Salalen Aluminium Complexes and their Exploitation for the Ring Opening Polymerisation of rac-Lactide

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In this paper we report the first use of Al(III) salalen complexes for the ring opening polymerisation of rac-lactide. Poly lactides with narrow polydispersities (PDLs range from 1.04 – 1.65) and moderate degrees of stereoselectivity were formed. Eight salalen Al(III) complexes have been prepared and fully characterised by solution-state NMR spectroscopy and where appropriate single crystal X-ray diffraction. With ligand 3H₂ either a monomeric or dimeric Al(III) species was formed, the dimeric species was favoured at low concentrations. The complexes were tested for the ring opening polymerisation of rac-lactide in toluene at 80 °C or 100 °C. Interestingly, various tacticities of polymer were formed, which were dependent upon the nature of the group bound to the amine nitrogen centre.

Introduction

In the last decade there has been an explosion of interest in the field of single-site catalysts for the ring opening polymerisation (ROP) of rac-lactide (rac-LA) to afford poly lactide (PLA). The polymer itself is not only sourced from sustainable materials but is biodegradable. In addition the polymer properties can be tuned by judicious choice of the catalyst, which can invoke stereoselectivity in the resultant polymerisation. For example, stereoblock isotactic PLA has a melting point of ca. 230 °C whereas poly-L-lactide has a melting point of ca. 180 °C. There have been many impressive advances in catalysts within the area and metals such as those in Groups 1–4, Zn(II), and pertinent to this study Al(III) have all been utilised. For example, Gibson has shown that minor alterations to the ligand can have significant effects on the stereochemistry of the resulting polymer. The use of Al(III) for the ROP of rac-LA is well established. One of the earliest such reports is that of Spassky and co-workers who used a complex based on a chiral Schiff base ligand of R-(+)-1,1’-binaphthyl-2,2’-diamine. This was active for the production of isotactically enriched PLA. The vast majority of Al(III) initiators for the production of PLA are based on either salan or salen ligands; we have recently demonstrated that Group 4 salalen complexes are active for the polymerisation of rac-lactide under both solution and melt conditions. The results herein represent the first example of the use of salalen ligands with Al(III) for the polymerisation of rac-LA. Catalytic reactions involving aluminium salalen complexes are rare and notable examples are by Katsuki et al who have shown that they are active for the oxidation of sulfides and the hydrophosphonylation of aldehydes. However, due to their facile nature of the preparation and degree of synthetic variability the use of salalen ligands is proving more popular.

Results and discussion

In this publication a series of Al(III) salalen complexes have been prepared and tested for the ROP of rac-LA. The ligands and complexes used in this study are shown in Scheme 1. The steric effects of the group on the amine, and the impact of changing the substituents (both electronic and sterics) on the salen phenoxide fragment have been investigated. The complexes were simply prepared by the reaction of 1 equivalent of AlMe₃ with 1 equivalent of the salalen ligand in toluene. Complexes based on ligands 2H₂, 3H₂, 7H₂ and 8H₂ were characterised by single crystal X-ray diffraction, Figure 1. The production of crystals of suitable quality for diffraction studies was challenging as these complexes were highly soluble in common organic solvents.

Scheme 1 Ligands and complexes prepared in this study.
The crystals were formed by slowly cooling a saturated solution of the complexes in hexane to −20 °C. For the crystallographically characterised complexes the Al(III) centre was seen to be in a highly distorted trigonal pyramidal geometry with C(1)-Al(1)-N(1) 113.68(13)°, C(1)-Al(1)-C(1) 124.68(14)° and O(2)-Al(1)-N(2) 165.45(12)°, for Al(3)Me, Figure 1, with the τ values for these complexes ranging from 0.56 – 0.80. This also suggests a bias towards the trigonal bipyramidal geometry. The phenoxy trans to the imine has the shortest Al-O bond distance and as expected the Al-Namine distance is considerably shorter than that of the Al-Namine. To the best of our knowledge these are the first examples of crystallographically characterised Al-alkyl salen complexes. The only previous Al(III)-salen complex characterised in the solid-state is the chiral Al-Cl system of Katsuki, in which an analogue of Jacobsen’s ligand was employed.12 It should also be noted that, to date, all Al(III) complexes of salan or salen ligands in the Cambridge Crystallographic data base are symmetric in their phenoxy substituents.13 There is a necessity for novel ligand systems, for Al(III), that can be easily prepared and derivatised.

The complexes have C₃v symmetry and all adopt a β-cis configuration in the solid-state. Upon complexation the tertiary amine becomes chiral and due to the chelation of the ligand the metal centre is also chiral; the S configuration at N(2) induces the Λ form in the complex where the R configuration corresponds to the Δ form. The complexes crystallise in centro-symmetric space groups so both forms are present.† The ¹H NMR spectra for these complexes are in agreement with the solid-state structures being maintained in solution, with resonances at ca. −0.5 ppm for the methyl group and at ca. 7.4 ppm for the imine proton, also the CH₂ groups are now diastereotopic indicating that the ligand is “locked” in position once coordinated to Al(III).†

If the reaction was performed at a lower concentration in toluene a second product was observed, Figure 2. Again this is a C₃v symmetric complex, however the Al(III) centres are now tetrahedral in geometry. In this case the salalen 3H₂ has reacted with two equivalents of AlMe₃ forming Al(3)Me₁₈. Under these lower dilution conditions both the 1:1 and 1:2 species were produced as evidenced by the ¹H NMR spectrum and it proved troublesome to separate the different forms. However, the 1:1 complexes could be isolated in high purities under more concentrated conditions.†

The complexes were tested for the ROP of rac-LA in solution at either 80 or 100 °C for 24 or 72 hours with the addition of 1 equivalent of benzyl alcohol (BnOH) to generate the alkoxide in-situ, the results of which are shown in Table 1.
All complexes were shown to be active for the polymerisation of rac-LA with the addition of 1 equivalent of BnOH. Relatively narrow polydispersity indices were observed, except with the polymers formed with complex Al(4)Me. MALDI-ToF mass spectrometry analysis of the polymers prepared with Al(3)Me indicate the presence of the benzyl alcohol end group (entries 6 and 7), which would be expected from the coordination insertion mechanism. Interestingly, the repeat unit of the polymer was seen to be 144 mass units. This is indicative of only a small degree of transesterification taking place. The initiators were also able to offer a degree of stereocontrol in the polymerisations. Complexes based on ligands 2H2, 4H2, 6H2 and 8H2 (entries 2-5, 8, 9, 12, 13 and 17) have a slight isotactic bias, whilst those based on 3H2, 5H2 and 7H2 (entries 6, 7, 10, 11, 14 and 15) afforded PLA with a moderate heterotactic bias, especially the polymer produced from Al(5)Me. Unlike previous work with Al(III) salan complexes where changing the substituents on the aromatic rings played a significant role in the stereoselectivity, it would appear in this case the group on the amine nitrogen R3 is more important. In this current work [except for Al(1)Me] when R3 = Ph slightly isotactic PLA was observed, but when this group was changed to Me poly lactide with a heterotactic bias was formed.

**Conclusions**

In conclusion we have shown for the first time that Al-salalen complexes are active for the ROP of rac-LA with narrow molecular weight distributions. We have also shown that there is a correlation between the group on the amine nitrogen and the tacticity of the resultant polymer.

**Acknowledgments**

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**Experimental**

For the preparation and characterisation of metal complexes, all reactions and manipulations were performed under an inert atmosphere of argon using standard Schlenk or glovebox techniques. rac-LA (Aldrich) was recrystallised from toluene and sublimed twice prior to use. All other chemicals were purchased from Aldrich. All solvents used in the preparation of metal complexes and polymerisation reactions were dry and obtained via SP5 (solvant purification system). 1H and 13C[1H] NMR spectra were recorded on a Bruker 250, 300 or 400 MHz instrument and referenced to residual solvent peaks. Coupling constants are given in Hertz. Elemental analyses were performed by Mr. A. K. Carver at the Department of Chemistry, University of Bath. The ligands were prepared according to standard literature procedures and the purity confirmed via 1H/13C[1H] NMR and HR-MS prior to use.

**Typical Polymerisation procedure**

For solution polymerisations a monomer:initiator ratio of 100:1 was used. In all cases toluene (10 ml) was added to a Schlenk followed by the initiator and 1 eq of BnOH, the lactide (0.72 g) was added and the flask heated for the desired time at the desired temperature. The reaction was quenched by the addition of methanol (20 ml). 1H NMR spectroscopy (CDCl3) and GPC (THF) were used to determine tacticity and molecular weights (Mw and Mn) of the polymers produced; P, (the probability of heterotactic linkages) were determined by analysis of the methine region of the homonuclear decoupled 1H NMR spectra.
Table 2 X-ray crystallographic data

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<tr>
<th>Compound reference</th>
<th>Chemical formula</th>
<th>Crystal system</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
<th>α°</th>
<th>β°</th>
<th>γ°</th>
<th>Unit cell volume/Å³</th>
<th>Temperature/K</th>
<th>Space group</th>
<th>Pcab</th>
<th>P</th>
<th>P2₁</th>
<th>P2₁/n</th>
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<tbody>
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<td>9.7286(7)</td>
<td>11.0181(4)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>7290.77</td>
<td>150(2)</td>
<td>Pcab</td>
<td>P</td>
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<td>P2₁/n</td>
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<tr>
<td>Al(3)(Me)</td>
<td>C₅H₅AlN₃O₂</td>
<td>Triclinic</td>
<td>12.5299(10)</td>
<td>10.7180(11)</td>
<td>14.6309(15)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>1295.98(17)</td>
<td>150(2)</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P2₁/n</td>
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<tr>
<td>Al(3)(Me)₂</td>
<td>C₆H₇Al₂N₃O₂</td>
<td>Triclinic</td>
<td>5.2266</td>
<td>5.0544</td>
<td>5.7856(5)</td>
<td>90</td>
<td>72.4385(5)</td>
<td>75.027(16)</td>
<td>1514.6(2)</td>
<td>150(2)</td>
<td>P</td>
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<td>5.2266</td>
<td>5.0544</td>
<td>5.7856(5)</td>
<td>90</td>
<td>72.4385(5)</td>
<td>75.027(16)</td>
<td>1514.6(2)</td>
<td>150(2)</td>
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<td>75.027(16)</td>
<td>1514.6(2)</td>
<td>150(2)</td>
<td>P</td>
<td>P</td>
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<td>P2₁/n</td>
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</table>

Complex Preparation

A representative procedure for the preparation of Al(3)Me is given, see supporting information for further details for all other complexes:

3H₂ (0.502 g, 1.22 mmol) was dissolved in toluene (20 cm³) to which AlMe₃ (0.6 ml of a 2.0 M solution in hexane, 1.22 mmol) was added and stirred for 2 hours. After which time the solvent was removed in vacuo and the product was recrystallised in hexane. After 5 days at –20 °C a crop of crystals were obtained which were filtered and dried. ¹H NMR (CD₂Cl₂) - 0.42 (3H, s, CH₃), 1.46 (9H, s, C(CH₃)₃), 1.65 – 1.76 (1H, m, CH₂), 1.79 (9H, s, C(CH₃)₃), 1.80 (3H, s, CH₃), 2.10 – 2.23 (1H, m, CH₂), 2.43 – 2.52 (1H, m, CH₂), 2.53 (3H, s, CH₃), 2.59 (1H, d J = 12.0 Hz, CH₂), 2.66 – 2.79 (1H, m, CH₃), 3.56 (1H, d J = 12.0 Hz, CH₂), 6.56 (1H, t J = 7.5 Hz, Ar-H), 6.76 (1H, dd J = 7.5 Hz, J = 1.0 Hz, Ar-H), 6.92 (1H, d J = 2.5 Hz, Ar-H), 7.23 (1H, d J = 7.0 Hz, Ar-H), 7.35 (1H, s, CH), 7.60 (1H, d J = 2.5 Hz, Ar-H). ¹C¹[H] (CD₂Cl₂) - 10.0, (Al-CH₃), 16.5 (CH₃), 30.1, 32.3 (C(CH₃)₃), 34.4, 35.5 (C(CH₃)₃), 44.1 (CH₃), 51.2, 54.4, 59.2 (CH₂), 115.3 (Ar-CH), 117.2, 122.1 (Ar-C), 123.8, 124.0 (Ar-CH), 131.2 (Ar-C), 131.4, 137.1 (Ar-CH), 138.2, 138.7 (Ar-C), 156.9, 167.2 (Ar-O), 172.7 (CH).

X-Ray Crystallography

Crystallographic data are summarised in Table 2. All data were collected on a Nonius Kappa CCD area detector diffractometer using Mo-Kα radiation (λ = 0.71073 Å) at a temperature of 150(2) K, and all structures were solved by direct methods and refined on all F² data using SHELXL-97.¹⁶ Hydrogen atoms were included in idealised position. Refinement was straightforward with the following noteworthy points – for Al(8)Me one ²Bu group was disordered over two positions in a 60:40 ratio the minor component was left isotropic, due to crystal quality the Rint for this structure was higher than desirable.

Notes and references