Chiral Salan Aluminium Ethyl Complexes and Their Application in Lactide Polymerization


Introduction

Poly(lactic acid)s (PLAs) prepared from renewable resources are important biodegradable materials for biomedical, pharmaceutical, and agricultural applications.[1] Although different methods for the synthesis of PLAs have been exploited, the most convenient is the ring-opening polymerization (ROP) of lactide (LA), the cyclic dimer of lactic acid. Current research in this area is particularly focused on the design and synthesis of single-site catalyst/initiators of gener-

Abstract: Synthetic routes to aluminium ethyl complexes supported by chiral tetradentate phenoxamine (salan-type) ligands \[\text{[Al} \text{OC} \text{C}_6 \text{H}_4 \text{(R-6-R-4)} \text{CH}_2 \text{N(CH}_3 \text{(C}_6 \text{H}_{10}) \text{NCH}_3 \text{]} \text{CH}_3 \text{]}\] (4, 7: \(R = \text{H}\); 5, 8: \(R = \text{Cl}\); 6, 9: \(R = \text{CH}_3\)) are reported. Enantiomerically pure salan ligands 1–3 with (R, R) configurations at their cyclohexane rings afforded the complexes 4, 5, and 6 as mixtures of two diastereoisomers (a and b). Each diastereoisomer a was, as determined by X-ray analysis, monomeric with a five-coordinated aluminium central core in the solid state, adopting a cis-(O,O) and cis-(Me,Me) ligand geometry. From the results of variable-temperature (VT) \(^1\text{H}\) NMR in the temperature range of 220–335 K, \(^1\text{H}–^1\text{H}\) NOESY at 220 K, and diffusion-ordered spectroscopy (DOSY), it is concluded that each diastereoisomer b is also monomeric with a five-coordinat-
ed aluminium central core. The geometry is intermediate between square pyramidal with a cis-(O,O), trans-(Me,Me) ligand disposition and trigonal bipyramidal with a trans-(O,O) and trans-(Me,Me) disposition. A slow exchange between these two geometries at 220 K was indicated by \(^1\text{H}–^1\text{H}\) NOESY NMR. In the presence of propan-2-ol as an initiator, enantiomerically pure (R, R) complexes 4–6 and their racemic mixtures 7–9 were efficient catalysts in the ring-opening polymerization of lactide (LA). Polylactide materials ranging from isotactically biased (\(P_m\) up to 0.66) to medium heterotactic (\(P_r\) up to 0.73) were obtained from rac-lactide, and syndiotactically biased polylactide (\(P_r\) up to 0.70) from meso-lactide. Kinetic studies revealed that the polymerization of \((S,S)-\text{LA}\) in the presence of 4/propan-2-ol had a much higher polymerization rate than (R, R)-LA polymerization (\(k_{SS}/k_{RR} = 10.1\)).

Keywords: aluminium · chirality · lactide · polymerization · salan

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al formula \( L_nMR^{[3]} \) in which \( M \) is a central metal atom, ligated with \( L_n \), which represents an ancillary ligand. \( R \) is the initiating group covalently linked through a remaining vacant orbital. The steric and electronic properties of the ligand affect the activity and the stereoselectivity of the catalyst. Appropriate combinations of \( L_n \) with \( M \) and \( R \) have generated numerous catalyst/initiators containing \( \text{Ca}^{[3]} \), \( \text{Al}^{[4]} \), \( \text{Zn} \) or \( \text{Mg}^{[5]} \), \( \text{Ti}^{[6]} \) or \( \text{Fe}^{[7]} \), as well as the rare earth elements \( [8] \) as central metal atoms. Most of these catalysts are highly efficient and lactide polymerization proceeds in a well-controlled manner. Moreover, in certain cases stereoregular PLAs have been obtained from rac-LA [an equimolar mixture of (S,S)-LA and (R,R)-LA] or meso-LA by use of these metal complexes. \([9–11]\) Some recent breakthroughs in the stereoselective polymerization of lactide in the presence of rare earth metals complexed by achiral phenoxyamine ligands have been achieved by the groups of Carpentier \([9]\) and Cui \([10]\) who have prepared highly heterotactic PLAs as central metal atoms. Most of these catalysts are highly efficient and lactide polymerization proceeds in a well-controlled manner. Moreover, in certain cases stereoregular PLAs have been obtained from rac-LA [an equimolar mixture of (S,S)-LA and (R,R)-LA] or meso-LA by use of these metal complexes. \([9–11]\) Some recent breakthroughs in the stereoselective polymerization of lactide in the presence of rare earth metals complexed by achiral phenoxyamine ligands have been achieved by the groups of Carpentier \([10]\) and Cui \([10]\) who have prepared highly heterotactic PLAs from rac-LA.

Tetradeinate phenoxyamine ligands are usually referred to as salan-type ligands, which can be considered fully reduced Schiff base (salen) ligands (Scheme 1). \([11]\) The salan-type ligands have more flexible structures than salen ligands, due to the sp\(^3\) hybridization of their amine nitrogen atoms. A salan ligand containing a trans-1,2-diaminocyclohexane bridge may lead to various kinds of interesting chiral metal complexes. Recently, chiral Fe(salan), \([12,13]\) Ti(salan), \([14,15]\) and V(salan) \([16]\) complexes have been studied and applied in the asymmetric oxidation of sulfides. Chiral Ti(salan) \([17–20]\) complexes have been exploited in the asymmetric addition of metal alkyls to aldehydes, whereas Mo(salan) \([21,22]\) complexes have been used in the enantioselective pinacol coupling of aryl aldehydes. Moreover, Kol and co-workers have demonstrated that chiral Zr(salan) complexes have the ability to initiate isospecific polymerization of hex-1-ene, 4-methylpent-1-ene, \([23]\) or vinylcyclohexane, \([24]\) as well as the cycopolymerization of hexa-1,5-diene. \([25]\)

The structures and catalytic applications of chiral Al(salan) complexes, however, have never been reported. \([25]\) Previously, we described a chiral Jacobsen salen aluminium isopropoxide, which exerts significant stereocentrol in rac-LA polymerization, affording highly isotactic PLAs with \( P_i \) values of up to 0.93. \([26–28]\) In this paper we describe the synthesis and structures of chiral salan aluminium ethyl complexes with regard to their ligand wrapping modes, as well as to their catalytic behavior in lactide polymerization in the presence of propan-2-ol as an initiator.

### Results and Discussion

#### Synthesis of chiral salan aluminium ethyl complexes: Enantiomeric (R,R)-1,2-diaminocyclohexane was obtained from trans-1,2-diaminocyclohexane by a procedure described by Larrow et al. \([29]\) The synthesis of the ligand precursors (R,R)-1 and rac-1 (Scheme 1) was accomplished by a three-step procedure. Firstly, a condensation between racemic or (R,R)-1,2-diaminocyclohexane and salicylaldehyde (2 equiv) yielded the salan intermediate. Subsequent reduction of the imine bonds in the presence of an excess of NaBH\(_4\) afforded the salan intermediate. The ligand precursors were obtained by condensation of the secondary amine groups with an excess of formaldehyde and reduction with an excess of NaBH\(_4\) (Scheme S1 in the Supporting Information). The syntheses of the ligand precursors rac-2, (R,R)-2, rac-3, and (R,R)-3 (Scheme 1) were carried out similarly, except that the salan intermediates were synthesized through Mannich condensations of 2,4-substituted phenols, formaldehyde, and racemic or (R,R)-1,2-diaminocyclohexane (Scheme S2 in the Supporting Information). All ligands were isolated as white crystalline solids in high yields after recrystallization from acetone.

Treatment of the enantiomeric pure salan ligand precursors (R,R)-1, (R,R)-2, or (R,R)-3 with equimolar amounts of AlEt\(_3\) in toluene at 70°C resulted in the formation of salan aluminium ethyl complexes 4, 5, and 6, respectively (Scheme 1). Interestingly, the \(^1\)H NMR spectroscopic data for 4, 5, and 6 in [\(D_8\)]toluene at 295 K clearly revealed the presence of two species in each case. One species (a) gives a disymmetric resonance pattern, whereas the other (b) gives a symmetric resonance pattern. The molar ratios of \(a/b\) in 4, 5, and 6 were 10:4, 10:2.5, and 10:3, respectively. As an example, in the \(^1\)H NMR spectrum of 4 (Figure 1), the appearance of four doublets for the benzylic ArCH\(_2\)-NCH\(_2\) protons at 3.70, 3.60, 3.19, and 2.71 ppm with a 2J(H,H) coupling constant of 13.0 Hz, together with the two singlets at 1.84 and 1.72 ppm for the N–CH\(_3\) protons (Figure 1, top), both indicated disymmetric surroundings of these groups in the salan complex, which was denoted 4a. On the other hand, the symmetric resonance pattern includes two doublets for the benzylic ArCH\(_2\)-NCH\(_2\) protons appearing at 3.44 and 3.28 ppm with the same 2J(H,H) value of 13.0 Hz and a singlet at 1.80 ppm for the N–CH\(_3\) protons (Figure 1, top), and this complex was denoted 4b. Moreover, the methylene protons in the aluminium ethyl groups in 4a or 4b displayed a significant difference in chemical shift (Figure 1, bottom), showing that these protons in 4a or 4b are all dia-stereotopic. Because of the gem-hydrogen effect, each quar-
tet is split into an unresolved double quartet. The $^1$H–$^1$H NOESY spectrum of 4 in [D$_8$]toluene at 295 K revealed no slow exchange between the species 4a and 4b on the NMR timescale (Figure S1 in the Supporting Information). Single crystals of 4a were isolated from a saturated toluene solution at room temperature and characterized by X-ray analysis (Figure 2; for crystallographic data see Table 1). Despite several attempts, only single crystals of species 4a were obtained.

The complex 4a was monomeric with a five-coordinated central aluminium atom (Figure 2). The geometry around such a five-coordinated aluminium atom would ideally be square pyramidal or trigonal bipyramidal and can be expressed by a $t$ value, which is 0 in the case of an ideal square pyramidal (sqp) and 1 in that of an ideal trigonal bipyramidal (tbp) geometry.[27] The $t$ value of 4a is 0.53, revealing a geometry intermediate between A, an ideal sqp, and B, an ideal tbp in this complex (Scheme 2, below). The $t$ value of 4a is higher than that of the corresponding chiral salen aluminium methyl complex ($t$ = 0.35),[28] indicating a more flexible ligand geometry, as a result of the sp$^3$ hybridization of the tertiary amine nitrogen atoms in the salen complex. The two phenolic oxygen atoms exist in a cis arrangement relative to the central aluminium. The Al1/C0 N1/C138 and Al1/C0 N2/C138 bond lengths (Table S1 in the Supporting Information) are both in the 2.01–2.26/C138 range, values generally observed for Al/C0 N bond lengths in tetradentate salen aluminium ethyl complexes.[29] The two methyl groups on the nitrogen atoms are in a cis configuration relative to the five-membered ring formed by Al1, N1, N2, C1, and C6. The nitrogen atoms have become chiral, due to the coordination with Al. The configurations of the two nitrogen atoms are R for N2 and S for N1.

To clarify the structure of 4b further, additional NMR characterization was performed. In $^{27}$Al NMR, four-coordinated aluminium complexes give resonance signals at ~70 ppm, whereas five- or six-coordinated aluminium complexes give resonance signals at ~40 and ~0 ppm, respectively.[30] The $^{27}$Al NMR spectrum of 4 did not exhibit any peaks in the ~70 to 280 ppm range, perhaps due to the asymmetric coordination of the salen ligand around the aluminium center.[31] However, DOSY NMR measurements revealed that 4a and 4b have comparable diffusion coefficients, indicating similar effective molecular radii, and further demonstrating that 4b is also monomeric. This also indicates that 4b may be a diastereoisomer of 4a. The VT $^1$H NMR spectra of 4 ([D$_8$]toluene) in the 295–335 K temperature range did not reveal any tendency for the resonances of the benzylic ArCH$_2$–NCH$_3$ protons of 4b to coalesce (Figure S2 in

Table 1. Crystallographic data for 4a and 9a.

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the Supporting Information). This indicates that the two Al–N bonds in 4b are stable at room temperature or even higher temperatures. The symmetric resonance pattern for the four benzylic ArCH₂–NCH₃ protons of 4b at 295 K indicates that these protons are symmetrically arranged in the complex. From this information, either the highly symmetric sqp geometry C or the tbp geometry D, or even a geometric intermediate between C and D, was considered the most probable for 4b (Scheme 2, below). Because of the presence of only one singlet for the N-methyl groups of 4b at 295 K, it is assumed that the two N-methyl groups exist in a trans arrangement. To reveal the structure of 4b fully, 1D and 2D NMR experiments were carried out.

Firstly, VT ¹H NMR analysis of 4 in [D₈]toluene was performed. With decreasing temperature the two doublets for the four benzylic ArCH₂–NCH₃ protons of 4b seen at 295 K split into two doublets (partly overlapping) and a broad peak at 220 K (Figure 3). It is speculated that with a further decrease in the temperature this broad peak should also split into two doublets. Moreover, the singlet representing the N–CH₃ protons at 295 K split into two broad peaks at 220 K (Figure S3 in the Supporting Information).

The ¹H–¹H NOESY NMR spectrum of 4 at 220 K displayed positive off-diagonal cross-peaks (with the diagonal cross-peaks phased in positive sign, and the NOE cross-peaks observed at opposite sign) between the ArCH₂–NCH₃ protons (Figure 4) as well as the N–CH₃ protons of 4b (Figure S4 in the Supporting Information). All of these observations indicate that at 220 K a slow exchange takes place between two geometries of 4b. From these data, it is assumed that diastereoisomer 4b adopts a geometry intermediate between C and D with the N-methyl groups existing in a trans orientation (Scheme 2). At 295 K, diastereoisomer 4b shows a fast exchange between the sp geometry C and the tbp geometry D on the NMR timescale. At low temperatures, the exchange between these two geometries was slow enough to be observable by NMR. So far, however, we have not been able to conclude whether either the (R,R) or (S,S) configurations (with respect to the nitrogen centers) or even mixtures of the two are present in 4b (Scheme 2).

On the basis of the NMR and X-ray analysis, it is reasonable to assume two different pathways by which these chiral salan aluminium ethyls were formed. Because the conformation of the cyclohexane ring is fixed upon formation of the five-coordinated aluminium complex, the positions of the methyl groups on the nitrogen atoms will also be fixed. Once the free ligand in the solution coordinates the aluminium atom with the N-methyl groups in a cis position, a wrapping mode with a cis-(O,O) geometry in-between A (sqp) and B (tbp) should be favored. The chiral salan ligand generates diastereoisomer 4a with (R,S) chiral nitrogen centers. On the other hand, if the free ligand in the solution adopts a conformation with the N-methyl groups in a trans position, a geometry intermediate between C (sqp) and D (tbp) as in

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**Figure 3.** VT ¹H NMR spectra of 4 in [D₈]toluene between 220–295 K (ArCH₂–NCH₃ region).

**Figure 4.** ¹H–¹H NOESY NMR spectrum of 4 at in [D₈]toluene 220 K (ArCH₂–NCH₃ region). Evidence for the exchange between the two geometries of 4b is provided by the presence of additional exchange-NOE cross-peaks labeled X.

**Scheme 2.** Schematic representation of the geometries adopted by diastereoisomers a and b.
The salan aluminium complexes 7–9 were obtained from racemic mixtures of the ligands 1–3 (Scheme 1). Only single crystals of 9a could be isolated from a saturated toluene solution at room temperature. X-ray analysis of 9a (Figure 5; Table 1) revealed that the complex was also dissymmetric with a five-coordinated central aluminium atom as in 4a. The packing modes in the unit cell of 9a show that a racemate crystallization had occurred. A τ value of 0.90 is calculated, indicating a trigonal bipyramidal geometry with N1 and O2 occupying the axial positions, and N2, C17, and O1 located in the equatorial plane. The central aluminium atom deviates from the equatorial plane by ca. 0.201 Å in the direction of O2. The axial bond length for Al1–O2 [1.7931(18) Å] is slightly longer than that for its equatorial counterpart Al1–O1 [1.7631(17) Å]. Moreover, in relation to N2, placed in the equatorial plane with a bond length of 2.039(2) Å from Al1, the N1 atom located at the axial site is weakly coordinated to Al1 with a longer Al1–N1 distance [2.448(2) Å]. Similar weak interactions were also observed in an aluminium complex ligated by an achiral salan ligand reported by Gibson and co-workers and in an aluminium complex stabilized by a 1,10-phenanthroline-bridged bis(phenolate) ligand reported by Okuda et al. As in 4a, the methyl groups on the nitrogen atoms exist in a cis arrangement relative to the five-membered ring formed by C6, C1, N2, N1, and Al1. The configurations of the two nitrogen atoms are R for N2 and S for N1.

**Ring-opening polymerization of rac- and meso-LA in solution:** Because it had so far not been possible to separate diastereoisomers a and b, complexes 4–6 and 7–9 were each treated with propan-2-ol (1 equiv) to generate the active isopropoxide initiators for the ROP of rac- or meso-LA in situ. All polymerizations were carried out in toluene at 70°C, and the levels of conversion were monitored by 1H NMR determination of samples withdrawn from the reaction mixtures. In the presence of propan-2-ol as an initiator, 4–6 and 7–9 furnished PLAs with similar number average molecular weights as calculated, as well as narrow molecular weight distributions, indicating well-controlled polymerization. Representative polymerization results are summarized in Table 2.

The tacticities of the resulting polymers were determined by inspection of the methine region in the homonuclear decoupled 1H NMR spectra. Compound 4/propan-2-ol and compound 7/propan-2-ol polymerized rac-LA to form isotactically biased polymers with $P_m$ values of 0.66 (Figure 6a) and 0.62, respectively. In contrast, 6/propan-2-ol and 9/propan-2-ol, with methyl substituents at the ortho and para positions of their phenolic groups, furnished atactic materials from rac-LA with $P_m$ values of 0.55 and 0.57, respectively. Interestingly, 5/propan-2-ol afforded heterotactically biased PLAs with a $P_m$ value of 0.64. Heterotactic PLAs cannot be obtained from rac-LA through a site control mechanism (SCM) with use of an enantiomeric pure complex, so this reveals the existence of a chain-end control mechanism (CEM) with use of 5/propan-2-ol in the rac-LA polymerization. The heterotacticity of the PLAs resulting from rac-LA increased to 0.73 when 6/propan-2-ol was used (Figure 6b), which probably indicates the operation of a propagating chain exchange mechanism as proposed by Coates and co-workers. In this case, the heteroselectivity of 8/
propan-2-ol should be enhanced relative to that of 5/propan-2-ol because of a more frequent positive cooperation effect between a CEM and a SCM, resulting from the occurrence of rapid exchange between propagating chains bound to each different enantiomeric ligand before insertion of a subsequent monomer unit (Scheme 3). The 4/propan-2-ol, 5/propan-2-ol, and 6/propan-2-ol systems afforded syndiotactically biased PLAs from meso-LA with P values of 0.64, 0.70 (Figure 6c), and 0.69, respectively. This clearly confirms the operation of a SCM in meso-LA polymerization with use of these chiral complexes.

To gain a better insight into the polymerization mechanism, detailed kinetic studies of rac-LA in the presence of 4–6 and 7–9 together with propan-2-ol as initiator were performed. Conversion of rac-LA over time at various concentrations of 7/propan-2-ol in toluene at 70°C were monitored by 1H NMR spectroscopy ([LA]₀ = 0.534 M, [Al]₀ = 10.7 to 21.4 mm, and [LA]₀ = 0.267 M, [Al]₀ = 8.9 mm). In each case, first-order kinetics in monomer were observed and the appropriate semilogarithmic plots are shown in Figure 7a. The polymerization of rac-LA in the presence of 7/propan-2-ol as catalyst/initiator thus proceeds according to:

$$-\frac{d[LA]}{dt} = k_{\text{app}}[LA]$$  \hspace{1cm} (1)

where $k_{\text{app}} = k_p[Al]^x$, and $k_p$ is the propagation rate constant. To determine the order in aluminium ($x$), $k_{\text{app}}$ was plotted against [Al]₀ (Figure 7b). In this plot, $k_{\text{app}}$ increased linearly with the aluminium concentration, indicating a first order in aluminium ($x$). Therefore, the polymerization of rac-LA in the presence of 7/propan-2-ol followed the overall kinetic equation:

![Figure 6. Methine regions of homonuclear decoupled 1H NMR spectra of PLAs produced: from rac-LA by use of a) 4/propan-2-ol, b) 8/propan-2-ol, and c) from meso-LA with 5/propan-2-ol as catalyst/initiator system.](image)

![Scheme 3. Proposed polymer exchange mechanism for the explanation of the enhancement of heteroselectivity and activity of 8 compared to 5 (* indicates the aluminium isopropoxides formed by 8 upon addition of propan-2-ol).](image)
Conversion versus time data were also collected for the polymerization of rac-LA in the presence of 4-propan-2-ol (toluene, 70°C, [LA]₀ = 0.534 mm, [Al]₀ = 10.7 mm, and [LA]₀ = 0.267 mm, [Al]₀ = 6.68 mm). In each case, a significant deviation from a first-order plot for ln[LA]₀/[LA]ₜ versus time was observed at high levels of conversion (Figure S5 in the Supporting Information), suggesting a kinetic preference of 4 for a certain lactide enantiomer. The polymerization of (S,S)- or (R,R)-LA with application of 4-propan-2-ol revealed a difference between kₚ values of one order of magnitude at the same aluminium concentration much lower than that of other reported chiral Schiff base aluminium systems [kₚ(R) ≈ 20 reported by Spassky for (R)-(SalBinap)AlOCH₃][28] and kₚ(S)/kₚ(R) ≈ 14 reported by us for (R,R)-cyclohexylsalen-AlOPr[30]. Moreover, the introduction of chlorine atoms or methyl groups both lead to decreased kinetic resolution for 5 and 6 with (R,R)- and (S,S)-LA. Unlike 4, which shows a preference towards (S,S)-LA, 5 has a preference toward (R,R)-LA with a kₚ(S)/kₚ(R) value of 0.62 (Table 4, entry 2, Figure S7), as does 6, with a kₚ(S)/kₚ(R) value of 0.82 (Table 4, entry 3, Figure S8).

Finally, conversion versus time data were collected for the polymerization of rac-LA in the presence of 5-propan-2-ol or 8-propan-2-ol and of 6-propan-2-ol or 9-propan-2-ol (toluene, 70°C, [LA]₀ = 0.534 mm, [Al]₀ = 10.7 mm). In each case, first-order kinetics in monomer were observed, and the semilogarithmic plots for these polymerizations are shown in Figure 8a and b, respectively. The kₚ and kₚ values determined are collected in Table 3. The kₚ and kₚ values for 8-propan-2-ol (kₚ = 5.26 m⁻¹ h⁻¹) and 9-propan-2-ol (kₚ = 3.32 m⁻¹ h⁻¹) are both slightly higher than those for 5 (kₚ = 3.49 m⁻¹ h⁻¹) and 6 (kₚ = 2.88 m⁻¹ h⁻¹), respectively, which further confirms a positive cooperation effect between a CEM and a SCM resulting from the occurrence of polymer exchange. The substituents on the salan ligand phenolate rings also affect the polymerization rate significantly. Introducing methyl groups results in a remarkable decrease in kₚ from 23.8 m⁻¹ h⁻¹ for 7 to 3.32 m⁻¹ h⁻¹ for 9. The kₚ values for 5 and 8 are much lower than the kₚ value for 7 (23.8 m⁻¹ h⁻¹).

This indicates that the introduction of chlorine substituents does not enhance the polymerization rate. Several studies have indicated that electron-withdrawing chlorine substituents on ligands increase Lewis acidities of metal centers, thereby enhancing rates of lactone polymerization.[25] These results indicate that the polymerization rate constant includes several steps, including monomer approach and binding, nucleophilic addition through the metal–alkoxide bond, and rearrangement causing the cleavage of the acyl-oxygen bond. Although the enhancement of the Lewis acidity of the metal center most probably leads to a more facile approach.
and binding of the monomer, other changes resulting from the introduction of chlorine atoms may reduce the rates of other steps.

Conclusions

In conclusion, a series of aluminium ethyl complexes ligated by chiral salan ligands has been reported. The structures of other steps.

Experimental Section

General conditions: All manipulations requiring a dry atmosphere were performed under dry argon by use of standard Schlenk techniques or in a glovebox (M. Braun, Germany). Solvents were dried by heating at reflux over sodium/benzophenone (toluene and hexane) or calcium hydrate (propan-2-ol) for at least 24 h. Anhydrous deuterated solvents ([D$_6$]toluene and [D$_6$]benzene, Aldrich) were kept under nitrogen over molecular sieves (4 Å). Starting materials for the synthesis of ligand precursors 1-3 were purchased from Aldrich and were used without further purification. The ligands 1-3 were synthesized by literature procedures.[21] Triethylaluminium from Aldrich was used as received. ([S,S]- rac-, and [meso]-LA (Purac Biochem b.v., the Netherlands) were purified by recrystallization three times from anhydrous toluene, followed by drying under vacuum at 30°C for 24 h before use.

Instruments and measurements: Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV 400 MHz instrument at 298 K or a Varian Inova 600 MHz spectrometer at 295 K. [D$_6$]Chloroform, [D$_6$]benzene, and [D$_6$]toluene were used as solvents. Homonuclear decoupled 1H NMR, 1H-1H COSY, 1H-1H NOESY, and diffusion-ordered DOSY spectra were recorded on a Bruker Avance II 600 MHz spectrometer operating at 600.13 MHz. The spectrometer was fitted with a Great 3/10 gradient amplifier and a triple-nucleus TXI probe with z-gradient. All experiments were performed at 295 K with use of standard pulse sequences from the Bruker library. Pulsed field gradient stimulated echo (PFGSE) diffusion experiments were performed by use of the bipolar stimulated echo sequence with 32 increments in the gradient strength (2-95%), typically 16 averages per increment step, and 100 ms diffusion time. Levels of monomer conversion were determined from the integrals of signals at 1.65 ppm, representing lactide monomer, and 1.59 ppm, representing PLA. $P_m$ (the probability of meso linkages) and $P_r$ values (the probability of racemic linkages) were calculated from different tetrad intensities measured by homonuclear decoupled 1H NMR. Gel permeation chromatography (GPC) measurements were conducted with a Waters 410GPC instrument with THF as the eluent (flow rate: 1 mL min$^{-1}$, 35°C). The molecular weights were determined relative to polystyrene standards.

Compound (R,R)-1: [H NMR (400 MHz, CDCl$_3$, 298 K): $\delta = 10.33$ (br, 2H; ArOH), 7.18 (td, 3J(H,H) = 1.2 Hz, 3J(H,H) = 8.4 Hz, 2H; ArH), 6.98 (d, 3J(H,H) = 7.2 Hz, 2H; ArH), 6.80 (m, 4H; ArH), 3.84 (d, 3J(H,H) = 13.2 Hz, 2H; ArCH$_2$(NCH$_3$)), 2.71 (d, 3J(H,H) = 12.9 Hz, 2H; ArCH$_2$(NCH$_3$)), 2.23 (s, 6H; NCH$_3$), 2.02 (d, 3J(H,H) = 10.2 Hz, 2H; cyclohexene hydrogens), 1.81 (d, 3J(H,H) = 6.9 Hz, 2H; cyclohexene hydrogens), 1.15 ppm (m, 4H; cyclohexene hydrogens); 13C NMR (100 MHz, CDCl$_3$, 298 K): $\delta = 157.84$ (ArCOH), 129.03 (ArCH), 128.61 (ArCH), 122.31 (ArCH), 119.03 (ArCH), 116.49 (ArCH), 61.91 (cyclohexane carbons), 56.97 (ArCH$_2$(NCH$_3$)), 35.53 (NCH$_3$), 25.27 (cyclohexane carbons), 22.32 ppm (cyclohexane carbons); elemental analysis calcd (%) for C$_{24}$H$_{30}$N$_2$O$_2$: C 74.54, H 8.53, N 7.90; found: C 74.99, H 8.32, N 7.94.}

Figure 8. a) First-order kinetic plots for the ROP of rac-LA in the presence of 8 or 5 and propan-2-ol in toluene at 70°C with [LA]$_0$ = 0.534 m, [Al]$_0$ = 10.7 mm. b) First-order kinetic plots for the ROP of rac-LA in the presence of 9 or 6 and propan-2-ol in toluene at 70°C with [LA]$_0$ = 0.534 m, [Al]$_0$ = 10.7 mm.
Compound 1: A solution of triethylaluminium in toluene (2.0 mL, 2 mL) was added dropwise by syringe at room temperature to a solution of (R,R)-1 (1.42 g, 4 mmol) in toluene (2 mL). Instantaneous evolution of ethane was observed. The colourless reaction mixture was stirred at 70°C overnight and allowed to cool slowly to room temperature. The solvent was removed under reduced pressure, and the residue was repeatedly washed with anhydrous n-hexane to afford the product as colourless crystals (1.09 g, 2.68 mmol, 67%). The 1H NMR spectra clearly indicated the presence of two complexes. 1H NMR (complex 4a, 500 MHz, [D6]toluene, 295 K): δ = 7.17 (dd, 2J(H,H) = 12.0 Hz, 2J(H,H) = 7.2 Hz, 2H; ArH), 7.07 (t, 2J(H,H) = 7.2 Hz, 2H; ArH), 6.84 (t, 2J(H,H) = 5.4 Hz, 2H; ArH), 6.74 (m, 2H; ArH), 3.70 (d, 2J(H,H) = 13.0 Hz, 1H; ArCH(NCH3)), 3.65 (d, 2J(H,H) = 13.0 Hz, 1H; ArCH(NCH3)), 3.19 (d, 2J(H,H) = 13.0 Hz, 1H; ArCH(NCH3)), 2.71 (d, 2J(H,H) = 13.0 Hz, 1H; CH2ArCH(NCH3)), 2.29 (td, 2J(H,H) = 1.2 Hz, 2J(H,H) = 3.6 Hz, 1H; CH), 2.02 (td, 2J(H,H) = 1.2 Hz, 2J(H,H) = 3.6 Hz, 1H; CH), 1.76 (3H, NCH3), 1.54 (t, 3H, NCH3), 1.51 (d, 2H, cyclohexane hydrogens), 1.34 (m, 2H, cyclohexane hydrogens), 0.58 (m, 4H, cyclohexane hydrogens), 0.10 (dq, 1H; AlCH2CH3), 0.05 (dq, 1H; CH), 1.69 (s, 3H; NCH3), 1.58 (d, 2H; cyclohexane hydrogens), 1.44 (t, 3H; CH2), 1.37 (m, 4H; cyclohexane hydrogens), 0.45 (m, 4H; cyclohexane hydrogens), 0.23 (dq, 1H; AlC(CH3)2), 0.20 ppm (dq, 1H; AlCH2CH3). 13C NMR (100 MHz, [D6]toluene, 298 K): δ = 153.59 (ArCOH), 130.60 (ArCH), 127.32 (ArCH), 127.12 (ArCH), 125.07 (ArCH), 121.81 (ArCH), 61.46 (cyclohexane carbons), 57.00 (ArCH(NCH3)), 35.31 (C2H5), 25.32 (cyclohexane carbons), 22.27 (cyclohexane hydrogens), 20.47 (C6D6), 15.66 ppm (ArCH); elemental analysis calcd (%) for C43H41AlCl4N2O2: C 52.77, H 5.35, N 5.13; found: C 52.56, H 5.42, 35.83, 24.53, 11.43, 0.86 ppm; elemental analysis calcd (%) for C43H41AlCl4O2N2: C 52.77, H 5.35, N 5.13; found: C 52.56, H 5.42, 35.83, 24.53, 11.43, 0.86 ppm; elemental analysis calcd (%) for C43H40AlCl4N2O2: C 52.77, H 5.35, N 5.13; found: C 52.56, H 5.42, 35.83, 24.53, 11.43, 0.86 ppm.

General procedure for lactide polymerization: In a typical polymerization experiment, 1.0 g (6.94 mmol, 0.26 mmol, 67%). The 1H NMR spectra clearly indicated the presence of two complexes. 1H NMR (complex 4b, 600 MHz, [D8]toluene, 295 K): δ = 7.02 (d, 2J(H,H) = 12.0 Hz, 2H; ArH), 6.56 (d, 2J(H,H) = 6.0 Hz, 2H; ArH), 3.71 (d, 2J(H,H) = 12.0 Hz, 1H; ArCH(NCH3)), 3.66 (d, 2J(H,H) = 12.0 Hz, 1H; ArCH(NCH3)), 3.27 (d, 2J(H,H) = 12.0 Hz, 1H; ArCH(NCH3)), 2.70 (d, 2J(H,H) = 12.0 Hz, 1H; ArCH(NCH3)), 2.60 (3H; ArCH3), 2.46 (s, 3H; ArCH3), 2.36 (s, 6H; CH2Ar), 2.01 (td, 1H; cyclohexane hydrogens), 1.89 (s, 2H; NCH3), 1.73 (s, 3H; NCH3), 1.57 (t, 3H; CH2ArCH3), 1.39 (m, 4H; cyclohexane hydrogens), 0.60 (dq, 1H; AlCH2CH3), −0.05 ppm (dq, 1H; AlCH2CH3). 13C NMR (complex 6b, 600 MHz, [D8]toluene, 295 K): δ = 7.03 (s, 2H; ArH), 1.64 (s, 2H; ArH), 3.46 (br, 2H; ArCH(NCH3)), 3.32 (d, 2J(H,H) = 12.0 Hz, 2H; ArCH(NCH3)), 2.59 (s, 6H; ArCH3), 2.34 (s, 6H; ArCH3), 2.09 (2H, CH2), 1.79 (s, 6H; NCH3), 1.44 (t, 3H; CH2ArCH3), 1.37 (m, 4H; cyclohexane hydrogens), 0.21 (dq, 1H; AlCH2CH3). 13C NMR (100 MHz, [D6]benzene, 298 K): δ = 157.08, 156.45, 131.79, 131.59, 131.41, 126.85, 126.54, 125.24, 122.84, 62.84, 61.17, 59.42, 53.16, 42.09, 35.19, 24.30, 22.69, 22.20, 21.76, 16.29, 11.50, 11.12 ppm; elemental analysis calcd (%) for C25H21AlCl4O3: C 72.38, H 8.89, N 6.05; found: C 72.09, H 9.02, N 6.26.

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Lactide Polymerization


For the formation of syndiotactic PLAs, see references [9b,10a,12b].

For the formation of racemic PLA PLAs, see references [9b,10a,12b].

For the formation of isotactic or stereoblock PLAs, see: a) N. Spasman, A. P. Dove, V. C. Gibson, E. L. Marshall, A. J. P. White, D. J. Williams, Carpentier, Inorg. Chem. 2007, 46, 2280; and references [9b,12,13].

For the formation of syndiotactic PLAs, see references [9b,10a,12b].

[9] For the formation of syndiotactic PLAs, see references [9b,10a,12b].


[11] For the formation of syndiotactic PLAs, see references [9b,10a,12b].


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