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Metal influence on the iso- and hetero-selectivity of complexes of bipyrrrolidine derived salan ligands for the polymerisation of *rac*-lactide†

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In this paper we have prepared a series of Ti(IV), Hf(IV) and Al(III) complexes based on bipyrrrolidine salan pro-ligands. The Hf(IV) complexes have all been characterised in the solid-state, the chiral ligands coordinate to Hf(IV) in an α -*cis* manner whereas the *meso* ligand coordinates in a β -*cis* geometry. The Hf(IV) complexes are all active for the ROP of *rac*-lactide in the melt, with the fluxional *meso* complex affording a strong isotactic bias $P_m = 0.84$. As expected Hf(3)(OⁱPr)₂ polymerised L-LA faster than *rac*-LA ($k_{app} = 5.9 \times 10^{-3} \text{ min}^{-1}$ vs. $3.8 \times 10^{-3} \text{ min}^{-1}$). For Ti(IV) complexes atactic PLA was formed. The salan pro-ligands have also been complexed to Al(III), and the novel Al-Me and Al-OⁱPr complexes were characterised in the solid and solution state. Al(1)(OⁱPr) was fluxional on the NMR timescale, whereas Al(3)(OⁱPr) was locked in solution with no exchange. Interestingly, the Al(III) complexes of 3H₂ produce PLA with a very strong heterotactic bias P_r upto 0.87, whereas atactic PLA is produced with 1H₂. For Al(3)(OⁱPr) a linear relationship is observed with M_n and conversion. Experiments with the addition of an equivalent of *rac*-LA to the selective initiators have also been performed and are discussed.

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Introduction

Over recent years there has been a concerted effort to find iso-selective initiators for the ROP of *rac*-LA.¹ Isotactic PLA from *rac*-LA has an enhanced melting point over PLA produced from the ROP of enantiopure monomers.² This coupled with the desirable biodegradation and the fact that the monomer can be prepared from annually renewable resources has spurred research in this area.³ The majority of iso-selective initiators are based on aluminium – for example early work of Feijen and Spassky employing chiral salen complexes.^{14,15} However, in recent years yttrium and lanthanide complexes have also shown promise in this area.⁵ Moreover, we have recently shown that a zirconium complex of a bipyrrrolidine salan ligand is able to produce PLA with a strong isotactic bias ($P_m = 0.84$).⁶ In this paper we have expanded further on this study with Ti(IV), Hf(IV) complexes and Al(III) systems.

It is difficult to predict the resulting stereochemistry of the polymer that an initiator may produce. Al(III) complexes have a propensity to produce highly isotactic PLA.⁷ For example, in 2004 Gibson prepared aluminium salan complexes based on an *N,N'*-dimethylethylenediamine with H-substituents on the phenoxide and this afforded moderate isotactic PLA ($P_m = 0.68$).^{1c} However, when this was changed to a Cl-substituted phenolate heterotactic PLA was produced, P_r of 0.88. However, with the *N,N'*-dibenzylethylenediamine version with H-substituents highly isotactic PLA ($P_m = 0.79$) was observed.^{1c} We have shown that with Al(III) salalen complexes the tacticity can be changed from moderate heterotacticity to moderate isotacticity by altering the substituent on the amine nitrogen.¹¹ In 2012 Williams prepared a series of yttrium phosphasalens initiators and it was observed that on varying the backbone either isotactic or heterotactic PLA could be produced.^{5a} Kol and Okuda have, with a series of ONSO ligands complexed to Zr(IV), shown that the selectivity can be dependent upon the fluxionality of the complex, with rigid ligands forming isotactic PLA and fluxional catalysts heterotactic PLA.⁸ However, it has recently been reported that with phenylene ONSO ligands the tacticity was determined by the substituents on the phenolate and not fluxionality.⁹ There are limited examples in the literature of ligands which when complexed to different metals afford different tacticities. Ma has shown a switch in stereoselectivity with a series of ONN derived salan ligands complexed to either zinc or magnesium.¹⁰ With magnesium a hexa-coordinated

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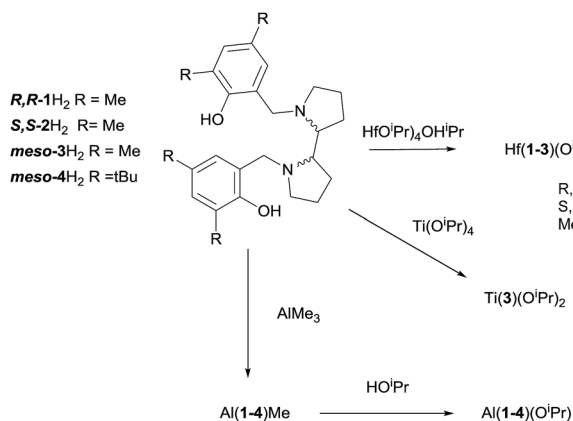
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Ligands and complex preparation

The Hf(IV) complexes, Fig. 1, are analogues to the previously reported zirconium complexes.⁶ As before the *meso* ligand is coordinated in a β -*cis* geometry and the chiral species as the α -*cis* isomers.^{6,12} Solution state NMR spectroscopic measurements are in agreement with the solid state structures being maintained in solution. For the enantiopure complexes the ligands are “locked” in position as indicated by discrete doublets for the methylene CH₂ moieties and there are no exchange peaks observed in the NOESY/EXSY spectrum at 298 K (CDCl₃). However, from NOESY/EXSY experiments on Hf(3)(OⁱPr)₂, there is evidence of ligand exchange on the NMR timescale. There are exchanges processes not only of the aliphatic back bone but also in the aromatic region of the spectrum, for instance the resonance at 6.51 ppm interchanges with that at 6.67 ppm. Furthermore, DOSY NMR (CDCl₃) was performed on the complex further suggesting one species in solution with a diffusion coefficient of $7.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ being observed, this equates to a hydrodynamic radii of *ca.* 5.1 Å. The *meso*-3H₂ ligand was also reacted with Ti(OⁱPr)₄ to form Ti(3)(OⁱPr)₂ which was recrystallised in hexane. As expected the β -*cis* geometry was observed in the solid-state. Solution state NMR spectroscopy confirmed this was the solution structure with two distinct isopropoxide methine resonances.

Initially the prolignans **1H₂** and **3H₂** were reacted with AlMe₃ to generate Al(**1** or **3**)Me.^{7c} The solid-state structures have been determined for Al(**1** or **3**)Me and are shown in Fig. 2.^{7c} The tau



Scheme 1 Ligands and complexes used in this study.

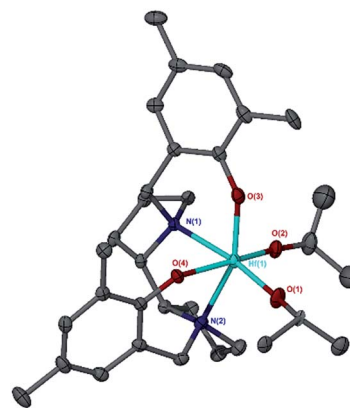


Fig. 1 Solid state structure of $\text{Hf}(\mathbf{3})(\text{O}i\text{Pr})_2$. Ellipsoids are shown at the 30% probability level, hydrogen and disordered moieties have been removed for clarity.

value for Al(1)Me is 0.97 indicating a strong preference for the R,R -ligand to form a trigonal bipyramidal structure, this is exemplified by the O(1)–Al(1)–N(2) and O(2)–Al(1)–C(1) angles of $168.66(6)^\circ$ and $122.09(8)^\circ$ respectively.¹³ There is a clear difference between Al(1)Me and Al(3)Me with the bipyrrrolidine rings of the *meso* ligand forming a “bowl” shape around the metal centre, this is observed in the space filling model (see ESI†). For Al(3)Me there are three crystallographically independent aluminium centres, with tau values of 0.37, 0.28 and 0.76 indicating there is no clear preference for either square pyramidal or trigonal bipyramidal in this case. This is exemplified by the O(1)–Al(1)–N(2) and O(2)–Al(1)–C(1) angles of $154.81(6)^\circ$ and $113.08(6)^\circ$ for one of the Al(3)Me moieties *cf.* $136.55(6)/105.95(8)^\circ$ and $162.79(6)/119.09(7)^\circ$ for the analogous angles in the other crystallographic unique Al(III) centres. The solution state ^1H NMR spectrum (298 K, $\text{C}_6\text{D}_5\text{CD}_3$) for Al(3)Me showed two aromatic resonances and two sharp doublets for the methylene Ar–CH₂–N moieties. Furthermore, six aromatic, four CH₂ and one CH resonance were observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR, indicating that both aryl rings and pyrrolidine rings are chemically equivalent. This is in contrast to the solution state NMR spectrum of Al(1)(Me) which was very broad and fluxional at 298 K. However, at 233 K the spectrum sharpened and four aromatic resonances were observed in the ^1H NMR spectrum, in the $^{13}\text{C}\{^1\text{H}\}$ spectrum eight CH₂, two CH and four Ar–CH₃ resonances were observed indicating that, once coordinated, each half of the ligand are no longer equivalent.

To generate species that are capable of acting as ROP initiators in the melt the Al–Me complexes were reacted with HOⁱPr to afford discrete alkoxide species.¹⁴ Al(1)(OⁱPr) crystallises in the orthorhombic space group $P2_12_12_1$. The aluminium centre is in a pseudo trigonal bipyramidal motif with a tau value of 0.70. Al(3)(OⁱPr) crystallises in the cubic space group $Pa\bar{3}$ and the aluminium centre is in a pseudo trigonal bipyramidal motif with a tau value of 0.64. The solution state behaviour mirrors that of the alkyl complexes. At 298 K (CDCl₃) Al(3)(OⁱPr) the solution state ¹H NMR spectrum consisted of two aryl resonances and discrete resonances for the Ar-CH₂-N moieties. Cooling to 233 K (CDCl₃) or heating to 353 K (C₆D₅CD₃) had no

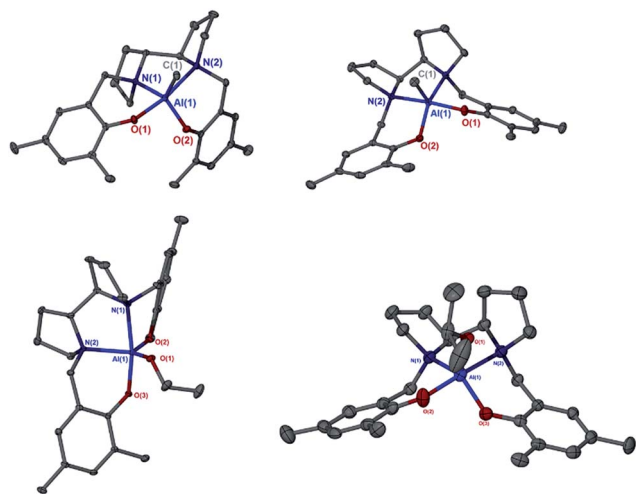


Fig. 2 Solid state structures for the aluminium complexes, ellipsoids are shown at the 30% probability level, all hydrogen atoms and disorder have been removed for clarity. Top left: Al(1)Me, Top right: Al(3)Me, bottom left Al(1)(OⁱPr) bottom right Al(3)(OⁱPr).

effect on the spectrum. Furthermore, there were no exchange peaks observed in the NOESY/EXSY spectrum. However, resonances for Al(1)(OⁱPr) at 298 K (CDCl₃) were broad, upon cooling to 253 K these sharpened significantly, as with Al(1)Me, both halves of the ligand are not equivalent once coordinated. NOESY/EXSY at 253 K and 298 K show the presence of exchange peaks. Furthermore, DOSY NMR (CDCl₃) was performed on Al(3)(OⁱPr) suggesting one major species in solution with a diffusion coefficient of $7.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ being observed. DFT studies were also in agreement with the isolated structure being the most stable form, see ESI.† It should also be noted that there is the possibility of one phenoxide arm orienting itself towards or away from isopropoxide, see ESI.† The difference between the two is small ($\Delta G = 2.4 \text{ kcal mol}^{-1}$) but adds further to the complexity of the system. The complex Al(4)(OⁱPr) was also prepared, its solid state structure is similar to Al(3)(OⁱPr) and its NMR is consistent with the desired structure being dominant in solution. However, it must be noted that it was difficult to fully convert Al(4)Me into the isopropoxide analogue; even with heating and five equivalents of isopropanol, *ca.* 5% of the Al(4)Me complex was co-isolated. This was not the case with the Me-substituted ligand and presumably reflects the steric difference between the two systems.

Polymerisation

In this study we have simply used recrystallised monomer to mimic more industrially relevant conditions. The results for the solution and melt ROP of *rac*-LA, with the Hf(IV) and Ti(IV) complexes are shown in Table 1. As observed for the Zr(IV) complexes isotactic PLA was produced, with Hf(IV). Analysis of the microstructure showed a small contribution from the *sis* tetrad and the *sii*, *iis* and *isi* are approximately 1 : 1 : 1 indicating that a chain end control mechanism is operative which would lead to a stereoblock structure of the PLA.^{1f,5a} DSC analysis of the PLA produced from Hf(3)(OⁱPr)₂ in solution showed a

Table 1 Polymerisation data for *rac*-LA with initiators Ti(3)(OⁱPr)₂ and Hf(1–3)(OⁱPr)₂

Initiator	Time (h)	Conv. (%) ^d	<i>M</i> _n ^e	PDI ^e	<i>P</i> _m ^f
Hf(1)(O ⁱ Pr) ₂ ^a	1	57	33 700	1.09	0.71
Hf(2)(O ⁱ Pr) ₂ ^a	1	55	33 250	1.07	0.71
Hf(3)(O ⁱ Pr) ₂ ^a	0.17	92	33 000	1.27	0.68
Ti(3)(O ⁱ Pr) ₂ ^a	24	48	15 700	1.06	0.50
Hf(1)(O ⁱ Pr) ₂ ^b	4	10	—	—	—
Hf(2)(O ⁱ Pr) ₂ ^b	4	10	—	—	—
Hf(3)(O ⁱ Pr) ₂ ^b	4	91	16 200	1.12	0.80
Hf(3)(O ⁱ Pr) ₂ ^c	4	87	14 100	1.06	0.84

^a Conditions: [M]/[I] = 300, 130 °C, solvent free. ^b Conditions: [M]/[I] = 100, toluene, *T* = 70 °C. ^c *T* = 50 °C. ^d As determined *via* ¹H NMR spectroscopy. ^e Determined from GPC (in THF) referenced to polystyrene. ^f *P*_m is the probability of isotactic enchainment, calculated from the ¹H homonuclear decoupled NMR spectra.

melting point of 181 °C (Table 1 entry 8) and 173 °C (Table 1 entry 7) indicating some crystallinity. Whereas, the PLA produced with Hf(1/2)(OⁱPr)₂ (*P*_m = 0.71) from bulk polymerisation had no defined melting point. The Ti(3)(OⁱPr)₂ complex produced atactic PLA and was significantly slower.

Hf(3)(OⁱPr)₂ was significantly faster than the chiral initiators, which is exemplified by the polymerisation tests at 70 °C. The kinetics for *L*-LA and *rac*-LA polymerisation were investigated with Hf(3)(OⁱPr)₂, Fig. 3. There is a first order dependency on the monomer, upto a conversion of 90%, and *L*-LA is faster than *rac*-LA. MALDI-ToF analysis on the PLA formed from solution (50 °C) shows a major polymer series with a repeat unit of 144 g mol^{−1} and a minor series with a 72 g mol^{−1} difference, indicating a small degree of transesterification. This also demonstrated the presence of an OⁱPr end group as expected from the classical coordination insertion mechanism. The mechanism for the polymerisation is presumably similar to that of the zirconium complex, which we have previously postulated is a ligand mediated chain end control mechanism with complementary chirality being maintained by virtue of the complex fluxionality. This is a “self-correcting” method to produce isotactic PLA. If the wrong isomer inserts then the initiator “switches” from $\Delta \rightleftharpoons \Lambda$, Fig. 4.

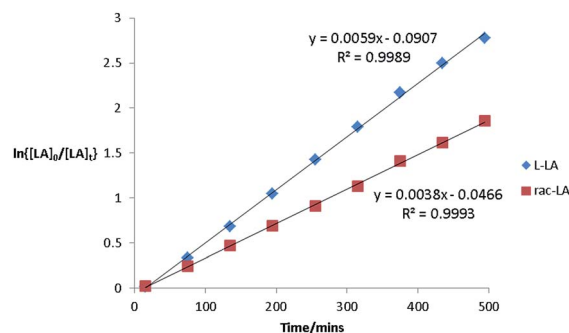


Fig. 3 Semi-logarithmic plots of the polymerisation of *L*-LA and *rac*-LA ([LA]₀ = 0.56 mol dm^{−3}) [LA] : [Init] 100 : 1 init = Hf (3)(OⁱPr)₂. CDCl₃ 298 K.



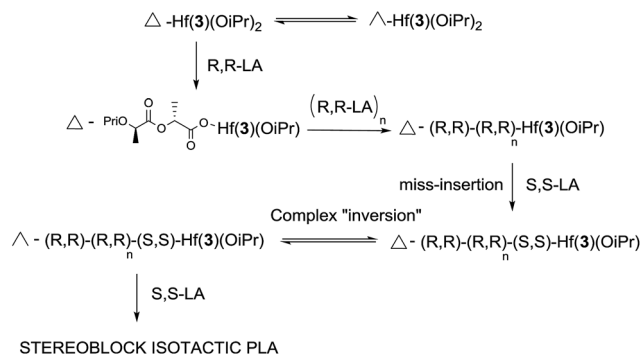


Fig. 4 Proposed mechanism to illustrate the stereocontrolled nature of the polymerisation using the $\text{Hf}(3)(\text{O}^i\text{Pr})_2$ initiator.⁶

When $\text{Hf}(3)(\text{O}^i\text{Pr})_2$ is reacted with 1 equivalent of *rac*-LA a complex mixture is observed (see ^1H NMR ESI[†]). However, the aromatic resonances are in a roughly 2 : 1 : 1 relationship which is indicative of the Hf(IV) centre remaining in a six coordinate octahedral β -*cis* geometry (as seen in the parent initiator). DOSY NMR spectroscopic analysis gave a diffusion coefficient of $6.4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. As expected this is reduced from the parent initiator due to the increased resistance caused by the ring opened lactide moiety. There appeared to be only one species in solution, which was presumably $\text{Hf}(3)(\text{O}^i\text{Pr})(\text{OC}(\text{HMe})\text{C}(\text{O})\text{OC}(\text{HMe})\text{C}(\text{O})\text{O}^i\text{Pr})$. NOESY/EXSY NMR shows a similar exchange pattern as for the parent initiator.

It is well known in the literature that aluminium complexes have a strong tendency to produce isotactic PLA.^{16,4a} However, heterotactic PLA was produced with $\text{Al}(3)(\text{O}^i\text{Pr})$ and atactic with $\text{Al}(1)(\text{O}^i\text{Pr})$, both in solution and in the melt, Table 2. The aluminium alkyl complexes required the addition of benzyl alcohol as co-initiator to form active species. PLA exhibiting a narrow dispersity was formed, with the *meso* complex affording a strong heterotactic bias, $P_r = 0.87$. Analysis of the PLA prepared with $\text{Al}(3)\text{Me}$ with the addition of HOCH_2Ph *via* MALDI-ToF MS indicated the presence of the H- and $-\text{OCH}_2\text{Ph}$ end groups as expected. Furthermore, the major series has a

Table 2 Polymerisation data for *rac*-LA with initiators $\text{Al}(1/3/4)\text{Me}/(\text{O}^i\text{Pr})$

Initiator	Time (h)	Temp/ $^\circ\text{C}$	Conv. ^d (%)	M_n^e	PDI ^e	P_r^f
$\text{Al}(1)\text{Me}^a$	120	80	86	29 150	1.08	0.49
$\text{Al}(3)\text{Me}^a$	120	80	87	21 550	1.05	0.87
$\text{Al}(1)(\text{O}^i\text{Pr})^b$	24	130	37	14 700	1.07	0.50
$\text{Al}(3)(\text{O}^i\text{Pr})^b$	24	130	82	59 650	1.25	0.69
$\text{Al}(4)(\text{O}^i\text{Pr})^b$	48	130	75	45 500	1.09	0.50
$\text{Al}(3)(\text{O}^i\text{Pr})^c$	168	70	72	18 850	1.05	0.87
$\text{Al}(3)(\text{O}^i\text{Pr})^c$	120	80	72	16 279	1.07	0.82
$\text{Al}(3)(\text{O}^i\text{Pr})^c$	90	90	71	17 900	1.10	0.79
$\text{Al}(3)(\text{O}^i\text{Pr})^c$	90	100	69	17 150	1.11	0.76

^a Conditions: $[\text{M}] : [\text{I}] : [\text{BnOH}] = 100 : 1 : 1$, toluene. ^b Conditions: $[\text{M}]/[\text{I}] = 300$, solvent free. ^c $[\text{M}] : [\text{I}] = 100 : 1$, toluene. ^d As determined *via* ^1H NMR spectroscopy. ^e Determined from GPC (in THF) referenced to polystyrene. ^f P_r is the probability of heterotactic enchainment, calculated from the ^1H homonuclear decoupled NMR spectra.

repeat unit of 144 g mol^{-1} (a minor series with 72 g mol^{-1} is also detected) indicating little inter-molecular transesterification is occurring. However, at low mass (*ca.* 2000 Da) a minor series of cyclic PLA is observed (up to 16 LA units) with a repeat unit of 72 g mol^{-1} implying a degree of intra-molecular transesterification was occurring.

As in solution the $\text{Al}(3)(\text{O}^i\text{Pr})$ initiator produced heterotactic PLA, whereas the chiral complex afforded atactic polymer under melt conditions (Table 2 entries 3 and 4). Furthermore, $\text{Al}(3)(\text{O}^i\text{Pr})$ was far more active in the melt than $\text{Al}(1)(\text{O}^i\text{Pr})$ and displayed a linear relationship between conversion and M_n , indicative of a well-controlled polymerisation, Fig. 5. When *L*-LA was polymerised with $\text{Al}(3)(\text{O}^i\text{Pr})$ under melt conditions a conversion of 47% ($M_n = 27\,450 \text{ g mol}^{-1}$, $M_w/M_n = 1.19$, 24 h) was achieved which is significantly lower than that obtained with *rac*-LA, as expected from a heteroselective initiator. A melt test with $\text{Al}(4)(\text{O}^i\text{Pr})$ afforded atactic PLA with a high conversion only achievable after 48 h. This indicated that a combination of steric bulk and the *meso* chirality are key in the production of heterotactic PLA in this case.

In solution there is a strong preference for heterotactic PLA with P_r upto 0.87. MALDI-ToF analysis of the PLA prepared at 70°C (Table 2 entry 6) showed a major series with the H- and $-\text{O}^i\text{Pr}$ end groups and a repeat unit of 144 g mol^{-1} (with a minor series of 72 g mol^{-1}), again a small amount of cyclic PLA was observed. Analysis of the PLA produced with $\text{Al}(3)(\text{O}^i\text{Pr})$ at 80°C after 48 h afforded a P_r value of 0.85 and conversion of 25%, indicating a strong heterotacticity from initiation. $\text{Al}(3)(\text{O}^i\text{Pr})$ was also trialled for the ROP of *rac*- β -butyrolactone, after 8 h at 80°C at 300 : 1 in the absence of solvent, a conversion of 78% was achieved ($M_n = 28\,400 \text{ g mol}^{-1}$, PDI = 1.03) unfortunately the polymer produced was atactic.

When $\text{Al}(3)(\text{O}^i\text{Pr})$ is reacted with 1 equivalent of *rac*-LA at 353 K (on the NMR scale *ca.* 20 mg of initiator), there are significant changes in the ^1H NMR spectrum (see ESI[†]). Four resonances (1 : 1 : 1 : 1) are observed for the aryl protons, a series of 1H doublets for the backbone, two clear quartets for the opened lactide and there is a slight downfield shift in the isopropoxide methine proton. There was little change in the ^{27}Al NMR with a resonance at *ca.* 44 ppm being observed at 353 K. When a further 3 equivalents were added there was still no change in the ^{27}Al NMR at 353 K implying that the aluminium centre remains 5 coordinate as the polymer chain is growing.¹⁵

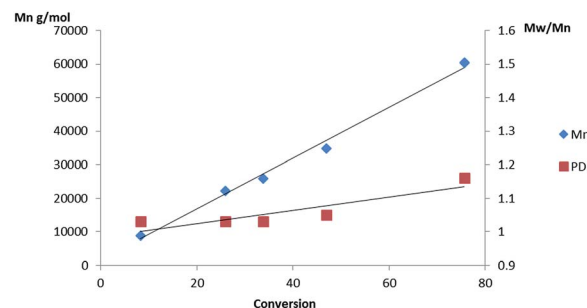


Fig. 5 Plot of M_n and PDI vs. conversion for the melt polymerisation of *rac*-LA initiated with $\text{Al}(3)(\text{O}^i\text{Pr})$.



Upon cooling back to 298 K the ^1H NMR spectrum was sharp and showed analogous features as the 353 K spectrum, but no signal could be observed in the ^{27}Al NMR spectrum. From analysis of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum two carbonyl resonances were observed at 170.4 and 180.8 ppm respectively. This compares to the signal at 180.7 previously observed for a five coordinate Schiff base Al-lactate complex.¹⁵ To probe the coordination of the active species further Al(3)Me was reacted with (S)-methyl-lactate. The ^{27}Al NMR had a broad resonance at 42.4 ppm (*cf.* 46.5 for Al(3)(OⁱPr)) which is indicative of a five coordinate Al(III) centre.¹⁵ We have also probed the complexes formed by the reaction of Al(3)Me with (S)-methyl-lactate *via* DFT calculations, which supports the notion of the five coordinated intermediate being favoured. However, it was clear that there were more than one species present in solution, this is exemplified by the presence of two CH₃ resonances for the methoxy and methyl groups of the lactate (at room temperature). This may be due to the presence of various stereoisomers, as well as the different possible orientations of the phenoxide arms being present. DOSY NMR gave a diffusion constant of $8.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (*cf.* $7.4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for Al(3)(OⁱPr)) and the NOESY NMR showed no exchange processes. These gives a hydrodynamic radii for Al(3)(OⁱPr) of *ca.* 5.3 Å (NB the solid-state diameter is ≈ 12 Å) and for the lactate complex the radii is *ca.* 5 Å both indicating monomeric species in solution.¹⁶ Al(1)Me was also treated with 1 equivalent of (S)-methyl-lactate at room temperature a broad spectrum was obtained, cooling to 233 K sharp signals were observed. The ^{27}Al NMR spectrum has a resonance at 42.2 ppm, which again implies a five coordinate Al(III) centre. In an attempt to rationalise the heterotacticity the Gibbs free energies of the different possibilities for the Al(3)-OⁱPr complexes with growing PLA chains were calculated. Again these showed that the Al(III) centre is 5 coordinate, it is interesting to note that the isomer with the PLA chain growing alongside the phenoxide arm (see ESI†) is more stable and there is a weak van der Waal interaction between the chain and the ortho substituent. However, given the complexities of this system future work will aim to rationalise the observed stereochemistry of the PLA produced. Very recently Kol and co-workers have shown that a racemic version of the 2,2'-bipyrrrolidine (Cl substituted) ligand produced heterotactic PLA, the mechanism proposed was based on polymeryl exchange between the different isomers matching the chirality of the polymer to the chirality at the metal.^{7c} In this case there are inactive and active diastereomers, which become awoken by polymer exchanges.^{7c} It is assumed that the same mechanism is in operation with the *meso* version of the ligand in this case.

Conclusions

A series of salan complexes based on a bipyrrrolidine backbone have been prepared and characterised in solution and solid state. There is a switch in selectivity from highly isotactic for hafnium initiators to heterotactic for aluminium initiators. It has previously been seen with Lu(III) and La(III) that there is a switch in selectivity with the smaller atomic radii metal forming isotactic PLA.^{5b} In this case the opposite is observed with the

larger Hf(IV) producing isotactic PLA and the smaller Al(III) heterotactic PLA. Moreover, Ma has shown that the tacticity is dependent upon coordination number, which may also account for the differences observed in this study. This illustrates the rich and diverse chemistry still to be explored and understood for the ROP of *rac*-LA. The *meso*-3H₂ is unique in the literature as either isotactic, heterotactic or atactic PLA can be prepared by simply changing the metal centre.

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