeric chains.\(^{18}\) The \(^1\)H NMR spectrum of the polymer (Fig. 9) indicated polymer chains

![Fig. 9](image)

**Fig. 9** \(^1\)H NMR spectrum (CDCl\(_3\), 400 MHz, 25 °C) of the PCL-b-PLA copolymer.

Table 4: Formation of block copolymer catalyzed by complex 2f

| Entry | \([\text{Cat.}]_0 : [\text{M}_1]_0 : [\text{M}_2]_0\) | Time (h) | T (°C) | Conv. \(^b\) (M\(_1\)) | Conv. \(^b\) (M\(_2\)) | \(M_{n,\text{GPC}}^c\) (kg mol\(^{-1}\)) | \(\delta^f\) |
|-------|---------------------------------|----------|-------|-----------------|-----------------|---------------------------------|----------|
| 1     | 2f : CL : BL                     | 1.5 + 12 | 25 + 70| 99              | 82              | 15.0                             | 1.24     |
| 2     | 2f : CL : LA                     | 1.5 + 24 | 25 + 70| 99              | 99              | 21.0                             | 1.16     |
| 3     | 2f : LA : BL                     | 24 + 12  | 70     | 93              | 11              | 13.2                             | 1.18     |
| 4     | 2f : BL : LA                     | 12 + 24  | 70     | 98              | 84              |                                  |          |

\(^a\) The polymerization reactions were carried out in toluene, [Cat.] = 0.01 M. \([\text{Cat.}]_0 : [\text{M}_1]_0 : [\text{M}_2]_0 = 1 : 100 : 100\). \(^b\) Measured by \(^1\)H NMR spectra. \(^c\) \(M_n\) and \(\delta\) of copolymer was obtained from GPC analyses, GPC \(M_n\) without correction.
end-capped with a benzyloxy group and a hydroxyl group. End group analysis of PCL-b-PHB copolymer by $^1$H NMR spectroscopy also showed the polymer chains end-capped with a benzyloxy group and a hydroxyl group (Fig. S5, ESI†).

Conclusions

We have synthesized and characterized a series of aluminum complexes supported by 2-(1,10-phenanthroline-2-yl)phenolate ligands. In the presence of BnOH, the complexes efficiently catalyzed the ROP of ε-CL, rac-LA and rac-β-BL. The catalytic activity of the complexes is affected by the substituents on the ligands. In each case the 2-position substituent on the phenanthroline ring of the ligand is unfavorable. The pluses and minuses of the bulky ortho-position substituent on the aromatic ring of phenoxy group depend on reaction substrates that they catalyzed, but too bulky substituent is often unfavorable. The polymerization reaction led to PCL with good molecular weight control and narrow molecular weight distribution. Isotactic enriched PLA were obtained when 2b, 2c, 2e and 2f were used as the catalysts, while atactic poly(hydroxybutyrate) was got no matter which complex was employed. Kinetic analysis using 2f as the catalyst revealed that the polymerization of ε-CL was first-order dependence on monomer concentration, and the polymerization of rac-LA proceeded with first-order dependence on both monomer and catalyst concentration. The block polymerization were also performed utilizing the “living” character of the aluminum catalysts, forming block copolymers including PCL-b-PHB, PCL-b-PLA, and PHB-b-PLA.

Experimental

All air or moisture sensitive manipulations were performed under dry N$_2$ using standard Schlenk techniques. Solvents were distilled under N$_2$ over sodium/benzophenone (n-hexane and diethyl ether) or sodium (toluene) and degassed prior to use. AlEt$_3$ was purchased from Acros Organics and used as received. C$_6$D$_6$ and CDCl$_3$ were purchased from Cambridge Isotope Laboratories, Inc., and were degassed and stored over Na/K alloy (C$_6$D$_6$) or 4 Å molecular sieves (CDCl$_3$). ε-CL and rac-β-BL were stirred over CaH$_2$ for 24 h and distilled under vacuum. rac-LA was recrystallized three times from toluene prior to use. o-Bromophenols and 2-buty1-1,10-phenanthroline were prepared according to the reported methods." Other chemicals and solvents were purchased from commercial vendors. NMR spectra were recorded on a Bruker av400 spectrometer at ambient temperature. The chemical shifts of $^1$H and $^{13}$C NMR spectra were referenced to TMS or internal solvent resonances. Elemental analyses were performed on an Elementar Vario EL cube analyzer. Gel permeation chromatography (GPC) measurements were performed on a Waters 150C instrument equipped with UltraStyragel columns (103, 104, and 105 Å) and a 410 refractive index detector, using monodispersed polystyrene as the calibration standard. THF (HPLC grade) was used as an eluent at a flow rate of 1 cm$^3$ min$^{-1}$.

Synthesis of 1a

To a stirred solution of 2-bromo-4-(4-tert-butyl)phenol (1.37 g, 6.0 mmol) in Et$_2$O (20 cm$^3$), BuLi (2.5 M solution in hexane, 5.3 cm$^3$, 13.25 mmol) was added dropwise at $-78$ °C. After stirring for 2 h at room temperature, the resulting mixture was added dropwise to 1,10-phenanthroline (0.90 g, 5.0 mmol) in toluene (30 cm$^3$). The dark purple solution was stirred at the same temperature for additional 20 h. The reaction mixture was quenched with water (20 cm$^3$) and extracted with ethyl acetate. The combined organic layers were dried over Na$_2$SO$_4$ and then removed solvent by rotary evaporation. The residue was used for the next step without further purification. To a stirred solution of the crude product in ethyl acetate (20 cm$^3$), MnO$_2$ (8.7 g, 100 mmol) was added at room temperature. The black suspension was stirred at 60 °C for 12 h. The resulting mixture was dried over MgSO$_4$ and filtered through a celite pad to remove MnO$_2$. The organic layers were evaporated and purified by column chromatography (eluting with hexane/ethyl acetate = 2 : 1) to afford 1a as a yellow solid in overall 26.8% yield (0.44 g, 1.34 mmol). Anal. calcd for C$_{22}$H$_{20}$N$_2$O: C, 79.95; H, 6.29; N, 8.31%. Found: C, 79.95; H, 6.29; N, 8.22%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 16.13 (s, 1H, OH), 9.16 (d, J = 4.2 Hz, 1H, Ar), 8.30 (d, J = 8.7 Hz, 1H, Ar), 8.24–8.17 (m, 2H, Ar), 7.96 (d, J = 2.2 Hz, 1H, Ar), 7.73 (s, 2H, Ar), 7.60 (dd, J = 8.0, 4.3 Hz, 1H, Ar), 7.45 (dd, J = 8.6, 2.3 Hz, 1H, Ar), 7.14 (d, J = 8.6 Hz, 1H, Ar), 1.41 (s, 9H, Bu$^t$). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 159.49, 157.70, 150.74, 144.80, 142.87, 140.80, 137.25, 135.86, 129.70, 128.98, 126.39, 126.31, 125.75, 123.41, 122.68, 118.83, 118.36, 117.93, 34.33, 31.74.

Synthesis of 1b

Compound 1b was synthesized using the same procedure as for 1a. Thus, 2-bromo-4,6-di-tert-butylphenol (1.42 g, 5 mmol) was treated successively with Bu$^t$Li (4.4 cm$^3$, 2.5 M solution in hexane, 11 mmol) and 1,10-phenanthroline (0.90 g, 5.0 mmol). The resulting species was oxidized with MnO$_2$ to afford, after purified by column chromatography (eluting with hexane/ethyl acetate = 5 : 1), 1b as an orange solid in overall 41.3% yield (0.794 g, 2.06 mmol). Anal. calcd for C$_{26}$H$_{28}$N$_2$O: C, 82.01; H, 5.65; N, 8.34%. Found: C, 82.00; H, 5.70; N, 8.30%.
A solution of \(1a\) (0.328 g, 1.0 mmol) in toluene (15 cm\(^3\)) was cooled to 0 °C. A solution of \(\text{AlEt}_3\) (0.72 mmol, 0.6 M solution in heptane, 0.43 mmol) was added to the cooled solution. The color of the solution instantaneously changed from light yellow to deep red.

The resultant mixture was warmed to room temperature and stirred for 12 h. The solution was filtered and the filtrate was concentrated to afford deep red crystalline solid of \(2a\) (0.198 g, 48%). Anal. calc. for \(\text{C}_{56}\text{H}_{47}\text{AlNO}_2\): C, 75.70; H, 7.09; N, 6.79%. Found: C, 75.43 H, 6.84; N, 6.59. \(^1H\) NMR (400 MHz, \(\text{C}_6\text{D}_6\)); \(\delta\) 8.57 (dd, \(J = 4.7, 1.4\) Hz, 1H, Ar), 7.64 (\(J = 8.9\) Hz, 1H, Ar), 7.60 (\(J = 2.4\) Hz, 1H, Ar), 7.48 (\(J = 8.8\) Hz, 1H, Ar), 7.39 (dd, \(J = 8.8, 2.5\) Hz, 1H, Ar), 7.35 (dd, \(J = 8.8\) Hz, 1H, Ar), 7.30 (dd, \(J = 8.2, 1.3\) Hz, 1H, Ar), 6.99–6.94 (m, 2H, Ar), 6.73 (dd, \(J = 8.1, 4.7\) Hz, 1H, Ar), 1.54 (t, \(J = 8.0\) Hz, 6H, Me), 1.32 (s, 9H, \(\text{Bu}^\text{t}\)), 0.75–0.64 (m, 2H, \(\text{Al}-\text{CH}_2\)), 0.53–0.43 (m, 2H, \(\text{Al}-\text{CH}_2\)). \(^{13}\text{C\ NMR}\) (101 MHz, \(\text{C}_6\text{D}_6\)); \(\delta\) 165.23, 161.07, 164.34, 140.91, 140.03, 138.22, 138.12, 136.78, 132.71, 127.98, 126.14, 125.55, 124.56, 124.30, 124.01, 123.28, 119.39, 34.16, 31.75, 11.96, 6.98.

**Synthesis of \(2b\)**

A solution of \(1b\) (0.23 g, 0.60 mmol) in toluene (15 cm\(^3\)) was cooled to 0 °C. \(\text{AlEt}_3\) (1.1 cm\(^3\), 0.6 M solution in heptane, 0.66 mmol) was added to the cooled solution. The resultant mixture was warmed to room temperature and stirred for 12 h. The solution was filtered and the filtrate was concentrated to afford deep red crystalline solid of \(2b\) (0.28 g, 81%). Anal. calc. for \(\text{C}_{56}\text{H}_{47}\text{AlNO}_2\): C, 76.89; H, 7.96; N, 5.98%. Found: C, 76.78 H, 7.94; N, 6.80. \(^1H\ NMR\) (400 MHz, \(\text{C}_6\text{D}_6\)); \(\delta\) 8.60 (dd, \(J = 4.7\) Hz, 1H, Ar), 7.84 (dd, \(J = 24.5\) Hz, 1H, Ar), 7.63–7.56 (m, 1H, Ar), 7.54 (s, 1H, Ar), 7.29 (dd, \(J = 8.8\) Hz, 2H, Ar), 6.98–6.90 (m, 2H, Ar), 6.76–6.69 (m, 1H, Ar), 1.99 (s, 9H, \(\text{Bu}^\text{t}\)), 1.43 (s, 9H, \(\text{Bu}^\text{t}\)), 1.39 (t, \(J = 8.1\) Hz, 6H, Me), 0.78–0.67 (m, 2H, \(\text{Al}-\text{CH}_2\)), 0.54–0.43 (m, 2H, \(\text{Al}-\text{CH}_2\)). \(^{13}\text{C\ NMR}\) (101 MHz, \(\text{C}_6\text{D}_6\)); \(\delta\) 164.31, 161.70, 146.49, 141.78, 140.67, 140.23, 137.84, 137.42, 136.70, 129.18, 127.91, 126.14, 125.31, 124.60, 124.14, 123.92, 123.16, 119.88, 36.18, 34.49, 31.92, 30.40, 11.82, 6.97, 6.52.

**Synthesis of \(\text{C}_{2}\)**

A solution of \(\text{C}_{2}\) (0.182 g, 0.36 mmol) in toluene (10 cm\(^3\)) was cooled to 0 °C. To the solution was added \(\text{AlEt}_3\) (0.72 mmol, 0.6 M solution in heptane, 0.43 mmol). The resultant mixture was warmed to room temperature and stirred overnight. The solution was filtered and the filtrate was concentrated to afford deep red crystalline solid of \(\text{C}_{2}\) (0.161 g, 76.4%). Anal. calc. for \(\text{C}_{40}\text{H}_{31}\text{AlNO}_2\cdot\text{C}_2\text{H}_5\text{C}\): C, 82.42; H, 7.21; N, 4.09%. Found: C, 82.25 H, 6.98; N, 4.25. \(^1H\ NMR\) (400 MHz, \(\text{C}_6\text{D}_6\)); \(\delta\) 8.56 (dd, \(J = 4.8, 1.4\) Hz, 1H, Ar), 7.77 (dd, \(J = 2.4\) Hz, 1H, Ar), 7.72–7.67 (m, 2H, Ar), 7.50 (dd, \(J = 2.4\) Hz, 1H, Ar), 7.49–7.42 (m, 3H, Ar), 7.36 (t, \(J = 7.8\) Hz, 2H, Ar), 7.29–7.08 (m, 7H, Ar), 7.07–7.00 (m, 3H, Ar), 6.87 (s, 2H, Ar), 6.65 (dd, \(J = 8.1, 4.8\) Hz, 1H, Ar), 2.12 (s, 6H, Me), 2.11 (s, toluene), 1.78 (s, 6H, Me), 1.12 (t, \(J = 8.1\) Hz, 6H, Me), 0.43–0.33 (m, 2H, \(\text{CH}_2\)), 0.24–0.14 (m, 2H, \(\text{CH}_2\)). \(^{13}\text{C\ NMR}\) (101 MHz, \(\text{C}_6\text{D}_6\)); \(\delta\) 163.96, 161.19, 151.91, 151.84, 146.35, 141.72, 140.66, 140.22, 137.89, 137.58, 136.83, 136.59, 131.35, 129.33, 128.57, 128.45, 128.19, 127.94, 127.37, 126.62, 126.02, 125.98, 125.70, 125.58, 125.25, 125.20, 124.37, 124.11, 123.89, 119.72, 43.22, 43.00, 31.41, 30.08, 11.43, 6.16.
Synthesis of 2d
A solution of 1d (0.47 g, 1.07 mmol) in toluene (15 cm³) was cooled to 0 °C. ALEt₃ (2.0 cm³, 0.6 M solution in heptane, 1.2 mmol) was added to the cooled solution. The resultant mixture was warmed to room temperature and stirred overnight. The solution was filtered and the filtrate was concentrated to afford red crystalline solid of 2d (0.26 g, 46.3%). Anal. calcd for C₁₄H₂₅AlN₂O: C, 77.83; H, 8.64; N, 5.34%. Found: C, 77.77 H, 8.70; N, 5.21.

CH₃NMR (400 MHz, C₆D₆): δ 8.71 (d, J = 7.0 Hz, 1H, Ar), 2.47 (s, 9H, Bu), 1.34 (m, 8H, CH₂ + Me), 0.90 (t, J = 7.3 Hz, 3H, Me), 0.81–0.68 (m, 2H, CH₂), 0.52–0.43 (m, 2H, CH₃), 1.43–1.34 (m, 8H, CH₂), 2.5 Hz, 1H, Ar), 7.67 (d, J = 8.9 Hz, 1H, Ar), 7.56 (d, J = 2.3 Hz, 2H, Ar), 7.29 (t, J = 8.8 Hz, 2H, Ar), 6.98–6.92 (m, 2H, 2H, Ar), 2.77 (dd, J = 8.1, 4.7 Hz, 1H, Ar), 2.13–2.01 (m, 2H, CH₂), 1.97 (s, 9H, Bu), 1.42 (s, 9H, Bu), 1.13 (d, J = 6.5 Hz, 6H, Me), 1.02 (d, J = 6.5 Hz, 6H, Me), 0.75 (dd, J = 13.2, 7.5 Hz, 2H, CH₂), 0.48 (dd, J = 13.2, 6.5 Hz, 2H, CH₂). ¹³C NMR (101 MHz, C₆D₆): δ 164.06, 162.53, 161.59, 141.30, 141.05, 140.18, 138.24, 137.58, 136.75, 128.97, 126.76, 125.70, 125.17, 125.07, 124.86, 124.61, 123.44, 120.78, 36.70, 36.18, 34.50, 32.37, 31.96, 30.35, 23.33, 14.22, 11.71, 6.50.

Polymerization of ε-caprolactone
A typical polymerization procedure was exemplified using 2a/BnOH as the catalyst. Complex 2a (24.5 mg, 0.0594 mmol) was dissolved in toluene (5.4 cm³) at 50 °C. To the stirred solution BnOH (0.60 cm³, 0.1 M solution in toluene, 0.06 mmol) and ε-CL (0.63 cm³, 5.94 mmol) were successively added. The polymerization reaction was terminated after 5 h by addition of several drops of glacial acetic acid. The mixture was stirred at room temperature for 30 min. The resulting solution was dropped into cool methanol with stirring. The white precipitate was filtered under reduced pressure and washed with cool methanol. For GPC analysis, the sample was dissolved in THF, passed through a short neutral aluminum oxide column, precipitated in methanol, and dried under vacuum.

Polimerization of rac-β-BL followed the same procedure as for the ROP of ε-CL.

Table 5 Details of the X-ray structure determination of complex 2c

| Complex | Empirical formula | fw | Crystal system | Space group | a (Å) | b (Å) | c (Å) | α (deg) | β (deg) | γ (deg) | V (Å³) | Z | Dcalcd (g cm⁻³) | F(000) | μ (mm⁻¹) |
|---------|------------------|----|----------------|-------------|-------|-------|-------|---------|---------|---------|-------|---|----------------|--------|--------|
| 2c·C₄H₄ | C₄H₆NOAl        | 684.86 | Monoclinic     | P2₁/a       | 13.1762(12) | 12.9320(11) | 23.471(2) | 90 | 96.3170(10) | 3975.1(6) | 4 | 1.144 | 1464 | 0.088 |
|         |                  |     |               |             |       |       |       |       |         |         |    | 2.21 to 25.02 | 19 732 |         |
|         |                  |     |               |             |       |       |       |       |         |         |    | 6997 (Rint = 0.0910) | 0/532 |         |
|         |                  |     |               |             |       |       |       |       |         |         |    | 1.019 |         |       |

Final R indices [I > 2σ(I)]
R₁ = 0.0596, wR₂ = 0.0853

R indices (all data)
Largest diff peak and hole [e Å⁻³]
0.156 and −0.159

R = Σ||Fo||−|Fc||/Σ|Fo|, wR = [Σw(Fo² − Fc²)/Σw(Fo²)]¹/².
toluene (2.1 cm$^3$) at 70 °C. The polymerization reaction was terminated after 24 h by adding several drops of glacial acetic acid. The mixture was stirred at room temperature for 30 min. The resulting solution was dropped into cool methanol with stirring. The white precipitate was filtered under reduced pressure and washed with cool methanol. For GPC analysis, the sample was dissolved in THF, passed through a short neutral aluminum oxide column, precipitated in methanol, and dried under vacuum.

X-ray crystallography

Single crystals of complex 2c were mounted in Lindemann capillaries under N$_2$. Diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo K$_\alpha$ radiation (λ = 0.71073 Å). The structure was solved by direct methods using SHELXS-97 (ref. 20) and refined against $\mathbf{F}^2$ by full-matrix least squares using SHELXL-97.\(^{21}\) Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determination are listed in Table 5.

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