Journal Name

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Al(III) Homopiperazine Complexes and their Exploitation for the Production of Polyesters

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

In this paper we report the synthesis and characterisation of a series of Al(III) homopiperazine complexes. The ortho substituent has been varied from H, Me, *t*Bu to investigate the effect this has on the solid-state structures and on the catalytic activity. Aluminium-methyl complexes involving ligands **1**H$_2$, **3**H$_2$ and **5**H$_2$ have been characterised in the solid-state and the aluminium centres are in pseudo trigonal bipyramidal geometries. The aluminium-methyl complexes were further reacted with benzyl alcohol to generate alkoxide complexes, which have been fully characterised by multinuclear NMR spectroscopy and elemental analysis. The alkoxide complexes were tested in the ring opening polymerisation of *rac*-lactide, δ-valerolactone and ε-caprolactone. Furthermore, triblock polyesters were also prepared with these initiators.

Introduction

Ring opening polymerisation (ROP) of lactide to produce polylactide (PLA) has received a remarkable degree of attention in recent years.[1] This is due to the biocompatibility of the final polymer and the fact that the starting lactide can be prepared from sustainable sources.[1b, 1d, 2] This is truly making PLA a viable alternative to crude oil based polymers for commodity applications. Furthermore, PLA and its copolymers are currently being exploited for high value biomedical applications.[3] Initiators for ROP based on Al(III),[4] Zn(II),[5] lanthanides,[6] group 4 metals[7] and group 2 metals[5g, 8] are prevalent in the literature. One of the most studied monomers is *rac*-lactide (a 50:50 mix of the D- and L- enantiomers), this is due to the fact that different (stereoblock isotactic, heterotactic and atactic) stereo-forms of PLA can be prepared. The physical properties of the final polymer are directly related to its microstructure.[1b, 2e] However, the properties of the polymer can also be varied by the copolymerisation of lactide with other monomers – such as ε-caprolactone or δ-valerolactone.[7c, 9] One of the main driving forces of this approach is to produce polymers which have desirable gas/drug permeability and mechanical strength properties.[1b]

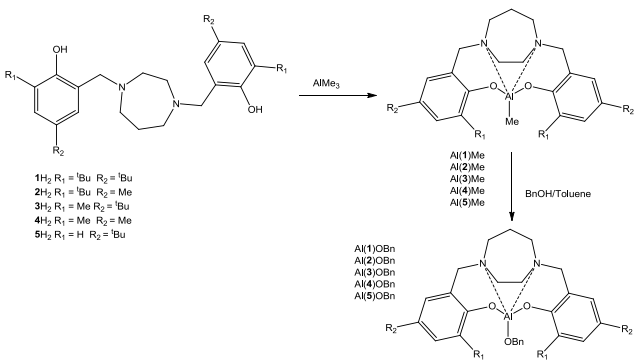
A significant number of aluminium complexes that are active for the ROP of *rac*-LA or other cyclic esters are based on either salan or salen ligands.[4c, 10] One such class of salan ligands are those utilising a piperazine or homopiperazine backbone. For example, Fulton and Wang have shown that bimetallic Al(III) complexes of piperazine derived phenolates show activity for the polymerisation of ε-caprolactone.[10] Furthermore, we have previously shown that amine bis(phenolate) ligands based on homopiperazine ligands complexes to group 4 metals are active initiators for the controlled ROP of *rac*-lactide.[7b, 11]

In the vast majority of aluminium examples an alkoxide initiator is generated *in-situ* from the aluminium-alkyl and thus the resultant polymerisation is performed in solution.[3c, 4c] However, this has a significant disadvantage in the fact that the polymerisation cannot be performed under the industrially preferred melt conditions. Therefore, in this study we have chosen to prepare a series of aluminium-homopiperazine alkoxide complexes for the application in ROP with a variety of monomers for melt polymerisation studies.

Results and Discussion

Synthesis of Complexes

The ligands were prepared by modified Mannich reactions and complexes were prepared *via* standard literature procedures, scheme 1.[7b, 11-12] The choice of ortho substituent allows us to probe the effect of steric influence on catalysis and solid-state structure. All ligands were characterised *via* multi-nuclear NMR spectroscopy and HR-MS.



Scheme 1 Synthesis of ligands and complexes used in this study.

The Al(Me) complexes were prepared by addition of 1

equivalent of $AlMe_3$ to 1 equivalent of ligand and it was noted that products of higher purity were isolated when the reactions was conducted at 80 ºC. Complexes Al(**1,3,5**)Me were characterised by single crystal diffraction studies, see Figure 1 for Al(**3**)Me and Table 1 for selected bond distances and angles. The aluminium centres are in a highly disordered trigonal bipyramidal geometry. For complex Al(**1**)Me a significant degree of disorder was observed in the homopiperazine ring moiety. For complexes Al(**3**)Me and Al(**5**)Me the methyl group bound to the aluminium centre can be thought of as being 'cis' to the -N(CH_2)(CH_2)N- fragment of the homopiperazine ring. However, for Al(**1**)Me two forms were observed in the solid-state; one with the Me group being 'cis' to the -N(CH_2)(CH_2)N- fragment and another with the Me 'cis' to the -N(CH_2)(CH_2)(CH_2)N- fragment. These were superimposed upon each other in a 50:50 ratio.

Furthermore, in the case of Al(**1**)Me if the isomer with the Me 'cis' to the -N(CH_2)(CH_2)N- is examined in more detail, in comparison to Al(**3,5**)Me, there is a significant 'twist' in the ligand. This is perhaps necessary to minimise steric clashes between opposing ortho *t*Bu moieties in Al(**1**)Me. This can be visualised by analysis of the space filling models, Figure 1. The metric data for the complexes reported herein are in agreement with Al-alkyl piperazine complexes prepared by Fulton and Wang.[10]

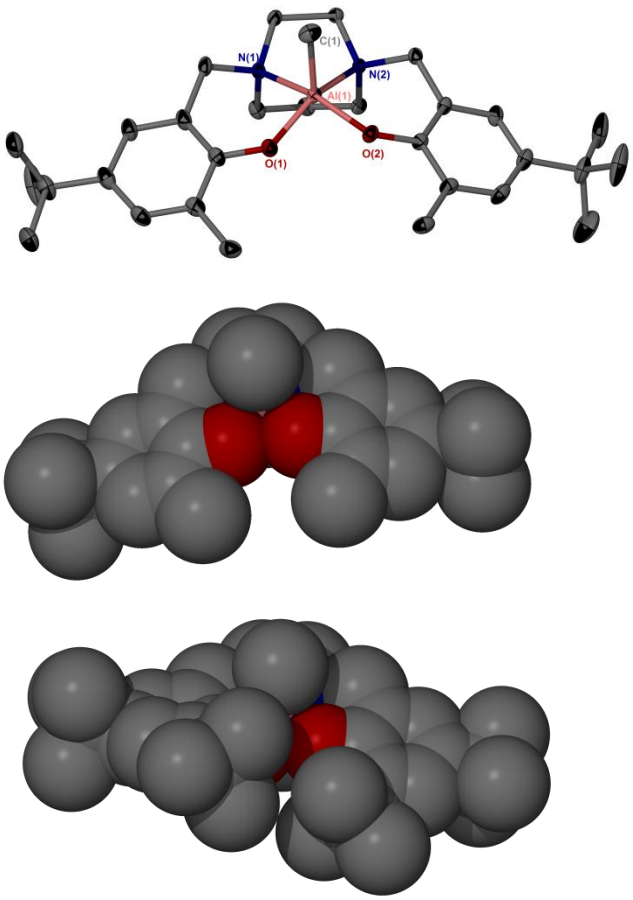


Fig. 1 Top: Solid-state structure for Al(**3**)Me, the ellipsoids are shown at the 50% probability level, the hydrogen-atoms and solvent molecules have been removed for clarity. **Middle**: Space fill model for Al(**3**)Me. **Bottom**: Space fill model for Al(**1**)Me, with the hydrogen atoms for the space fill model being removed for clarity

Table 1 Bond lengths (Å) and angles (º) for complexes Al(**1**,**3**,**5**)Me

	Al(**1**)Me[a]	Al(**3**)Me	Al(**5**)Me
Al(1)-C(1)	1.959(5)	1.980(3)	1.966(7)
Al(1)-O(1)	1.797(3)	1.7873(19)	1.786(4)
Al(1)-O(2)	1.767(2)	1.7975(18)	1.796(4)
Al(1)-N(1)	2.192(7)	2.132(2)	2.109(5)
Al(1)-N(2)	2.240(6)	2.108(2)	2.101(5)
O(1)-Al(1)-O(2)	89.77(13)	91.79(9)	90.2(2)
N(1)-Al(1)-N(2)	71.9(2)	73.74(8)	74.48(17)
O(1)-Al(1)-C(1)	104.5(2)	114.29(13)	111.8(3)
N(1)-Al(1)-C(1)	96.7(3)	100.09(12)	102.0(2)

[a] This complex exhibits disorder in the homopiperazine fragment. The metric data given is for the -N(CH_2)(CH_2)N 'cis' to the Me bound to the aluminium centre.

The NMR spectra of the complexes were none trivial at room temperature due to significant broadening and the diastereotopic nature of the methylene groups. However, at 233 K, NMR spectra in agreement with monomeric structures were observed in solution, with discrete doublets for the CH_2 moieties. Variable temperature NMR spectra were recorded ($C_6D_5CD_3$) in an attempt to elucidate the fluctionality, see Figure 2 for Al(**1**)Me. From such experiements it is clear that the aluminium species exhibit complex fluctional behaviour. Noteworthy, for Al(**1**)Me DFT calculations indicated there was no discernible difference in energy between the two isomers. Once the Al-Me complexes were prepared these were treated with $PhCH_2OH$ to generate the alkoxide complexes which for ligands **1**H_2-**3**H_2 were isolated as white solids after recrystallisation. Interestingly, to replace all the Al-Me groups an excess (3 equivalents) of benzyl alcohol was required and the reaction required heating to 80 ºC for three hours. It was noted, however, that the alkoxides prepared with ligands **4**H_2 and **5**H_2 were oily in consistency.

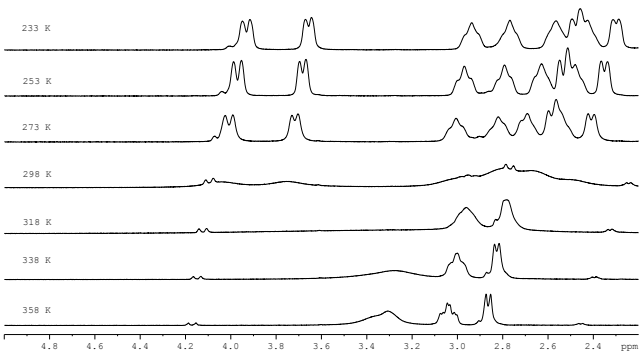


Fig. 2 Variable temperature NMR spectra Al(**1**)Me (only methine region shown).

Polymerisation

Initially the Al-Me complexes were trialled for the polymerisation of *rac*-LA in a solution of toluene at 80 ºC with 1 equivalent of benzyl alcohol as the co-initiator. However, under these conditions no polymeric material was formed. Therefore, the alkoxide complexes were prepared which could be utilised more effectively under melt conditions (130 ºC), Table 2. All tests were run at 130 ºC, regardless of the monomer in question.

Table 2 Polymerisation data

Entry	Initiator	Mon.	Con. (%)[a]	M_n[b]	PDI[b]
1	Al(**1**)OBz	*rac*-LA	87	54400	1.31
2	Al(**1**)OBz	VL	88	24800	1.77
3	Al(**1**)OBz	CL	97	73100	1.54
4	Al(**1**)OBz	CL-VL-*rac*-LA	99, 95, 98	42400	1.66
5	Al(**2**)OBz	*rac*-LA	88	58200	1.40
6	Al(**2**)OBz	VL	31	10100	1.12
7	Al(**2**)OBz	CL	30	11400	1.15
8	Al(**2**)OBz	CL-VL-*rac*-LA	88, 43, 64	29500	1.63
9	Al(**3**)OBz	*rac*-LA	81	56400	1.40
10	Al(**3**)OBz	VL	94	33000	1.54
11	Al(**3**)OBz	CL	94	71900	1.63
12	Al(**3**)OBz	CL-VL-*rac*-LA	99, 95, 22	47800	1.76
13	Al(**4**)OBz	*rac*-LA	87	42100	1.42
14	Al(**4**)OBz	VL	90	39600	1.50
15	Al(**4**)OBz	CL	94	54100	1.42
16	Al(**5**)OBz	*rac*-LA	56	16800	1.08
17	Al(**5**)OBz	VL	81	16000	1.25
18	Al(**5**)OBz	CL	83	25800	1.48

[a] Determined *via* ^{1}H NMR spectroscopy. [b] Determined *via* GPC at 35 °C in THF at 1 ml/min using polystyrene as the standards. For the homopolymerisation the monomer:initiator ratio was 300:1, Caprolactone = 30 mins, δ- Valerolactone = 1 h, *rac*-lactide = 2h. For the triblock the monomer:initiator ratio was 100:1 for each monomer, ie 300:1 overall.

The polymerisations were very efficient for all complexes with all monomers, with the exception of Al(**2**)OBz with lower conversion for δ-valerolactone (VL) and ε-caprolactone (CL). In all cases atactic PLA was produced. Noteworthy is that the molecular weight (after similar conversions) are significantly lower for Al(**5**)OBz compared to the other initiators. This is perhaps related to the reduced steric demand of this ligand facilitating multiple chain attachment to each metal centre. Attempts then focused on the production of triblock polymers with the complexes. In this case the monomers were added in a sequential manner. It was noted that the addition of the monomers was critical to the polymerisation success. For example, if lactide was polymerised first followed by either δ-valerolactone or ε-caprolactone then only PLA was isolated, so a VL or CL will not insert into an Al-LA linkage. Therefore, in the preparation of the triblock *rac*-LA was added last as LA can insert into an Al-CL or Al-VL linkage. The molecular weights of the triblocks were in agreement with the expected values based on the GPC values for the homopolymers and the conversion, indicating that the triblock had formed. Furthermore, the GPC traces were unimodal. The ^{1}H NMR spectra were complex due to overlapping of the resonances for the CL and VL blocks. In the ^{13}C{^{1}H} NMR there was one resonance for each carbonyl of the CL and VL blocks and the carbonyl region for *rac*-LA block was typical of an atactic PLA block.

Conclusions

In conclusion a series of Al-Me and Al-OBz complexes have been prepared and characterised. Monomeric complexes were isolated, with the geometry of the ligand being influenced by the steric effects of the ortho substituent. All complexes are active for the ROP of cyclic esters under solvent free conditions.

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* SPS (solvent purification system). ^{1}H and ^{13}C{^{1}H} 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. CHN microanalysis was performed by Mr Stephen Boyer of London Metropolitan University. The ligands were prepared according to standard literature procedures and the purity confirmed *via* ^{1}H/^{13}C{^{1}H} NMR and HR-MS prior to use.[11-12] DFT calculations utilised optimised crystallographically determined structures with TightSCF conversion. Initial calculations used the BP86 functional with RI approximation and the def2-svp basis set. The final calculations were refined iteratively using B3LYP functional with the RIJCOSX algorithm firstly using the def2-svp basis set and finally the def2-TZVPP basis set. Empirical van der Waals corrections were applied alongside COSMO solvent effect at infinite dielectric constant.

Ligand Preparation

All ligands were prepared using previously established protocols except **5**H_2 which was prepared as follows[12]: Homopiperazine anhydrous (2.20g, 25 mmol) and formaldehyde (38% in H_2O) (5.30 ml, 75.4 mmol) were refluxed (2 h) in MeOH (40 ml). The solution was then cooled to room temperature and 4-tert-butylphenol (7.51 g, 50.0 mmol) in methanol (60 ml) was added slowly then refluxed (16 h) and then cooled to room temperature. The solid was filtered, washed in cold MeOH then dried under vacuum to yield a white powder (2.31 g, 5.5 mmol, 22 %). ^{1}H NMR ($CDCl_3$) δ: 1.27 (18H, s, CH_3), 1.94 (2H, quintet, J = 6.0 Hz, CH_2), 2.79 (4H, s, CH_2), 2.84 (4H, t, J = 6.0 Hz, CH_2), 3.78 (4H, s, CH_2), 6.76 (2H, d, J = 8.50 Hz, Ar-H), 6.95 (2H, d, J = 2.5 Hz, Ar-H), 7.19 (2H, dd, J = 8.5 Hz, J = 2.5 Hz, Ar-H), 10.47 (2H, br, O-H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 26.8 (CH_2), 31.6 (CH_3), 34.0 (C), 53.6 (CH_2), 54.7 (CH_2), 62.4 (CH_2), 115.5 (Ar-H), 121.0 (Ar), 125.4 (Ar-H), 125.6 (Ar-H), 141.9 (Ar), 155.4 (Ar). Calc. m/z. $[C_{27}H_{40}N_2O_2+H]^+$ 425.3168. Found 425.3233.

Complex Preparation

Al(**1**)Me. A solution of **1**H_2 (0.96 g, 1.8 mmol) in toluene (50 ml) was heated to 50°C and 2M $AlMe_3$ (1 ml, 1.8 mmol) was added slowly then stirred (30 mins, 50 °C), after which the solution was further heated and stirred (3 hrs, 80 °C). The crude mixture was recrystallised from a toluene:hexane (0.25 g, 0.43 mmol, 24 %). ^{1}H NMR (233 K) (C_4D_8O) δ : -0.87 (3H, s, Al-Me), 1.26 (18H, s, CH_3), 1.44 (9H, s, CH_3), 1.50 (9H, s, CH_3), 1.86 (1H, br, CH_2), 2.33 (2H, br, CH_2), 2.41 (1H, br, CH_2), 2.62 (1H, br, CH_2), 3.15 (2H, br, CH_2), 3.23 (2H, m, CH_2), 3.32 (2H, m, CH_2), 3.41 (1H, br, CH_2), 4.06 (1H, d, J = 11.5 Hz, CH_2), 4.27 (1H, d, J = 14.0 Hz, CH_2), 6.79 (1H, s, Ar-H), 6.86 (1H, s, Ar-H), 7.16 (1H, s, Ar-H), 7.20 (1H, s, Ar-H). ^{13}C{^{1}H} NMR (233 K) (C_4D_8O) δ : 21.9 (CH_2), 29.8 (CH_3), 29.1 (CH_3), 31.3 (CH_3), 31.4 (CH_3), 33.7 (C), 33.8 (C), 34.8 (C), 35.1 (C), 43.9 (CH_2), 51.9 (CH_2), 54.2 (CH_2), 55.6 (CH_2), 59.4 (CH_2), 65.0 (CH_2), 120.5 (Ar), 121.8 (Ar), 122.4 (Ar), 122.7 (Ar), 123.2 (Ar), 123.5 (Ar), 135.8 (Ar), 136.4 (Ar),

137.3 (Ar), 137.8 (Ar), 155.7 (Ar-O), 159.7 (Ar-O). Calc. (%) for $C_{36}H_{57}N_2O_2Al$; C 74.96, H 9.96, N 4.86. Found (%); C 74.96, H 9.90, N 4.81.

Al(**2**)Me. The crude mixture was recrystallised from a toluene:hexane mix to yield a white powder (0.21 g, 0.4 mmol, 43 %). ^{1}H NMR (233 K) ($C_6D_5CD_3$) δ : -0.59 (3H, s, Al-Me), 0.54 (1H, d, J = 13.5 Hz, CH_2), 0.92 (1H, br, CH_2), 1.08 (1H, br, CH_2), 1.16 (2H, br, CH_2), 1.30 (1H, d, J = 7.5 Hz, CH_2), 1.55 (1H. br, CH_2), 1.92 (9H, s, CH_3), 1.95 (9H, s, CH_3), 2.27 (1H, d, J = 11.5 Hz, CH_2), 2.40 (1H, d, J = 14.5 Hz, CH_2), 2.43 (1H, br, CH_2), 2.43 (3H, s, 2.76), 2.48 (3H, s, 2.76), 2.57 (1H, br, CH_2), 2.87 (1H, br, CH_2), 3.63 (1H, d, J = 11.5 Hz, CH_2), 3.81 (1H, d, J = 14.0 Hz, CH_2), 6.54 (1H, s, Ar-H), 6.60 (1H, s, Ar-H), 7.36 (1H, s, Ar-H), 7.41 (1H, s, Ar-H). ^{13}C{^{1}H} NMR (233 K) (C_4D_8O) δ : 21.3 (CH_3), 21.4 (CH_3), 22.9 (CH_2), 30.2 (CH_3), 30.9 (CH_3), 35.6 (C), 35.9 (C), 44.8 (CH_2), 52.7 (CH_2), 55.3 (CH_2), 56.8 (CH_2), 60.2 (CH_2), 65.6 (CH_2), 122.1 (Ar), 123.3 (Ar), 123.4 (Ar), 124.8 (Ar), 127.4 (Ar), 127.5 (Ar), 128.1 (Ar), 128.5 (Ar), 138.2 (Ar), 139.4 (Ar), 156.8 (Ar-O), 161.0 (Ar-O). Calc. (%) for $C_{30}H_{45}N_2O_2Al$; C 73.14, H 9.21, N 5.69. Found (%); C 73.02, H 9.25, N 5.73.

Al(**3**)Me: The crude mixture was recrystallised from a toluene:hexane mix to yield a white powder (0.25 g, 0.5 mmol, 51 %). ^{1}H NMR (233 K) ($C_6D_5CD_3$) δ : -0.45 (3H, s, Al-Me), 0.18 (1H, br, CH_2), 0.73 (1H, br, CH_2), 1.12 (2H, d, J = 7.5 Hz, CH_2), 1.39 (2H, d, J = 7.0 Hz, CH_2), 1.51 (18H, s, CH_3), 2.06 (1H, m, CH_2), 2.45 (2H, d, J = 13.0 Hz, CH_2), 2.54 (2H, br, CH_2), 2.64 (1H, br, CH_2), 2.82 (6H, s, CH_3), 3.97 (2H, d, J = 13.0 Hz, CH_2), 6.80 (2H, d, J = 2.0 Hz, Ar-H), 7.40 (2H, d, J = 2.0 Hz, Ar-H). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$) δ : 17.3 (CH_3), 21.9 (C), 32.2 (CH_3), 40.0 (CH_2), 49.4 (CH_2), 52.1 (CH_2), 63.2 (CH_2), 118.5 (Ar), 122.3 (Ar-H), 127.8 (Ar), 127.9 (Ar-H), 137.5 (Ar), 157.6 (Ar-O). Calc. (%) for $C_{30}H_{45}N_2O_2Al$; C 73.14, H 9.21, N 5.69. Found (%); C 72.99, H 9.09, N 5.78.

Al(**4**)Me: The crude mixture was recrystallised from a toluene:hexane mix to yield a white powder (0.45 g, 1.1 mmol, 59 %). ^{1}H NMR (298 K) ($C_6D_5CD_3$) δ : -0.59 (1.5H, s, Al-Me), -0.43 (1.5H, s, Al-Me), 0.50 (0.5H, d, J = 15.5 Hz, CH_2), 0.89 (1H, m, CH_2), 1.04 (0.5H, br, CH_2), 1.22 (1H, m, CH_2), 1.35 (2H, m, CH_2), 1.51 (1H. m, CH_2), 1.68 (1H, m, CH_2), 2.28 (3H, s, CH_3), 2.30 (3H, s, CH_3), 2.43 (3H, s, CH_3), 2.58 (2H, m, CH_2), 2.62 (3H, s, CH_3), 2.66 (2H, m, CH_2), 2.92 (1H, m, CH_2), 3.68 (1H, d, J = 13.0 Hz, CH_2), 4.04 (1H, d, J = 13.0 Hz, CH_2), 6.45 (2H, d, J = 4.5 Hz, Ar-H), 6.95 (2H, s, Ar-H). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$) δ : 16.7 (CH_3), 17.0 (CH_3), 20.8 (CH_3), 22.0 (CH_2), 22.4 (CH_2), 46.2 (CH_2), 49.5 (CH_2), 51.1 (CH_2), 55.5 (CH_2), 61.7 (CH_2), 62.8 (CH_2), 119.0 (Ar), 120.5 (Ar), 123.6 (Ar), 124.3 (Ar), 126.5 (Ar-H), 126.7 (Ar-H), 128.0 (Ar), 128.9 (Ar), 131.7 (Ar-H), 131.9 (Ar-H), 157.7 (Ar-O), 157.9 (Ar-O). Calc. (%) for $C_{24}H_{33}N_2O_2Al$; C 70.56, H 8.14, N 6.86. Found (%); C 70.68, H 8.08, N 6.69.

Al(**5**)Me: The crude mixture was recrystallised from a toluene:hexane mix to yield a white powder (0.55 g, 0.58 mmol, 58 %). Please check again ^{1}H NMR (233 K) (C_4D_8O) δ : -0.53 (3H, s, Al-Me), 1.23 (18H, s, CH_3), 1.23 (2H, br, CH_2), 2.30 (2H, m, CH_2), 2.94 (2H, br, CH_2), 3.04 (2H, br, CH_2), 3.13 (2H, br, CH_2), 3.40 (2H, d, J = 13.5 Hz, CH_2), 4.30 (2H, d, J = 13.0 Hz, CH_2), 6.58 (2H, d, J = 8.5 Hz, Ar-H), 6.87 (2H, d, J = 2.0 Hz, Ar-H), 7.07 (2H, dd, J = 8.5 Hz, J = 2.0 Hz, Ar-H). ^{13}C{^{1}H} NMR (C_4D_8O) δ : 22.5 (CH_2), 31.6 (CH_3), 33.7 (C), 50.2 (CH_2), 52.7 (CH_2), 63.1 (CH_2), 119.3 (Ar-H), 119.7 (Ar), 124.6 (Ar-H), 126.0 (Ar-H), 137.5 (Ar), 159.4 (Ar-O). Calc. (%) for $C_{28}H_{41}N_2O_2Al$; C 72.38, H 8.89, N 6.03. Found (%); C 72.35, H 8.88, N 6.17.

Al(**1**)OBz. A solution of **1H$_2$** (0.53 g, 1.0 mmol) in toluene (30 ml) was heated to 50 °C and 2M $AlMe_3$ (0.5 ml, 1.0 mmol) was added slowly then stirred (30 mins, 50 °C), after which the solution was further heated and stirred (3 hrs, 80 °C). Excess benzyl alcohol (0.31 ml, 3.0 mmol) was carefully added to the hot solution and allowed to stir (3 hrs, 80 °C) the reaction was cooled then the crude mixture was recrystallised from a toluene:hexane mix to yield a white powder (0.24 g, 0.36 mmol, 36 %). ^{1}H NMR (233 K) ($C_6D_5CD_3$) δ : 0.29 (1H, br, CH_2), 0.76 (1H, br, CH_2), 1.48 (4H, br, CH_2), 1.51 (18H, s, CH_3), 2.00 (18H, s, CH_3), 2.56 (4H, m, CH_2), 2.64 (2H, m, CH_2), 4.32 (2H, d, J = 13.5 Hz, CH_2), 5.26 (2H, s, CH_2), 6.77 (2H, s, Ar-H), 7.15 (1H, s, Ar-H), 7.21 (2H, t, J = 7.5 Hz, Ar-H), 7.36 (2H, d, J = 7.5 Hz, Ar-H), 7.66 (2H, s, Ar-H). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$) δ : 22.1 (CH_2), 30.1 (CH_3), 32.1 (CH_3), 34.2 (C), 36.1 (C), 50.7 (CH_2), 52.3 (CH_2), 63.7 (CH_2), 65.9 (CH_2), 119.8 (Ar), 122.8 (Ar-H), 124.0 (Ar-H), 126.1 (Ar-H), 126.7 (Ar-H), 128.1 (Ar-H), 137.9 (Ar), 139.0 (Ar), 147.0 (Ar), 157.6 (Ar-O). Calc. (%) for $C_{42}H_{61}N_2O_3Al$; C 75.41, H 9.19, N 4.19. Found (%); C 75.37, H 9.04, N 4.12.

Al(**2**)OBz The reaction was recrystallised from a toluene:hexane mix to yield a white powder (0.20 g, 0.3 mmol, 34 %). ^{1}H NMR (233 K) ($C_6D_5CD_3$) δ : 0.40 (1H, d, J = 13.5 Hz, CH_2), 0.76 (1H, br, CH_2), 1.20 (2H, d, J = 9.0 Hz, CH_2), 1.40 (2H, br, CH_2), 1.96 (18H, s, CH_3), 2.43 (6H, s, CH_3), 2.51 (4H, m, CH_2), 2.66 (2H, m, CH_2), 4.27 (2H, d, J = 13.0 Hz CH_2), 5.25 (2H, s, CH_2), 6.48 (2H, s, Ar-H), 7.14 (1H, s, Ar-H), 7.21 (2H, t, J = 7.5 Hz, Ar-H), 7.40 (4H, m, Ar-H). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$) δ : 21.0 (CH_3), 22.1 (CH_2), 30.9 (CH_3), 35.7 (C), 50.6 (CH_2), 52.2 (CH_2), 63.2 (CH_2), 65.9 (CH_2), 120.3 (Ar), 124.3 (Ar), 126.1 (Ar-H), 126.7 (Ar-H), 126.9 (Ar-H), 127.8 (Ar-H), 128.1 (Ar-H), 139.4 (Ar), 146.7 (Ar), 157.6 (Ar-O). Calc. (%) for $C_{36}H_{49}N_2O_3Al$; C 73.94, H 8.45, N 4.79. Found (%); C 73.86, H 8.51, N 4.75.

Al(**3**)OBz: The crude mixture was recrystallised from a toluene:hexane mix to yield a white powder (0.47 g, 0.8 mmol, 81 %). ^{1}H NMR (233 K) ($C_6D_5CD_3$) δ : 0.11 (1H, d, J = 12.0 Hz, CH_2), 0.70 (1H, br, CH_2), 1.10 (2H, d, J = 8.0 Hz, CH_2), 1.47 (2H, br, CH_2), 1.50 (18H, s, CH_3), 2.43 (4H, m, CH_2), 2.71 (2H, d, J = 6.5 Hz, CH_2), 2.85 (6H, s, CH_3), 4.31 (2H, d, J = 12.5 Hz CH_2), 5.29 (2H, s, CH_2), 6.79 (2H, s, Ar-H), 7.15 (1H, br, Ar-H), 7.24 (2H, t, J = 7.5 Hz, Ar-H), 7.40 (4H, m, Ar-H). ^{13}C NMR ($C_6D_5CD_3$) δ : 17.6 (CH_3), 22.3 (CH_2), 32.5 (C), 32.6 (CH_3), 34.5(CH_2), 50.4 (CH_2), 52.9 (CH_2), 63.2 (CH_2), 66.7 (CH_2), 119.5 (Ar), 122.7 (Ar-H), 126.5 (Ar-H), 127.2 (Ar-H), 128.1 (Ar), 128.4 (Ar-H), 128.5 (Ar-H), 138.4 (Ar), 147.3 (Ar), 157.7 (Ar-O). Calc. (%) for $C_{36}H_{49}N_2O_3Al$; C 73.94, H 8.45, N 4.79. Found (%); C 73.91, H 8.50, N 4.72.

Al(**4**)OBz: The crude mixture was recrystallised from a toluene:hexane mix to yield a tacky solid (0.22 g, 0.4 mmol, 44 %). ^{1}H NMR (233 K) ($C_6D_5CD_3$) δ : 0.22 (1H, d, J = 13.5 Hz, CH_2), 0.75 (1H, br, CH_2), 1.10 (2H, br, CH_2), 1.45 (2H, br, CH_2), 2.40 (6H, s, CH_3), 2.45 (4H, m, CH_2), 2.71 (2H, br, CH_2), 2.81 (6H, s, CH_3), 4.30 (2H, d, J = 12.5 Hz CH_2), 5.25 (2H, s, CH_2), 6.51 (2H, s, Ar-H), 7.15 (1H, br, Ar-H), 7.15 (2H, br, Ar-H),

7.23 (2H, m, Ar-H), 7.41 (2H, d, J = 7.5 Hz, Ar-H). $^{13}C\{^{1}H\}$ NMR ($C_6D_5CD_3$) δ : 16.8 (CH_3), 20.8 (CH_3), 21.9 (C), 22.4 (C), 45.6 (CH_2), 50.0 (CH_2), 52.5 (CH_2), 55.7 (CH_2), 61.9 (CH_2), 62.4 (CH_2), 64.9 (CH_2), 66.4 (CH_2), 119.6 (Ar), 120.5 (Ar), 124.3 (Ar), 124.7 (Ar), 126.1 (Ar-H), 126.5 (Ar-H), 126.6 (Ar-H), 127.3 (Ar-H), 126.8 (Ar-H), 128.1 (Ar), 128.1 (Ar-H), 128.3 (Ar-H), 128.8 (Ar), 131.8 (Ar-H), 132.0 (Ar-H), 157.4 (Ar-O), 157.3 (Ar-O). Calc. (%) for $C_{30}H_{37}N_2O_3Al$; C 71.98, H 7.45, N 5.60. Found (%); C 72.12, H 7.50, N 5.52.

Al(**5**)OBz The crude mixture was recrystallised from a toluene:hexane mix to yield a tacky solid (0.15 g, 0.3 mmol, 27 %). ^{1}H NMR ($C_6D_5CD_3$) δ : 0.80 (1H, m, CH_2), 1.14 (1H, m, CH_2), 1.35 (18H, s, CH_3), 1.50 (4H, m, CH_2), 2.59 (2H, d, J = 7.5 Hz, CH_2), 3.22 (2H, d, J = 12.5 Hz, CH_2), 3.36 (2H, m, CH_2), 3.58 (2H, m, CH_2), 5.16 (2H, s, CH_2), 6.85 (2H, d, J = 2.5 Hz, Ar-H), 7.04 (1H, m, Ar-H), 7.12 (2H, m, Ar-H), 7.14 (1H, s, Ar-H), 7.14 (1H, br, Ar-H), 7.22 (1H, d, J = 2.5 Hz, Ar-H), 7.25 (1H, d, J = 2.5 Hz, Ar-H), 7.29 (1H, m, Ar-H), 7.32 (1H, br, Ar-H). $^{13}C\{^{1}H\}$ NMR ($C_6D_5CD_3$) δ : 22.1 (CH_2), 32.0 (CH_3), 34.0 (C), 46.8 (CH_2), 50.1 (CH_2), 52.4 (CH_2), 55.2 (CH_2), 62.6 (CH_2), 66.3 (CH_2), 120.9 (Ar-H), 121.4 (Ar), 125.3 (Ar-H), 126.3 (Ar-H), 127.6 (Ar-H), 127.7 (Ar-H), 128.4 (Ar-H), 139.3 (Ar), 147.3 (Ar), 159.6 (Ar-O). Calc. (%) for $C_{34}H_{45}N_2O_3Al$; C 73.35, H 8.15, N 5.03. Found (%); C 73.45, H 8.14, N 4.89.

Polymerisation Procedure:

For solvent-free homopolymerisations the monomer: complex ratio employed was 300:1 at a temperature of 130 °C, in all cases either 1 g of *rac*-lactide, 1 ml of δ-valerolactone, or 1 ml of caprolactone were used. After the reaction time methanol (20 ml) was added to quench the reaction and the resulting solid was dissolved in dichloromethane. The solvents were removed in-vacuo and the resulting solid washed with methanol (3 × 50 ml) to remove any unreacted monomer. For solvent-free triblock polymerisations the monomers were added in sequence under an argon gas flow with the ratios 100:100:100:1 of ε-caprolactone:δ-valerolactone:*rac*-lactide:complex respectively. First ε-caprolactone (0.77 ml) was stirred for 30 mins, then δ-valerolactone (0.64 ml) was introduced and stirred for 1 h, finally lactide (1 g) was added and reacted for 2 h. The polymerisation was held at 130 °C for the duration then quenched with methanol (20 ml) and the resulting solid was dissolved in dichloromethane. The solvents were removed in-vacuo and the resulting solid washed with methanol (3 × 50 ml) to remove any unreacted monomers. ^{1}H NMR spectroscopy ($CDCl_3$) and GPC (THF) were used to determine tacticity and molecular weights (M_n and M_w) of the polymers produced; $P_{r/m}$ (the probability of heterotactic/isotactic linkages) were determined by analysis of the methine region of the homonuclear decoupled ^{1}H NMR spectra. Gel Permeation Chromatography (GPC) analyses were performed on a Polymer Laboratories PL-GPC 50 integrated system using a PLgel 5 μm MIXED-D 300 x 7.5 mm column at 35 °C, THF solvent (flow rate 1.0 ml/min). The polydispersity index (PDI) was determined from M_w/M_n where M_n is the number average molecular weight and M_w the weight average molecular weight. The polymers were referenced to polystyrene standards.

Single Crystal Diffraction

All data were collected on a Nonius kappa CCD diffractometer with MoKα radiation (λ = 0.71073 Å) see Table 3. T = 150(2) K throughout and all structures were solved by direct methods and refined on F^2 data using the SHELXL-97 suite of programs.[13] Hydrogen atoms, were included in idealised positions and refined using the riding model. For Al(**1**)Me two isomers were present in a 50:50 ratio. One *t*Bu group was disordered over two positions in a 50:50 ratio while another *t*Bu was disordered over three positions with equal occupancies. The structure also had solvent accessible voids; however, the electron density therein was very diffuse. Therefore, the SQUEEZE programme was employed and this suggested that the residual electron density was consistent with a diffuse hexane moiety (recrystallisation solvent). For Al(**3**)Me one *t*Bu group was modelled over two sites in a 80:20 ratio a molecule of toluene was also seen in the asymmetric unit. There is also a small (43 $Å^3$) solvent accessible void but this was left in the final refinement. For Al(**5**)Me one *t*Bu group was modelled over two sites in a 60:40 ratio, while half of a molecule of toluene was observed straddling a centre of symmetry. In addition a toluene moiety with 50% occupancy was present for which the carbon atoms were modelled and refined isotropically. For both Al(**1**)Me and Al(**5**)Me distance restraints were employed in the disordered *t*Bu moieties and solvent molecules to aid convergence.

Cite this: DOI: 10.1039/c0xx00000x

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Table 3 Crystal structure of complexes Al(**1**)Me, Al(**3**)Me and Al(**5**)Me.

Compound reference	Al(**1**)Me	Al(**3**)Me	Al(**5**)Me
Chemical formula	$C_{36.75}H_{58.75}AlN_2O_2$	$C_{33.50}H_{49}AlN_2O_2$	$C_{35}H_{49}AlN_2O_2$
Formula Mass	587.59	538.73	556.74
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	*C*2/*c*	$P2_12_12_1$	*C*2/*c*
a/Å	35.6710(9)	14.7810(2)	32.935(3)
b/Å	10.4360(3)	15.1010(2)	7.0560(10)
c/Å	24.9340(8)	29.1190(4)	31.375(4)
α/°	90	90	90
β/°	116.4370(10)	90	114.289(5)
γ/°	90.00	90	90
Unit cell volume/Å^3	8311.3(4)	6499.59(15)	6645.8(14)
Temperature/K	150(2)	150(2)	150(2)
No. of formula units per unit cell, *Z*	8	8	8
Absorption coefficient, *μ*/mm^{-1}	0.075	0.092	0.092
No. of reflections measured	70559	81419	24788
No. of independent reflections	9479	14759	5755
R_{int}	0.0411	0.0780	0.1342
Final R_1 values ($I > 2\sigma(I)$)	0.1196	0.0619	0.1154
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.3258	0.1606	0.2713
Final R_1 values (all data)	0.1319	0.0676	0.1818
Final $wR(F^2)$ values (all data)	0.3350	0.1651	0.3088
Goodness of fit on F^2	1.090	1.091	1.077
Flack Parameter	-	0.06(14)	-

Notes and references

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† Electronic Supplementary Information (ESI) available: the X-ray data in the .cif format.. See DOI: 10.1039/b000000x/

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